Saturday Evening Poster Sessions, July 15, 2017

Atomic Layer Etching
Room Plaza Exhibit - Session ALE-SaP

Atomic Layer Etching Poster Session

ALE-SaP-1 Quasi-Atomic Layer Etching of Silicon Nitride with Tunable Directionality and Ultra-high Selectivity*, **Sonam Sherpa**, A Ranjan,* Tokyo Electron

Self-limiting etch processes have emerged as a viable approach to address the challenges associated with continuous or quasi-continuous plasma processes. To this end, we have previously reported the quasi-atomic layer etching of silicon nitride via sequential exposure to hydrogen and fluorinated plasma[1] . Our work was preceded by Posseme et al. who reported the etching of silicon nitride via exposure to hydrogen plasma followed by dilute hydrofluoric acid (DHF) treatment[2]. Commonality between the two approaches is the increase in reactivity of silicon nitride after the exposure to hydrogen plasma and the underlying assumption was the implantation of hydrogen ions into silicon nitride.

In this talk, we will demonstrate that similar enhancement in reactivity of silicon nitride can also be attained via diffusion of hydrogen atoms into silicon nitride. Comparison of the self-limiting etch via ion-implantation versus diffusion offers new insights into the mechanism for the increase in reactivity of silicon nitride after hydrogen plasma treatment. This process is isotropic and we will demonstrate its feasibility to etch silicon nitride encapsulation layer selective to underlying silicon, silicon oxide, and other materials. These results complement our previous work that reported the anisotropic version of this process[1] and, thus, confirm the realization of self-limiting etch of silicon nitride with tunable directionality and ultra-high selectivity.

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[2] N. Posseme, O. Pollet, and S. Barnola, Appl. Phys. Lett. **105**, 2 (2014).

ALE-SaP-2 Atomic Layer Etching with Gas Cluster Ion Beam Irradiation in Reactive Gas Vapor*, **Noriaki Toyoda**,* University of Hyogo, Japan*; A Ogawa,* University of Hyogo*; I Yamada,* Univeristy of Hyogo

Atomic layer etchings (ALE) with gas cluster ion beam (GCIB) irradiation in reactive gas vapor were investigated for the first time. Since the kinetic energy of gas cluster ions is shared by thousands of gas atoms or molecules, energy/atoms or energy/molecules can be easily reduced to several eV. As a result, low-damage surface modification is promoted. In additions, since gas cluster ions realize dense energy deposition without severe damage, chemical reaction enhancement at low substrate temperature is expected. By using these characteristics, ALE by GCIB irradiation was studied in this paper. In this study, ALE of Cu films with oxygen GCIB irradiation in acetic acid vapor were investigated. We separated each etching steps as following; (1) adsorption of acetic acid on Cu, (2) evacuation of residual acetic acid vapor, (3) reaction between acetic acid and Cu and subsequent removal of surface Cu layer by oxygen GCIB irradiations. Effects of the following etching parameters on ALE were investigated from real-time Cu thickness on a quartz crystal monitor; acceleration voltage of oxygen GCIB, irradiation time of GCIB, partial pressure of acetic acid, exposure time of acetic acid.

During a one cycle of ALE of Cu with oxygen GCIB in acetic acid vapor, very thin layer of adsorbed acetic acid was formed on Cu surface in the first place. Acetic acid remained on Cu surface after evacuation of residual acetic acid. Subsequently, chemically altered Cu on the surface layer were removed with oxygen GCIB irradiation. In the case of 20 kV oxygen GCIB irradiations, Cu atoms beneath surface layer were also physically sputtered after removal of the chemically modified layer. Consequently, the etching process with 20 kV oxygen GCIB was not self-limiting. It was also observed that there was surface smoothing of Cu by lateral sputtering effects, which arise from physical sputtering of GCIB. On the contrary, surface Cu atoms with adsorbed acetic acid were reactively removed by 5 kV oxygen GCIB as same as the case by 20 kV oxygen GCIB, however, Cu atoms beneath layer were not physically sputtered at 5 kV. Therefore, the etching with 5 kV oxygen GCIB is self-limiting, which is crucial for ALE. Since there are various combination between adsorbed molecules and target materials, it is expected that ALE with GCIB will be applicable for various materials.

ALE-SaP-3 Thermal Atomic Layer Etching of TiO_2 using Sequential Exposures of WF_6 and BCl_3*, P Lemaire, **Gregory N. Parsons**,* North Carolina State University

Controlled thin film etching is essential for further development of sub-10 nanometer semiconductor devices. Vapor-phase thermal etching of oxides is appealing for achieving highly conformal etching of high aspect ratio features. We show that tungsten hexafluoride (WF_6) dosing or sequential WF_6 and boron trichloride (BCl_3) exposures can be used for chemical vapor or atomic layer etching (ALE) of oxides. In particular, these processes were observed to selectively etch titania (TiO_2) films versus other oxides including alumina (Al_2O_3) because of different volatility of metal fluorides. The etch process was observed to be temperature dependent, with the etch rate decreasing as the temperature was reduced from 220°C because of reduced volatilization of the metal fluoride and WF_2O_2. XPS shows evidence for a WO_xF_y layer that forms on of the TiO_2 films during the etch process. In addition, the incorporation of BCl_3 enables the volatilization of the WO_xF_y, for controlled etching at lower process temperatures (170°C). Using quartz crystal microbalance (QCM) analysis, we further investigate how the reactant exposure times and process temperature affects the relative etch rate per cycle for the WF_6/BCl_3 process.

ALE-SaP-4 Etch Profile Control of ALD-SiO2 Film Assisted by Alternating ALE Process of Fluorocarbon Deposition and O2 Plasma Etching*, **Masaru Zaitsu**,* ASM, Japan*; T Tsutsumi,* Nagoya University, Japan*; A Kobayashi,* ASM*; H Kondo, M Hori,* Nagoya University, Japan*; T Nozawa, N Kobayashi,* ASM

It is demanded to form not only conformal film by ALD but also any desired shape on patterned structures with the assistance of ALE for advanced devices fabrication. We have recently developed a novel ALE of SiO2 based on alternating process of fluorocarbon deposition and O2 plasma etching, which features saturated etching thickness per cycle for both the fluorocarbon deposition time and O2 plasma etching time. In this time we demonstrate the profile control of ALD SiO2 film by controlling etch conformality of this ALE process.

Conformal SiO2 film is deposited on a Si trench by plasma-enhanced ALD and then followed by the ALE with 60 MHz CCP type etching chamber. We investigate the etch conformality (EC) which is defined as the ratio of the etched thickness of sidewall film and that of top film with varying the ALE process parameters. A standard condition results EC of 33% as shown in Figure 1, which shows relatively anisotropic etching. On the other hand, a different condition using Ar/O2 as the etching plasma gas instead of O2 plasma shows EC of >100%, where sidewall film is etched while almost no etching on top film. This is because more carbon polymer is formed only on top due to anisotropic ion bombardment and it prevents etching top SiO2 film. EC can be controlled depending on plasma gas and further tuned by varying process parameters such as pressure, RF power, and substrate bias.

ALE-SaP-5 *In Situ* Mass Spectrometer Studies of Volatile Etch Products During Thermal Al_2O_3 Atomic Layer Etching Using HF and Trimethylaluminum*, **Joel Clancey**, S George,* University of Colorado - Boulder

The technique for removing atomic layers using sequential, self-limiting reactions known as atomic layer etching (ALE) offers a new level of etching precision. This atomic precision is needed by the semiconductor industry as advanced devices continue to scale to the 10 nm technology node and beyond. Thermal ALE using sequential, self-limiting reactions is emerging as a new technique capable of isotropically etching challenging 3D and high aspect ratio device architectures.

Thermal ALE has been developed for Al_2O_3, HfO_2, ZrO_2, ZnO and AlN based on sequential fluorination and ligand-exchange reactions. For many of these ALE systems, the surface reactions during thermal ALE have been characterized by *in situ* quartz crystal microbalance (QCM) and FTIR spectroscopic measurements [1, 2]. These studies have identified the mass changes and surface species during thermal ALE. The volatile etch products have also been inferred based on the mass changes and surface species. However, these volatile etch products have not been directly confirmed using mass spectrometry.

In this presentation, we describe a new ALE reactor with an *in situ* quadrupole mass spectrometer (QMS) with high resolution and mass range. A schematic of this new ALE reactor is given in the supplemental figure. This new apparatus is then used to investigate the thermal ALE of Al_2O_3 using HF and trimethylaluminum (TMA) as the reactants [1]. We can identify the volatile etch products during each HF and TMA reaction. The volatile etch products for the fluorination and ligand-exchange reactions evolve during the reactant exposures and present some surprises.

[1] Younghee Lee, Jaime W. DuMont and Steven M. George, “Trimethylaluminum as the Metal Precursor for the Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions”, *Chem. Mater.* **28**, 2994 (2016).

[2] Younghee Lee, Jaime W. DuMont and Steven M. George, “Atomic Layer Etching of HfO_2 Using Sequential, Self-Limiting Thermal Reactions with Sn(acac)$_2$ and HF”, *ECS J. Solid State Sci. Technol*. **4**, N5013 (2015).

ALE-SaP-6 Cyclic Plasma Cleaning Process of SiO_2 Layers using Surface Fluorination*, **Kyongbeom Koh,** H Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Controlling impurities and particles is an important factor in determining the performance and yield of semiconductor devices. However, it becomes more challenging as the critical dimension shrinks. Many contaminants such as organic materials, inorganic materials and native oxide are generated in etching process. Among them, especially, native oxide can have an adverse effect on electronic devices. It can create higher contact resistance, which makes the IC inoperable. Other disadvantages of native oxide involve leakage current on gate oxide and inadequate formation of silicide in devices.[1] Various wet cleaning processes are mainly applied to remove the native oxide.[2-3] However, the conventional wet cleaning processes start show limitations in some applications. Therefore, various dry cleaning processes are actively being investigated in order to overcome the limitations of the wet cleaning processes in nanoscale patterns.[4]

In this work, cyclic plasma process was studied for SiO_2 (native oxide) removal with surface fluorination in an inductively coupled plasma (ICP) reactor with CHF_3, CF_4, Ar, O_2 chemistries. The cleaning rate of cyclic process was found to be lower than that of direct process, so we studied cyclic process for SiO_2 cleaning than direct process. The cyclic plasma cleaning process is composed of two steps. The first one is fluorination of SiO_2 surface by fluorocarbon radicals which are generated from CHF_3 or CF_4 plasmas. The other step is removal of fluorinated SiO_2 layers by ions and radicals which are generated from O_2 or Ar plasmas. Formation of fluorocarbon layer on SiO_2 surface was confirmed by SEM and XPS analysis. Cleaning rate was investigated by varying bias voltage and ion density by monitoring processes with a VI probe and an ion monitor. It is also confirmed that the cleaning rate becomes self-limited as the fluorination and cleaning time increase. Cleaning rates were compared at various process conditions and the cleaning rate could be controlled under 10 Å/cycle.

References

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Keywords: Cyclic plasma cleaning, native oxide, surface fluorination

ALE-SaP-7 Low Damage Cyclical Etching of GaN and AlGaN*, A Goodyear,* Oxford Instruments Plasma Technology, UK*; P Abrami,* University of Bristol, UK*; **Mike Cooke**,* Oxford Instruments Plasma Technology, UK*; M Loveday,* Oxford Instruments Plasma Technology

The AlGaN gate recess etch requires the removal of a controlled amount of material, up to 30nm thick, with minimal disruption to the few nanometres remaining in the layer. Other device structures call for etching GaN, without disrupting underlying AlGaN. We have studied the use of cyclical ALE-style etch processes for these materials.

We find that both materials etch at around 1.5-4 Å /cycle in a Cl_2/Ar cycle, similar to that used for ALE of silicon^1, in an Oxford Instruments PlasmaPro100 Cobra^{300} ICP etch tool modified for ALE^2. The baseline of the cycle, using a continuous ICP plasma is:

10 – 100 msec chlorine dose; the dose can also be varied by changing the flow

2 – 20 seconds of purge

3 – 30 seconds of 13.56MHz RF bias at 0 – 50 Vdc self bias

We present graphs showing a synergistic effect of gas dose and ion bombardment, and a distinct plateau in etch per cycle v chlorine dose for both GaN and AlGaN. The synergy is seen by comparing the etch per cycle with and without a chlorine dose. Zero etching is observed if only the dose step is applied. Only a slight saturation behaviour in etch per cycle v etch step intensity (bias voltage or time) was observed, due to a low selectivity of etch rate under argon ion bombardment, between chlorinated and non-chlorinated surfaces. The etch step bias required to consume all the adsorbed reactant is very close to the onset of physical sputtering of the base material, so that no plateau is seen. The cyclical etch strategy provides a repeatable low etch rate using minimal ion energies, although it does not give a significant selectivity between GaN and AlGaN, using this chemistry.

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ALE-SaP-8 Thermal Atomic Layer Etching of ZnO by “Conversion-Etch” Using Hydrogen Fluoride and Trimethylaluminum*, **David Zywotko**, S George,* University of Colorado - Boulder

ZnO atomic layer etching (ALE) was demonstrated using hydrogen fluoride (HF) and trimethylaluminum (TMA) as the reactants [1]. ZnO thin films were grown by ZnO atomic layer deposition (ALD) at 150°C using diethylzinc (DEZ) and H_2O. The ZnO films were then etched using sequential exposures of HF and TMA. *In situ* quartz crystal microbalance (QCM) monitored the linear mass loss during etching at 265°C. The QCM also allowed for analysis of individual mass gains and losses during reactant exposures. In addition, ZnO ALD films were grown on Si(100) wafers for *ex situ* analysis. The ZnO ALE was measured between 205°C and 295°C using spectroscopic ellipsometry and x-ray reflectivity analysis . The etch rate was temperature dependent and varied from 0.01 Å/cycle at 205°C to 2.19 Å/cycle at 295°C.

The QCM measurements at 265°C showed that the sequential HF and TMA thermal reactions were self-limiting. In addition, the large mass loss during the TMA exposures could not be explained by simple ligand-exchange reactions that remove the AlF_3 fluoride layer following fluorination by the HF exposure. Instead, the large mass loss suggested that TMA was converting the ZnO surface to an Al_2O_3 layer. The HF then is believed to fluorinate the Al_2O_3 surface to an AlF_3 layer. Subsequently, the TMA exposure removes the AlF_3 layer by ligand-exchange reactions before continuing to convert more ZnO to Al_2O_3. This new strategy for thermal ALE can be called a “conversion-etch” mechanism.

The conversion of ZnO to Al_2O_3 during ZnO ALE may be one example of a fairly general phenomena. Conversion reactions may occur when the metal precursor used for ligand-exchange can form a metal oxide that is more stable than the initial metal oxide. These conversion reactions may be very useful in thermal ALE. For example, the conversion reaction could convert a metal oxide that has a volatile fluoride and would not display self-limiting fluorination to another metal oxide that may have a stable fluoride. The conversion reaction could also convert a metal oxide that may not have a volatile reaction product after ligand-exchange to another metal oxide that may have a volatile reaction product.

[1] David R. Zywotko and Steven M. George, “Thermal Atomic Layer Etching of ZnO by a “Conversion-Etch” Mechanism Using Sequential Exposures of Hydrogen Fluoride and Trimethylaluminum”, *Chem. Mater.* **2017**- DOI: 10.1021/acs.chemmater.6b04529.

ALE-SaP-9 Cryogenic Atomic Layer Etching of SiO_2*, N Holtzer, **Thomas Tillocher**, P Lefaucheux, R Dussart,* GREMI Université d'Orléans/CNRS, France

Atomic Layer Etching (ALE), that has been developed in the 90s, addresses new challenges in micro and nanoelectronics where high precision processes are required. This is typically a sequential process relying on a self-limited reaction of radicals created in the plasma phase and adsorbed on the material to be etched. Precursor radicals adsorb ideally on the first monolayer. Then, under a low energy ion bombardment, the etch products form and desorb until the adsorbed layer is depleted (self-limited reaction). This removes a few monolayers. By repeating the cycle, the material is etched monolayers by monolayers.

ALE of SiO_2 has already been demonstrated with a 3-step process. The first step is an Ar/C_4F_8 plasma with no RF self-bias voltage applied to the substrate holder. The oxide surface is then coated with a very thin fluorocarbon (FC) layer. The second step is a pure Ar plasma still with no RF self-bias voltage used to pump C_4F_8 out of the chamber. The third and final step is an Ar plasma with about 10V RF self-bias voltage. The ion energy must be kept below the sputtering threshold. If the thickness of the FC layer is accurately controlled, the process can be self-limited.

Such a process has been implemented and investigated on our ICP etching tool. It is observed that it is not reproducible since, depending on chamber wall conditions, it can switch from an etching regime to an unwanted deposition regime. A sequential 4-step process is proposed instead: after the etching step (step 3), an O_2-based cleaning plasma step is added and improves overall process reproducibility. The chamber itself, whereas it provides gas pulsing capability for alternated processes, requires very accurate control of gas flows to reach self-limiting etching and hence low thickness etched per cycle. Ultimately, an etch rate of 0.3 A/cycle has been obtained in our experimental conditions.

However, fluorocarbon contamination of chamber walls is an issue. We propose to run ALE at cryogenic temperature of the substrate as a potential solution. Different precursor chemistries are investigated (fluorine-based, fluorocarbon-based) for top layer adsorption. At such a low temperature, species are adsorbed only at cooled surface and hence wall pollution is mainly suppressed. In addition, the substrate temperature is expected to be an additional process knob that enables the adjustment of the adsorbed precursor layer thickness and hence the reduction of the etched thickness per cycle. Finally, since radical diffusion in the bulk material is reduced at cryogenic temperature, low structural damage is expected as well.

ALE-SaP-10 SF_4 as a New Fluorine Reagent for Thermal ALE: Application to Al_2O_3 and VO_2 ALE*, **Jonas Gertsch**, N Johnson, V Bright, S George,* University of Colorado - Boulder

Thermal ALE has been demonstrated recently for many materials including Al_2O_3, HfO_2, ZrO_2, ZnO, and AlN using fluorination and ligand-exchange reactions [1]. The fluorine reagent for the fluorination reactions has been HF from an HF-pyridine solution. HF-pyridine is a safer HF source than anhydrous HF. However, safety concerns, as well as the need for a stronger fluorination source, have motivated an exploration of SF_4 as the fluorine reagent.

This study examined Al_2O_3 and VO_2 ALE using SF_4 for fluorination together with $Sn(acac)_2$ (tin(II) acetylacetonate) as the metal precursor for ligand-exchange. Al_2O_3 and VO_2 ALD films were grown at 150 °C using trimethylaluminum and H_2O for Al_2O_3 ALD and tetrakis(ethylmethylamido) vanadium(IV) and H_2O for VO_2 ALD. These films were then etched using sequential SF_4 and $Sn(acac)_2$ exposures. An *in situ* quartz crystal microbalance was employed to monitor film growth and etching during the ALD and ALE reactions. *Ex situ* X-ray reflectivity (XRR) and spectroscopic ellipsometry (SE) were used to characterize film thicknesses on silicon substrates before and after etching.

The Al_2O_3 and VO_2 ALD films were removed with a linear etch rate of ~0.2 Å/cycle and ~0.3 Å/cycle, respectively, at 200°C. Both SF_4 and $Sn(acac)_2$ exhibited self-limiting reactions on Al_2O_3 and VO_2. The temperature dependence was also explored for Al_2O_3 ALE using SF_4 and $Sn(acac)_2$. The etch rates varied from 0.03 Å/cycle at 150 °C to 0.3 Å/cycle near 250 °C. To replace $Sn(acac)_2$, BCl_3 (boron trichloride) has also been explored as an alternative for VO_2 etching together with SF_4. Initial results have shown that BCl_3 and SF_4 can etch VO_2 by a "conversion-etch" mechanism [2]. BCl_3 is thought to convert the VO_2 surface to a B_2O_3 layer. SF_4 can then spontaneously etch the B_2O_3 surface layer.

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ALE-SaP-11 Demonstrating Manufacturability of Atomic Level Etch (ALE) through Accelerated Neutral Atom Beam (ANAB) Processing*, **Daniel Steinke**, B Sapp, S PapaRao,* SUNY Polytechnic Institute*; E Barth,* SEMATECH*; V Kaushik, M Rodgers, C Hobbs,* SUNY Polytechnic Institute*; M Walsh, S Kirkpatrick, R Svrluga,* Neutral Physics Corporation

Accelerated Neutral Atom Beam (ANAB) processing has been shown to be an effective method to achieve ALE in a cyclic process when combined with a selective removal step to form a SiN spacer [Barth *et al*, ALE Workshop 2016]. In this paper, we present the progress towards demonstrating manufacturability of the ANAB-enabled ALE process – in terms of factors such as process speed, control and stability, and ease of integration into a standard 300mm fabrication facility. In this work we will show several-fold improvement of wafer throughput by reduction of ANAB process times while still accomplishing the necessary surface modification by ANAB exposure. A detailed investigation of the applicability of various processes for the selective removal portion of the ALE cycle has shown that ANAB effectively reduces the surface roughness that is introduced by the selective removal process step. We also demonstrate the ability to affect the sidewall profile of the spacer etch by adjusting the ANAB process parameters throughout the cycled process, such as average neutral atom energy, the incorporation of chemically active species into the ANAB beam, etc. These improvements, combined with the installation of the first ANAB tool in the state of the art 300mm process line at the College of Nanoscale Science and Engineering (CNSE), are aiding wider implementation of ANAB-based ALE in semiconductor manufacturing lines.

ALE-SaP-12 Etching with Low Te Plasmas*, **Scott Walton**, D Boris,* U.S. Naval Research Laboratory*; S Hernández,* U.S.Naval Research Laboratory*; H Miyazoe, A Jagtiani, S Engelmann, E Joseph,* IBM TJ Watson Research Center

Processing with atomic layer precision requires the ability to not only add, remove or modify one monolayer of material but to also leave adjacent layers unchanged. This requires fine control over the flux of species and energy deposition at the surface. The appropriate threshold and process windows are certainly material specific but it is reasonable to assume many applications require low energy ions. Electron beam-generated plasmas are generally characterized by high charged particle densities (10^{10}- 10^{11} cm^{-3}), low electron temperatures (0.3 - 1.0 eV), and in reactive gas backgrounds, a relatively low radical concentration compared to discharges. As such, these sources are well-suited to explore processing space not commonly found in industrial tools. In this work, we discuss SiN etching using pulsed, electron beam generated plasmas produced in SF_6 backgrounds. We pay particular attention to the etch rates, selectivity (vs. carbon films, Si and SiO_2), and patterning as function of operating parameters such as relative gas concentration, operating pressure, and substrate bias. These results are compared with plasma diagnostics to gain a better understanding of the process requirements and windows for threshold etching of SiN. This work is partially supported by the Naval Research Laboratory base program.

ALE-SaP-13 Surface Cleaning of Gallium Antimonide Oxides: The Role of Hydrogen Atoms, Argon Ions, and Temperature*, **Thomas Larrabee**, S Prokes,* Naval Research Laboratory

Complete removal of surface oxides from GaSb and other III-V semiconductors may be accomplished by a variety of means, including thermal oxide desorption at high temperature, chemical reaction with atomic or molecular hydrogen, and physical sputtering by noble gas ion bombardment. It is often difficult to remove the oxide while preserving a low-defect surface, which is typically critical to limit Fermi-level pinning that degrades device performance, because one species desorbs faster than another or because the temperatures or ion energies involved cause physical surface defects. Plasmas, however, particularly mixtures of argon and hydrogen, have been shown to work well in surface preparation of GaSb interfaces at very low temperature.(1) What is not known clearly is which species of the plasma is the most critical, how low the temperature can be to effectively remove oxide, or whether there is a *synergistic* effect to multiple species in atomic layer surface cleaning at low temperature. To investigate this phenomenon, GaSb (001) surfaces have been prepared in an UHV chamber with in-situ photoelectron spectroscopies and low-energy electron diffraction (LEED).(2) The effects of atomic hydrogen exposure alone, low- and moderate-energy Ar+ ions alone, and *simultaneous* atomic hydrogen and low-energy Ar+ ions (like would be encountered in many plasma systems) on oxidized GaSb will be presented. The effectiveness of oxide stripping and re-oxidation has been evaluated with surface-sensitive electron-stimulated Auger spectroscopy and XPS, and has been studied as a function of temperature. LEED patterns confirm the ordering and crystallinity that may still be achieved, even after multiple oxidations and oxide removals. Controlled oxidation and selective, damage-free oxide stripping will also be explored as a route to a pseudo atomic layer etch process for GaSb. Such a process could be sped up considerably in plasma-based reactor at higher pressures, when the requirements on the plasma, such as ion energy and flux, hydrogen atom flux, and surface temperature are understood.

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ALE-SaP-14 Aluminum Native Oxide Surface Cleaning and Passivation in an Atmospheric Plasma System*, **John Mudrick**, M Pohl, K Knisely,* Sandia National Laboratories

Plasma cleaning is an integral part of electronics processing used for surface decontamination, wire bonding, wafer-to-wafer interconnect formation, preparation for film growth, and many other process steps. Plasma cleaning and passivation of aluminum is of particular importance because any degree of ambient exposure results in a rapidly-forming native oxide several nanometers in thickness, potentially deteriorating the electrical and morphological properties of the Aluminum surface. Careful control of this oxidized surface at the atomic scale is of paramount importance for many steps. In this work we use a flexible, low-damage dielectric barrier discharge atmospheric plasma treatment system to fully reduce oxidized aluminum surfaces and passivate against future re-oxidation. Wire bond pull tests and water contact angle (WCA) measurements were used to initially characterize the aluminum cleaning process. Aluminum wire bonds made to an untreated aluminum surface failed under a force of (10.1 ± 1.8) grams. Exposing the aluminum surface to a hydrogen-based plasma prior to wire bonding resulted in an increased bond strength, requiring a force of (13.2 ± 0.9) grams for failure. WCA measurements correlate this enhancement with native oxide removal: untreated aluminum samples show a weakly hydrophilic surface with a contact angle of (57 ± 2) degrees. Exposing the samples to the same hydrogen-based plasma reduces the WCA to (28 ± 5) degrees, suggesting the degree of oxidation is reduced. Further increasing the plasma exposure time results in a steady decrease in WCA until the native oxide is completely removed, Fig. (a) and (b). However, the WCA increases rapidly under ambient exposure. To combat this re-oxidation, nitrogen gas is added to the plasma in order to passivate broken Al-O bonds and improve process flexibility. Both mixed mode – hydrogen and nitrogen mixed gas flow - and sequential – separate hydrogen and nitrogen steps – passivation schemes are investigated in order to maximize the time with minimal WCA. Both schemes show improved resistance to aluminum re-oxidation. To date, best passivation is achieved in continuous mode: a modest WCA increase from 2 to 5 degrees is observed after 180 minutes of re-oxidation in cleanroom ambient conditions, Fig. (c). Cleaning and passivation mechanisms will be further characterized with x-ray photoelectron spectroscopy measurements. Extensions to aluminum nitride film growth on plasma-cleaned and passivated aluminum substrates are also underway.

ALE-SaP-15 Atomic Layer Etching in Reactive Ion Etching System for Nanoscale Pattern Transfer*, S Khan,* ***Dmitry Suyatin****, M Graczyk, A Kvennefors,* Lund University, Sweden*; E Kauppinen,* Aalto University, Finland*; M Huffman, I Maximov,* Lund University, Sweden*; J Sundqvist,* Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany

Today the characteristic size of advanced electronic components is already below 20 nm, which corresponds to less than 40 silicon atoms. Atomic Layer Etching (ALE) provides atomic precision material removal and is inherently a damage-free etch process. This makes ALE to be very important for fabrication of leading edge electronic components [1-3].

Here we present our study of ALE process in Plasmalab-100 etch system from Oxford Instruments for nanoscale pattern transfer. The ALE process for Si was based on surface activation with Cl_2 gas and removal of the activated layer in Ar plasma [4]. Nanoscale patterns with different geometries and feature sizes, see Figure 1, were fabricated with electron beam lithography in HSQ (hydrogen silsesquioxane) resist. Inspection of the nanoscale patterns after ALE allowed us to study different effects and limitations of the ALE process, for example loading, trenching and sidewall tapering.

References

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ALE-SaP-16 Selective Fluorocarbon-based Atomic Layer Etching in a Conventional Parallel-Plate, Capacitively Coupled Plasma*,* ***Stefano Dallorto****,* Ilmenau University of Technology*; A Goodyear, M Cooke,* Oxford Instruments Plasma Technology, UK*; S Dhuey, A Schwartzberg, S Sassolini,* Lawrence Berkeley National Laboratory*; C Ward,* Oxford Instruments*; D Olynick,* Lawrence Berkeley National Laboratory*; I Rangelow,* Ilmenau University of Technology*; S Cabrini,* Lawrence Berkeley National Laboratory

We study a Fluorocarbon(FC)-based ALE process for controlling the etching of several substrates at the atomic level in a conventional parallel-plate, capacitively coupled plasma tool. In a steady state Ar plasma, a periodic fluorocarbon gas injection enables control of the deposited FC layer thickness in the one to several Angstrom range and chemical modification of the surface. For low energy Ar^+ ion bombardment conditions, the physical sputter rate of the substrate vanishes, whereas the modified surface can be etched when FC reactants are present at the surface.

With the goal of achieving high selectivity FC-based ALE, we study the etching of different materials under different FC chemistry. Etching rate per cycle is first investigated using spectroscopy ellipsometer on unpatterned surfaces. Using CHF_3-based ALE for SiO_2 etching, the etching rate is 8.5Å/cycle. SiO_2 features with different critical dimensions has been etched under different conditions. The SiO_2 features etched using an ALE process (Row 1) are aspect-ratio independent compared to the features obtained with a continuous RIE process (Row 2). It is worth noticing how the results change when higher DC bias is used in the etch step of the ALE process (Row 3). This case is dominated by sputter etching with results in a high degree of physical/ionic etching.

A successful application of the cyclic ALE approach has been demonstrated. Overall, the cyclic FC/Ar etch has proven to pattern features well (Row 1), with great potential for significant improvement in overall etch performance.

ALE-SaP-17 RF Plasma Electrostatics: The Influence on Film Morphology and Carbon Incorporation*,* ***K. Scott Butcher****,* Meaglow Ltd, Canada*; P Terziyska,* Institute of Solid State Physics, Bulgarian Academy of Sciences, Bulgaria*; V Georgiev,* Meaglow Ltd, Canada*; D Georgieva,* Semiconductor Research Lab, Lakehead University, Canada*; R Gergova,* Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, Bulgaria*; P Binsted, S Skergetc,* Semiconductor Research Lab, Lakehead University, Canada

RF plasmas have a DC component that can affect the migration of species deposited during film deposition. Electrostatic interactions between the positive charge presented by RF plasmas and the negative charge of deposited layers can have a strong influence on film morphology. We have characterised some of these interactions and published some results that may be of interest [Butcher et al. J. Appl. Phys. **121** (2017) 013301].

Electrostatic field interactions can also play a strong role in reducing carbon contamination, we provide an example of GaN where carbon contamination using a nitrogen plasma is reduced below detection limits using controlled electrostatic interactions.

ALE-SaP-18 Atomic Layer Etching of Amorphous Silicon with Selectivity Towards MoS_2*,* ***Markus Heyne****,* KU Leuven, Belgium*; A Goodyear,* Oxford Instruments Plasma Technology, UK*; J de Marneffe,* IMEC, Belgium*; M Cooke,* Oxford Instruments Plasma Technology, UK*; I Radu,* IMEC, Belgium*; E Neyts,* University of Antwerp, Belgium*; S De Gendt,* KU Leuven, Belgium

Transition-metal dichalcogenides and their heterostructures enable promising architectures for novel device concepts. Nowadays, prototype structures are fabricated by manual stacking of exfoliated nanosheets or transferred CVD layers. This transfer approach has the advantage of reducing processing steps being detrimental to the sensitive 2D materials. However, it cannot be automated and it is not compatible with the geometrical scaling required for advanced CMOS applications. The exploration of selective patterning and selective growth is therefore essential to build heterostructures with defined geometries and electrical contacts to the individual nanosheets.

This paper describes the first critical step to fabricate a WS_2/MoS_2 heterostructure by selective conversion of sacrificial Si [1]. Large-area MoS_2 as the bottom MX_2 layer is deposited by sulfidation [2,3] and pre-patterned by optical lithography and conventional etch. Amorphous Silicon (aSi) is deposited on top of the MoS_2 and optical lithography is performed defining the top layer of the heterostack, which is converted to WS_2 [1]. The key part of the device prototyping is the selective etch of aSi without damage to the underlying MoS_2. To this end, we investigated an atomic layer etching (ALE) process based on Cl_2 plasma chemistry in an Oxford Instruments PlasmaPro 100 ICP reactor equipped with an ALE kit. The process was composed of alternating cycles of a Cl_2 pulse followed by low-bias Ar activation in a continuous ICP mode. The controllable silicon etch rate of the ALE process was 0.6 nm per cycle. The process stopped on the MoS_2 without degradation of its structure, enabling very high overetch. The exposed MoS_2 quality was characterized by Rutherford backscatter spectrometry, Raman spectroscopy, and X-ray photoelectron spectroscopy. No damage to the MoS_2 was detected. Finally, the developed aSi ALE with selectivity to MoS_2 was applied to samples with lithography patterns to demonstrate the applicability for pattern transfer. The presented work also covers the challenges of applying ALE to 2D materials, and focuses on the detrimental influence from adsorbed water on the carrier wafer and chamber walls, and the protecting effect of the heterostack's top layer during the plasma ignition. The established procedure opens a path to study the plasma-surface interaction on MX_2 materials without damaging the top molecular MoS_2 layer.

[1] M. Heyne et. al, Nanotechnology **28**, 04LT01 (2017)

[2] M. Heyne et. al, J. Mater. Chem. C **4**, 1295 (2016)

[3] D. Chiappe et al., Advanced Materials Interfaces **3(4)**, 1500635 (2016)

ALE-SaP-19 Simulation of New Material-Systems for Directional Atomic Layer Etching*, **Ivan Berry**, K Kanarik, T Lill, V Vahedi, R Gottscho,* Lam Research Corp.

Atomic layer etching (ALE) has recently been introduced into manufacturing of 10 nm logic devices. ALE is an etching technology that deploys separated and self-limited steps. In directional ALE, at least one of the two steps has to be directional, i.e., has to transfer momentum to the surface and/or be sensitive to line of sight. Ion bombardment is most commonly used to realize directional ALE. ALE exhibits the same ion-neutral synergy as RIE but the removal amount is not flux dependent due to the separation of the neutral (chemical) and ion fluxes /1,2/. Flux independence gives ALE its most important property: inherent uniformity across all length scales – across wafer, loading, ARDE and surface smoothness. As compared to conventional plasma etching, the separate steps in ALE also offers a simplified system in which to study the basic etching mechanisms. For example, recently, the process window of ALE was shown to be predictable based on the energy barriers relevant to the substrate-reactant combination, such as the surface binding energies of the chemically modified and bulk material /3/. The separate and independent steps make it particularly suitable to modelling efforts. Here we present the latest results in feature scale modelling of new material systems amenable to the ALE approach.

[1] H.F. Winters, J.W. Coburn, E. Kay, J. Appl. Phys. 48, 4973 (1977)

[2] K.J. Kanarik et al., J. Vac. Sci. Technol. A 33(2) (2015)

[3] K.J. Kanarik et al., J. Vac. Sci. Technol. Submitted Dec 2016

Plenary Session
Room Plaza ABC - Session PS1-SuM

Sunday Plenary Session I

Moderators: John Conley, Oregon State University, Charles Dezelah, EMD Performance Materials

8:30am **PS1-SuM-3 Future Applications and Challenges for ALD in Microelectronics*, Suvi Haukka,*** ASM, Finland **INVITED**

The number of different materials in semiconductor devices has been increasing nearly exponentially with the down-scaling of device dimensions. For decades the device consisted of mainly Si based materials, but by the late 1990´s it became clear these materials alone cannot enable the required scaling. Furthermore, the deposition methods used were unable to meet the ever more stringent requirements. Thus atomic layer deposition (ALD), although considered too slow at that time, started gaining increasing interest. ALD dielectrics were the first to be investigated, especially due to the need for ultra-thin and highly conformal films. In early 2000 first ALD Al2O3 and later ZrO2 were used in memory applications, while in 2007 ALD HfO2 replaced SiO2 as the gate oxide in transistors at the 45 nm node. Now ten years later the research community is facing even greater challenges in future device scaling, which calls for new ALD processes, or even completely new deposition methods. We all working in the deposition field are challenged to deposit high quality materials at low temperatures, such as low resistivity metals and patterning layers. Also we are requested to deposit many materials selectively only on certain surfaces, for instance to overcome lithography misalignment issues. Since there is less and less room for all the different layers, the thickness of each layer is approaching 1nm or less making the uniform deposition demanding. Furthermore, the materials should also be deposited conformally in extremely high aspect ratio, highly complicated and very high surface area structures. These industry needs drive new materials requirements which put great demands on the ALD chemistry. It is essential to understand the chemistry of the starting surfaces, interfaces and the interaction of precursors with the varying surfaces to make it possible to selectively deposit uniform and continuous layers less than 1 nm thick. Any of the challenges mentioned could be difficult to overcome, unless we understand in detail how to design and optimize our ALD reactors for the new chemistries. Thus not only the chemistry of ALD, but also the hardware play a big role in how successful we will be. In this presentation the various future applications and challenges are reviewed with the main focus on how the ALD chemistry is critical for developing solutions.

9:15am **PS1-SuM-6 Future Trends of Deposition Technologies in Semiconductor Industry*, Mei Chang,*** Applied Materials **INVITED**

3D transistor FinFET, 3D memory, and multiple patterning have been driving the semiconductor industry for the recent years. While Moore's Law is still on going, dimensional scaling has slowed down noticeably; instead, the focus has shifted toward stacking vertically. The challenges to deposit films conformally and to fill the features free of void are getting more severe. On top of them, the demand for various functional materials is continuously expanding on the periodic table.

In this talk, we will discuss several technologies: thin conformal coatings, void free filling, and selective deposition; their application and tradeoffs.

Plenary Session
Room Plaza ABC - Session PS2-SuM

Sunday Plenary Session II

Moderators: Steven M. George, University of Colorado at Boulder, Keren J. Kanarik, Lam Research Corp.

10:45am **PS2-SuM-12 Atomic Layer Etching – An Overview of Possibilities and Limitations*, Richard Gottscho,*** Lam Research Corp. **INVITED**

Exceeding expectations set back in the 1980s, today the field of plasma etching is more critical than ever to formation of nanometer-sized features in a $35-40 billion chip equipment industry. For most critical etch applications such as pattern-transfer and 3D structure formation, an essential requirement is the anisotropic removal of material. Plasma is important because it provides the energetic, directional ions that enable anisotropy, while also producing radicals to accelerate reactions. Conventional plasma etching was for many years considered a “black box” of coupled non-linear interactions between ions and radicals [1]. Atomic layer etching (ALE) is an advanced etch technique used in the fabrication of 10 nm logic. By virtue of its separated and self-limiting steps, ALE offers a simplified system in which to understand etch mechanisms. In this talk, we'll explore plasma ALE focusing on silicon ALE as a case study before expanding the concepts and applying them to a variety of other materials relevant to the industry such as Ge, C, W, GaN, and SiO_2 [2, 3]. A “synergy” parameter quantifies the degree to which each process approaches the ideal ALE regime and is related to the energetics of underlying surface interactions. By systematically studying a group of materials, we show that synergy scales with surface binding energy of the bulk material. This helps explain why some materials are inherently more (or less) amenable to the ALE approach. The insights will be vital for exploiting ALE in the fabrication of future devices.

[1] H.F. Winters, J.W. Coburn, E. Kay, J. Appl. Phys. 48, 4973 (1977)

[2] K.J. Kanarik et al., J. Vac. Sci. Technol. A 33(2), Mar/Apr 2015

[3] K.J.Kanarik et al, J. Vac. Sci. Technol. Submitted Dec 2016

ALD Fundamentals
Room Plaza E - Session AF-SuA

ALD Fundamentals: Precursors and Mechanisms (1:30-3:30 pm)/High Aspect Ratios & High Surface Areas (4:00-5:30 pm)

Moderators: Roy Gordon, Harvard University, Charles H. Winter, Wayne State University, Mato Knez, CIC nanoGUNE, Ola Nilsen, University of Oslo

1:30pm **AF-SuA-1 Atomic Layer Deposition of Silicon Dielectrics: Precursors, Processes and Plasmas***, Dennis Hausmann,* Lam Research **INVITED**

As the dimensions of modern semiconductor devices continue to shrink below the current 14 nm technology node, novel processes for the deposition of highly conformal, low temperature, silicon based dielectrics will be needed for applications that include sidewall spacers, barriers, and patterning layers. Atomic layer deposition (ALD) is an ideal method for achieving the high conformality and has been used in high volume manufacturing (HVM) to deposit high-k dielectric materials (HfO_2, ZrO_2 …) for several technology generations. Plasma assisted ALD is the best known method to meet low temperature (< 500 °C) requirements and is now being used for depositing conformal silicon dielectrics such as silicon oxide (SiO_2) and silicon nitride (Si_3N_4). In this presentation, the current state of the art of precursors, plasmas and process conditions required to deposit conformal silicon dielectrics by plasma ALD will be discussed. Theoretical and experimental data will be presented to explain the observed reaction characteristics for the plasma ALD of SiO_2, Si_3N_4, and the lack (so far) of silicon carbide (SiC). Although plasma enables low temperature deposition, they pose challenges for achieving isotropic film properties over the complex topography of today's semiconductor devices.

2:00pm **AF-SuA-3 Atomic Layer Deposition of Carbon Doped Silicon Oxide by Precursor Design and Process Tuning***, Meiliang Wang, H Chandra, A Mallikarjunan, K Cuthill, M Xiao, X Lei,* Versum Materials, Inc

Atomic Layer Deposition (ALD) of silicon oxide is commonly used in the semiconductor industry due to its excellent thickness control and conformality. For some applications, films deposited at low temperature with low wet etch rate relative to undoped silicon oxide are required, e.g., pattern definition using selective wet etch. Carbon doping is a known method to tune the wet etch rate of silicon oxide films. In this paper, the impact of precursor reactivity, the number of precursor silicon-carbon bonds, co-reactant concentration, and deposition temperature on deposited film's carbon content will be discussed.

Substituting the Si-H bonds by $Si\text{-}CH_3$ bonds on organoaminosilane precursors is considered to be able to introduce carbon doping into the silicon oxide film. In this paper, precursors with different numbers (1, 2 or 3) of Si-H bonds substituted by $Si\text{-}CH_3$ groups are compared. Figures 1 and 2 show the silicon oxide film growth per cycle (GPC) and carbon content in the film respectively with different precursors at different deposition temperatures. It is found that substituting the Si-H bond by $Si\text{-}CH_3$ bond reduces precursor reactivity and decreases GPC. At temperatures ≥ 225 °C, all the precursors could deposit silicon oxide films with reasonable GPC but very little carbon in the film (<1 at.% by XPS). At temperatures ≤ 150 °C, precursors with two or three $Si\text{-}CH_3$ bonds, eg. dimethylaminodimethylsilane (DMADMS) and dimethylaminotrimethylsilane (DMATMS), have almost no silicon oxide film deposition (GPC < 0.1 Å/cycle), while the newly designed precursor with only one $Si\text{-}CH_3$ bond substitution, eg. diisopropylaminomethylsilane, could deposit silicon oxide film with relatively high GPC and high carbon doping (1-10 at.%). The above example illustrates that tailoring the precursor structure is crucial to balance reactivity and desired film property. In addition, an alternative novel way of making carbon doped SiO_2 is presented in another talk by our group [1].

[1] Haripin Chandra, *et al.* ALD 2017

2:15pm **AF-SuA-4 Evaluation of Silicon Precursors for Low Temperature Silicon Nitride Deposition***, Shuang Meng, B Hendrix, T Baum,* Entegris Inc.*; D Hausmann,* Lam Research

The increased complexity of the next generation device structures challenges the widely used deposition technology of materials such as silicon nitride (Si_3N_4). New applications including double patterning spacer, liner, encapsulation layer, and gate spacer all require a conformal silicon nitride film deposited at low temperatures (<400°C); these films should display good etch resistance and/or etch selectivity in highly conformal films. Plasma-enhanced atomic layer deposition (PEALD) is the preferred deposition method due to its excellent conformality, thickness control, and the ability to deposit films at low temperatures with better film properties. Although many silicon containing precursors have been used and explored for silicon nitride deposition in the past, no precursor has been identified that can simultaneously meet all the technical requirements for low temperature deposition and be economically viable.

In this work we screen a variety of silicon precursors using PEALD with both N_2 and NH_3 plasmas. The precursors were selected with a variety of molecular structures (mono vs. di-silane, cyclic structures, linear structures) and functional groups (chloride, methyl, dimethyl amide, and N,N-dimethylhydrazido) to evaluate their effect on process performance and final film properties. FTIR and SIMS were used to characterize the resultant film composition and impurity level. Wet etch rate (WER) and step coverage were also measured and compared for different precursors under equivalent process conditions.

We found that the deposition characteristics and film properties displayed drastically different behaviors depending on precursor structure, types of co-reactants, RF power, as well as pressure and temperature settings. In particular, all aminosilane precursors tested require N_2 plasma for deposition, but do not deposit with NH_3 plasma. In contrast, chlorosilane precursors showed little deposition with N_2 plasma, while deposition rates with NH_3 plasma depend upon the relative position of chlorine within the precursor; terminal chlorine substituents display greater reactivity. Impurity levels are generally low for all PEALD deposited Si_3N_4 films. The notable exceptions relate to hydrogen content, which is always higher for NH_3 plasma deposited films. WER of the as-deposited films varies drastically with co-reactant species, RF power, as well as deposition temperature and pressure. Film conformality is generally better for NH_3 plasma deposited films relative to N_2 plasma films. However, WER of the NH_3 plasma films are substantially higher than that of the N_2 plasma deposited films.

2:30pm **AF-SuA-5 Atomic Layer Deposition of SiO_2 Using Tris(dimethylamino)Aminosilane Precursor and Ozone***, Charith* ***Nanayakkara,*** EMD Performance Materials*; A Dangerfield,* University of Texas at Dallas*; G Liu, C Dezelah,* EMD Performance Materials*; Y Chabal,* University of Texas at Dallas*; R Kanjolia,* EMD Performance Materials

Atomic layer deposition (ALD) of silicon oxide using aminosilanes has attracted wide attention due to their ability to overcome the challenges associated with chlorosilanes such as formation of reactive by products, particles, chlorine impurities and increased deposition rates due to the self-catalyzed reaction mechanisms of the amino groups.[1,2] Here, we have investigated the novel tris(dimethylamino)aminosilane (3DMAAS) for the ALD of SiO_2.

A cross-flow ALD reactor was used to deposit SiO_2 films on Si coupons with native oxide (~1.5 nm). 3DMAAS was delivered in vapor draw mode with ampoule at 38 - 39 °C. A typical ALD process cycle involves 2 s 3DMAAS pulse with 5 s trap time, 25 s N_2 purge, 5 s ozone pulse with 5 s trap time and 25 s N_2 purge. Saturation curves in Figure 1 suggest that 3DMAAS has a saturation behavior at 350 °C typical of an ALD precursor. There was no nucleation delay on Si(100) substrate with native oxide, with an average growth rate of about 0.94 Å/cycle at 350 °C. Post deposition XPS indicated C and N impurity levels in the bulk of the film are below the detection limit with the film composition agreeing with stoichiometric SiO_2.

Using *In-situ* FTIR spectroscopy we investigated the 3DMAAS and ozone ALD reaction mechanism on pre-annealed, OH-terminated and oxidized Si(111) surface at 250 °C. Figure 2 shows that first 3DMAAS pulse ("1st Si") reacts with surface OH groups (loss at 3745 cm^{-1}) to form $(O)_2\text{-}Si\text{-}(NMe_2)_2$ structure, as evidenced by a strong Si-O-Si band at 1110 cm^{-1}, bands associated with the C-H stretch at ∼2900 cm^{-1} and C-H asymmetric and symmetric bend modes at 1305 cm^{-1} and 1491 cm^{-1} and Si–N stretch mode at 1006 cm^{-1}. Weak absorption for the N-H stretch and bend modes of NH_2 at 3500 cm^{-1}, 3415 cm^{-1} and 1550 cm^{-1} was observed suggesting the surface termination is predominantly$(O)_2\text{-}Si\text{-}(NMe_2)_2$. First ozone pulse ("1st Oz") leads to a loss of the modes for $-(NMe_2)_2$ with the appearance of OH groups (gain at 3745 cm^{-1}). The steady state ALD process is characterized by $-(NMe_2)_2$ removal by ozone with densification of a more stoichiometric silicon oxide (TO and LO modes at 1070 and 1250 cm^{-1}), with hydroxyl termination sustaining the ALD process. The absorption at 2310 cm^{-1} could be result from CO_2 molecules resulted from ozone exposure.

This work provides insight into the ALD of SiO_2 thin film deposition using novel precursor 3DMAAS and ozone with film characterization and in-situ FTIR to further elaborate the details of the ALD reaction mechanism.

[1] Chem. Mat, 2016, 28 (5), 1247–1255

[2]Electrochem. Soc. Interface Winter 2011, 20, (4), 33-37

2:45pm **AF-SuA-6 *In situ* Infrared Absorption Study of Plasma-Enhanced ALD of Silicon Nitride using Di-*sec*-butylaminosilane and Bis(t-butylamino)silane on Silicon and Silicon Nitride Surfaces*, Fabian Pena,*** *E Mattson, C Nanayakkara, Y Chabal,* University of Texas at Dallas*; A Mallikarjunan, H Chandra, M Xiao, X Lei, R Pearlstein, A Derecskei-Kovacs,* Versum Materials, Inc

The demand for lower temperature deposition of silicon nitride (<300˚C), with the requirement that the films be uniform, conformal, and of controllable thickness, has led to the development of plasma-enhanced atomic layer deposition (PEALD). Silicon nitride films are typically deposited using aminosilane or chlorine-based silicon precursors and either NH_3 or N_2 plasma as co-reactants. In contrast to ALD using NH_3 plasma, for which the growth is hindered by the presence of hydrogen, the use of a N_2 plasma leads to good quality films at low temperatures. [ACS Appl. Mater. Interfaces, **2015**, 7 (35), 19857] However, the mechanisms involved in this process are not well understood. Experimental and theoretical work has suggested that aminosilane precursors (DSBAS and BTBAS) react on under-coordinated nitrogen bonds [J. Phys. Chem. Lett. **2015**, 6, 3610] generated by the N_2 plasma. The notion that plasma induced defects (or reactive sites) facilitate subsequent reactions has been well accepted. However, such reactive sites can also lead to recapture of the precursor by-products and oxygen contaminants, arising from plasma etching of the plasma chamber dielectric in inductively coupled plasma (ICP) sources.

In this work we use *in-situ* infrared spectroscopy to investigate each step of a PEALD process with DSBAS or BTBAS and Ar or N_2 remote plasmas. We find that, on fully H-terminated silicon Si(111) surfaces, these two aminosilane precursors do not react at temperatures up to 300˚C.[J. Phys. Chem. C, **2016**, 120 (20), 10927] Upon partial desorption of H with an Ar+ plasma, the reaction is possible, presumably due to Si dangling bonds (db). However, if most of the H is removed, DSBAS does not react as much, suggesting that the presence of both active sites (db) and hydrogen atoms is required for DSBAS reaction, as H is necessary for the release of the amino ligand (Fig. 1). The role of active sites is confirmed by time-dependent studies that allow poisoning of these sites. The situation is more complex with N_2 plasma because silicon nitride is initially formed in the surface region of the Si substrate. Therefore, we have also examined the PEALD process on high quality Si_3N_4 films. The data are consistent with the participation of surface H and active sites, but it is not possible to identify the nature of the active sites. Furthermore, the ion-induced desorption is strongly dependent on the surface composition, with no desorption (i.e. creation of active sites) when oxygen is in the Si-bond.

3:00pm **AF-SuA-7 First-Principles Understanding of Reaction Mechanisms in Plasma Enhanced Atomic Layer Deposition of Silicon Nitride*, Gregory Hartmann,*** *G Hwang,* The University of Texas at Austin*; P Ventzek,* Tokyo Electron America*; T Iwao, K Ishibashi,* Tokyo Electron Tohoku, Ltd., Japan

Atomic layer deposition (ALD) has recently received increasing attention for the growth of high-conformity silicon nitride (SiN) thin films. In particular, plasma enhanced ALD (PEALD) allows SiN deposition at substantially lower temperatures (< 400 °C) with better film properties compared to thermal ALD. These advantages make PEALD more attractive for ultra large scale integrated circuit (ULSI) device fabrication where the growth of aspect ratio independent and high-quality conformal thin dielectric films is tremendously important. The PEALD of SiN films involves a two-step process of i) silicon-containing precursor adsorption/decomposition and ii) nitridation. Chlorosilanes such as hexachlorodisilane, bis(tertiary-butyl-amino)-silane, and dicholorosilane (DCS, SiH_2Cl_2) have been utilized as Si precursors. Despite previous studies, the underlying reaction mechanisms of these Si precursors with a nitrogen containing surface during PEALD still remain uncertain. Parameters controlling the rate of growth and uniformity have been demonstrated experimentally, but without knowledge of the reaction mechanisms, direct contributions of specific process conditions cannot be explained. Using first-principles density functional theory (DFT) calculations, we have examined and identified a novel mechanism for the adsorption and decomposition of DCS on a hydrogenated SiN surface. Our study predicts that the DCS adsorption and dissociation can occur by overcoming a moderate barrier (< 0.7 eV), far lower than the prohibitively large barriers predicted for previously proposed mechanisms. Through a detailed electronic structure analysis of the reaction intermediates, we have elucidated the principles underlying the reaction mechanism, notably the hypervalent nature of Si which permits chlorosilanes to adsorb prior to dissociation. A proper model of the interactions between the SiN surface are necessary to explain the ALD process and also indicate the mechanism for the formation of side products, which has a considerable contribution to the thermodynamic favorability of the proposed mechanism. We have examined the same mechanism utilizing alternative precursors and the predicted trends are found to be corroborated with the important properties of the system. Understanding these principles allows us to develop guidelines for processing conditions, such as the importance of maintain the proper surface composition to support Si precursor adsorption and dissociation. Our study provides insight into the SiN ALD process via chlorosilanes and guidelines to control the deposition for high-quality SiN films and provides a framework for future theoretical studies of ALD mechanisms.

3:15pm **AF-SuA-8 Atomic Layer Deposition of AlN from $AlCl_3$ using NH_3 and Ar/NH_3 Plasma as Co-reactant*, Ville Rontu,*** *P Sippola, M Broas,* Aalto University, Finland*; T Sajavaara,* University of Jyväskylä, Finland*; M Paulasto-Kröckel, H Lipsanen, S Franssila,* Aalto University, Finland

ALD AlN has been typically deposited using $AlMe_3$ as the Al precursor. This has resulted in films with high amounts of carbon and hydrogen impurities, non-stoichiometric composition and poor crystalline quality although some of them have been epitaxial [1]. We report here thermal and remote plasma-enhanced processes to deposit AlN from $AlCl_3$ and NH_3 or Ar/NH_3 plasma using Picosun R200 PEALD tool.

The films were characterized with ellipsometry for thickness and refractive index, wafer curvature for stress, XRR for thickness and density, XRD for crystallinity, TOF-ERDA for stoichiometry and impurity content, and TEM for crystallinity and interfacial structure.

Growth per cycle (GPC) for the thermal process was 0.058 nm at 475 °C and 0.072 nm at 500 °C using the same parameters. GPC is limited by poor NH_3 reactivity and long NH_3 pulses are required since reactor temperature cannot be increased further. The films have refractive index of 1.9 and density of 2.8-2.9 g/cm^3. The films are partly crystalline with weak preferred orientation as seen in Supp.Fig. 1. Stresses in thermal thin films were ca. 1 GPa tensile.

Previous studies have shown both film quality [2] and stress [3] to be affected by plasma. We used Ar/NH_3 plasma at 500 °C to check these. The resulting films had a low GPC of < 0.05 nm. However, the crystallinity was much improved and stronger preferred orientation was measured with electron diffraction as shown in Supp.Fig. 2. Density was 3.2 g/cm^3 (very close to bulk value 3.26 g/cm^3) and the refractive index increased to 2.0. Typical range for ALD AlN films is 1.85-2.05 [1, 4-5]. Films had very little impurities: 6.5 at. % H, 1.7 at. % O, and 0.1 at. % Cl as measured by TOF-ERDA. These values are much lower than those obtained with $AlMe_3$ precursors, where >10 % hydrogen and few percent carbon are commonly observed [1, 4-5].

The largest effect of plasma was the stress level. It changed from highly tensile in thermal process to very high compressive stresses (-2 GPa) in the PEALD process. This is thought to originate from a subplantation effect where energetic ions hitting the surface are entrapped into growing film distorting lattice and causing compressive stresses [6]. Subplantation is supported by TOF-ERDA measurement of 0.058 at. % of argon in the film.

References:

[1] N. Nepal, et al., Appl. Phys. Lett. 103, 082110 (2013)

[2] H. B. Profijt, et al., J. Vac. Sci. Technol. A 29, 050801 (2011)

[3] H. B. Profijt, et al., J. Vac. Sci. Technol. A 31, 01A106 (2013)

[4] A. P. Perros, et al., J. Phys. D: Appl. Phys. 46, 505502 (2013)

[5] H. V. Bui, et al., J. Vac. Sci. Technol. A 33, 01A111 (2015)

[6] Y. Lifshitz, et al., Phys. Rev. B 41, 10468 (1990)

4:00pm **AF-SuA-11 Nanoscale Gettering of Excess O in CuO Nanowires via ALD Al_2O_3*,*** *S Banerjee, Z Gao, Y Myung,* ***Parag Banerjee,*** Washington University, St. Louis

CuO nanowires are an attractive platform for energy-based applications including photoelectrochemical splitting of H_2O and photocatalysis. However, there is limited understanding of the surface chemistry of these nanowires. It has been shown that CuO nanowires surfaces can be reduced stoichiometrically[1] as Cu_2O or non-stoichiometrically[2] as $Cu_{2-d}O$ depending on the severity of the thermal reduction process.

Here, we progressively map the chemical reduction of CuO nanowires, *ex situ,* by sequentially adding few monolayers of Al_2O_3 on a single CuO nanowire. The CuO nanowire is contacted electrically via electron beam lithography (**Figure 1a**), prior to the deposition experiments. Using atomic layer deposition (ALD), Al_2O_3 is deposited using trimethyl aluminum (TMA) and H_2O as reactants. The chemical changes on the nanowire surface are studied by X-ray photoelectron spectroscopy (XPS) and electrical properties of the nanowire are recorded after every monolayer deposition.

XPS fine spectra of Cu 2p reveal a clear reduction of Cu^{2+} to Cu^{1+} after only a single pulse of TMA. The O 1s fine spectra reveals the formation of Al-O and Cu^{+1}-O bonds and removal of adsorbed O species after 1 cycle of Al_2O_3 **(Figure 1b).** The Al 2p fine spectra shows a clear Al-O bond formation after ~ 3 cycles of ALD. Thus, a clear surface reduction of CuO nanowire and subsequent formation of Al_2O_3 is noted in XPS studies. This change in surface chemistry manifests itself in the electrical characteristics as a detectable photocurrent response under ambient (760 Torr) conditions; where, for a pristine CuO nanowire, no such response is previously observed (**Figure 1c**). (Figures are in the supplemental material)

References:

1. Wu, F.; Myung, Y.; Banerjee, P., Rayleigh Instability Driven Nodular Cu O Nanowires via Carbothermal Reduction of CuO Nanowires. 2015, 15, 1588-1595.

2. Wu, F.; Banerjee, S.; Li, H.; Myung, Y.; Banerjee, P., Indirect Phase Transformation of CuO to Cu2O on a Nanowire Surface. 2016, 32, 4485-4493.

4:15pm **AF-SuA-12 Temperature Dependent Growth of Alumina on Tungsten Nano-Powder***, **Kedar Manandhar**, J Wollmershauser, B Feigelson,* U.S. Naval Research Laboratory

Use of nanopowders for technological applications is growing because of their size specific properties, such as high surface area to volume ratio and quantum confinement effects, which can lead to unique physical, optoelectronic, catalytic, mechanical, and chemical properties when compared to their bulk counterpart. However for many nanopowders, a key obstacle in their path to technical application is a danger of the deterioration of their size specific properties by the environment in which they will be used. To protect such properties, nano-powder surfaces are modified by growing thin films of metal oxides. Alumina film is preferred over other metal oxides films because of easiness of forming pinhole free films. The work on growth of alumina on nano-powder is not that common as that on the flat surfaces and the few available reports have grown alumina at around 200 °C. Many nano-materials, such as polymers and PbSe are temperature sensitive, so a growth of alumina on such materials needs to be done at temperature lower than 200 °C. Our recent studies on ALD of alumina on nano-particles have demonstrated that the growth of films on nano-powder is different from that on flat surfaces, which is due to size specific properties of nano-powder1, 2. Therefore, systematic studies on temperature dependent growth of alumina film on nano-material is essential.

As a model substrate for the study of temperature dependent growth of alumina, tungsten (W) powder was utilized because this substrate/film provides high contrast between the core and shell in transmission electron microscope micrographs providing clear delineation between the film and substrate and we selected trimethylaluminum/water chemistry because it is most commonly used chemistry. Thin alumina (Al_2O_3) films from 50 ALD cycles were grown at reaction temperatures ranging from 50 to 300 °C on W-nanopowders with an average particle size of 50 nm using rotary reactor (RR) ALD. The results for alumina deposition demonstrated conformal coating of alumina with varying growth per cycle as a function of temperature. The as-prepared samples were investigated with x-ray photoelectron spectroscopy (XPS), scanning and transmission electron microscopy (SEM and TEM). Growth per cycle and properties of ALD grown alumina films on W-nanopowders as a function of reaction temperature will be presented and discussed.

Work is supported by NRL Base Program and DARPA

1. K. Manandhar, J. A. Wollmershauser., B. N. Feigelson In preparation .

2. K. Manandhar, J. A. Wollmershauser., J. E. Boercker, B. N. Feigelson J. Vac. Sci. Technol A 2016, 34, (2), 021519.

4:30pm **AF-SuA-13 Critical Aspects in Fluid Bed ALD***, **Markus Bosund**, R Peltonen, E Maiorov,* Beneq Oy, Finland*; M Jauhiainen,* Beneq Oy*; E Salmi,* Beneq Oy, Finland*; S Sneck,* Beneq Oy

Atomic layer deposition is an effficient method for conformal particle coating specially if the particle size is small and the grown layer is thin. One of the most critical factors in many particle coating methods is the amount of particles coated (APC=coated particles/total particles). It is possible to coat very small quantities of particles using a traditional flow type ALD reactor whereas, a special reaction chamber design is required when high APC values with greater particle quantities are required. Especial attention should be given to the separation of the particles during coating. Fluid bed reactor (FBR) ALD with continuous vibration and fluidization of the particles is a well-known method to achieve this.

The limits of fluid bed ALD were studied by investigating the effect of following process parameters on the APC value: pulse time, purge time, fluidization flow and amount of particles. The precursor molecules and by-products were analyzed during the deposition using a MKS residual gas analyzer (RGA). Beneq TFS 200 equipped with double wall FBR reactor was used in the depositions. Commercially available SiO_2 spheres 9-13 mm (Sigma Aldrich) were coated with Al_2O_3 using trimethylaluminum and water as the precursors. A scanning electron microscope with energy-dispersive X-ray spectroscopy was used for the particle analysis.

The limits of FBR ALD were studied by investigating the effect of process parameters on the APC value. The precursor molecules and by-products were analyzed during the deposition using a MKS residual gas analyzer (RGA). Beneq TFS 200 equipped with double wall FBR reactor was used in the depositions. Commercially available SiO_2 spheres 9-13 mm (Sigma Aldrich) were coated with Al_2O_3 using trimethylaluminum and water as the precursors. A scanning electron microscope with energy-dispersive X-ray spectroscopy was used for the particle analysis. Pulse time, purge time, fluidization flow and amount of particles were observed to have a significant effect on the APC value.

4:45pm **AF-SuA-14 Super-Conformal Growth by ALD***, **Roy Gordon**,* Harvard University, USA*; J Feng,* Harvard University

ALD normally covers substrates conformally, with the outer surfaces of the films faithfully replicating the topography of the substrates. We now report that a process for aluminum-catalyzed ALD of silicon dioxide actually produces super-conformal growth. This means that the growth per cycle is larger inside recessed, concave features than it is on flat surfaces or on protruding, convex features. One result of this “bottom-up” growth mode is that the top surface of the film becomes smoother than the surface of the substrate on which it was grown.

Another consequence of this growth mode is that trenches with strictly parallel sides can be filled without any trace of a seam or void at the center-line of the trench.

A mechanism is proposed for this super-conformal ALD process, based on ALD of silica catalyzed by aluminum.[1] Smoothening or leveling effects have also been observed in “bright” metal electroplating, and in chemical vapor deposition of metals. The underlying mechanisms for all of these super-conformal coating processes will be compared and contrasted.

1. Dennis Hausmann, Jill Becker, Shenglong Wang and Roy G. Gordon, *Science***298**, 402 (2002)

5:00pm **AF-SuA-15 Thin Film Conformality Profile Analysis with Microscopic All-Silicon Lateral High Aspect Ratio Structures***, **Riikka Puurunen**, O Ylivaara, K Grigoras, M Ylilammi,* VTT Technical Research Centre of Finland, Finland

The downscaling of future semiconductor devices with increasing 3D character leads to increasing demand of highly conformal thin films. Atomic layer deposition (ALD), based on the use of repeated, self-terminating reactions of typically at least two compatible reactants on a solid substrate, is often the only technique that can meet the conformality specifications. Conformal films made by ALD are also needed in other fields with intrinsic three-dimensionality requirements, such as microelectromechanical systems (MEMS), energy applications, and high-surface-area catalysts.

This work continues on earlier work on conformality analysis [1–3]. All-silicon microscopic lateral high-aspect-ratio (LHAR) structure prototypes have been designed and fabricated with an improved design (PillarHall Prototype 3). The LHAR structures consist of a lateral gap of typically 500 nm (in some cases, 100 to 2000 nm) in height under a polysilicon silicon membrane, supported by silicon pillars. The gap length varies from 1 to 5000 µm, giving aspect ratios (length vs height) for the typical ~500 nm gap of 2:1 to 10 000:1.

In this work, we analyse how sensitive the measured thickness profile is to changes in (i) test-structure-related factors, such as test structure length, and (ii) analysis-related factors, such as spot size of the measurement, using the widely-studied [4,5] Me_3Al/H_2O and $TiCl_4/H_2O$ ALD processes as test vehicles. According to preliminary results, the test structure length in the range 500 to 5000 µm has no significant impact on the results. An increasing measurement spot size leads to a softer apparent film termination profile and a smaller negative slope value at the half-thickness-penetration-depth (HTPD). A sufficiently small spot size of the measurement is critical for extracting kinetic parameters from the thickness profile.

Acknowledgements: The authors are grateful to Mari Laamanen and Jaakko Saarilahti for help with process integration, Meeri Partanen and Tuomo Honkaharju for clean room processing, Harri Pohjonen for mask drawing, James Dekker for dry etch specialist advice and Virpi Korpelainen for discussions regarding error analysis. Funding for this work comes from Academy of Finland's Finnish Centre of Excellence in Atomic Layer Deposition and Tekes PillarHall project.

[1] Gao et al., J. Vac. Sci. Technol. A, 33 (2015) 010601 (5 pages).

[2] Mattinen et al., Langmuir 32 (2016) 10559-10569.

[3] Puurunen, IEEE Xplore, in press (2016).

[4] Puurunen, J. Appl. Phys. 97 (2005) 121301.

[5] Miikkulainen et al., J. Appl. Phys. 113 (2013) 021301.

5:15pm **AF-SuA-16 ALD onto Particles: Batch and Continuous Processes for Industry***, **Joseph Spencer II**,* ALD NanoSolutions, Inc. **INVITED**

Process and equipment design are critical components to the emerging field of ALD onto particles. While industrial semiconductor ALD processes and tools are designed for standardized, reproducible rigid substrates, the diversity of particle substrates necessitates a variety of engineering approaches. As ALD coated powder products require different ALD cycle thicknesses, production quantities, particle sizes, and possible substrate/precursor interactions, there is no single best design. This talk will focus on various process approaches for ALD onto particles, ranging from prototype batch reactors to continuous, spatial production systems for high volume industries.

Atomic Layer Etching

Room Plaza D - Session ALE-SuA

Atomic Layer Etching Session I (1:30-3:30 pm) and II (4:00-5:30 pm)

Moderators: Geun Young Yeom, Sungkyunkwan University, Korea, Satyarth Suri, Intel Corporation, Ankur Agarwal, KLA-Tencor

1:30pm **ALE-SuA-1 Atomic Layer Processes to Enable the Atomic Scale Era***, **Robert Clark**, K Tapily, J Smith, N Mohanty, S Kal, D Newman, S Consiglio, D O'Meara, K Maekawa, A Mosden, A deVilliers, P Biolsi, T Hurd, C Wajda, G Leusink,* TEL Technology Center, America, LLC **INVITED**

As Figure 1 below demonstrates, the implementation of FinFETs at the 22nm node introduced a new minimum patterned feature size, fin half pitch, into CMOS high volume manufacturing. In addition, the 22nm node marked the initial use of self-aligned multiple patterning for CMOS features, which was required in order to pattern features below the limit of resolution of 193nm immersion (193i) lithography. At the 14nm node Intel's patterned fin feature size fell below 100 atoms in width, marking the beginning of what can be termed the atomic scale era in CMOS manufacturing.[1] Continued scaling is expected to drive all of the critical feature sizes below 100 atoms wide in the near future for CMOS and memory devices as well. Considering features in terms of atoms illuminates a fundamental roadblock to continuing linear scaling: atoms do not scale.

Depositing and etching films used to manufacture atomic scale devices requires atomic level control. Atomic layer deposition and etch (ALD and ALE), including quasi-ALD and quasi-ALE, processes are therefore finding increasingly more use within semiconductor manufacturing. Patterning and aligning features below the lithographic limit requires clever process designs and the inherent control, conformality, and uniformity afforded by ALD and ALE. Likewise, depositing and etching functional films which are in many cases an order of magnitude thinner than the smallest feature sizes can only be controlled using ALD and ALE. Highly selective ALD and ALE processes including area and material selective processes, as well as anisotropic depositions and etches are sought to reduce the reliance and overburden needed for chemical mechanical planarization (CMP) in order to realize bottom up alignment. In this talk we will describe the challenges driving ALD and ALE into manufacturing and provide examples of how we are meeting those challenges with processes that will enable scaling to the 3nm node and beyond.

Figure 1. Historical and Projected Atomic Feature Sizes (half pitch/0.235 nm/Si atom) in CMOS High Volume Manufacturing. Projected feature sizes are based on Intel historical trend

S. Natarajan *et al*, IEDM Tech Dig., pp. 71-73, 2014.

2:00pm **ALE-SuA-3 Thermal Atomic Layer Etching of SiO_2 by a "Conversion-Etch" Mechanism***, J DuMont, A Marquardt, A Cano, **Steven M. George**,* University of Colorado

SiO_2 is an important semiconductor material and SiO_2 etching is needed in many steps during semiconductor manufacturing. SiO_2 atomic layer etching (ALE) has been demonstrated earlier using periodic exposures of C_4F_8 plasma synchronized with Ar^+ ion bombardment [1]. In this work, we report a thermal process for SiO_2 ALE based on sequential exposures of trimethylaluminum (TMA) and hydrogen fluoride (HF) at 300°C. The etching mechanism involves the conversion of SiO_2 to Al_2O_3/aluminosilicate by TMA and the subsequent etching by sequential fluorination and ligand-exchange reactions [2].

Ex situ x-ray reflectivity measurements revealed that the etch rate was dependent on reactant pressure. SiO_2 etch rates of 0.027, 0.15, 0.20, and 0.31 Å/cycle at 300°C were observed at reactant pressures of 0.1, 0.5, 1.0 and 4.0 Torr, respectively. *Ex situ* spectroscopic ellipsometry measurements agreed with these etch rates versus reactant pressure. *In situ* Fourier transform infrared (FTIR) spectroscopy investigations also observed SiO_2 etching that was dependent on reactant pressure. The FTIR studies showed that the TMA and HF reactions displayed self-limiting behavior. In addition, the FTIR spectra revealed that an Al_2O_3/aluminosilicate intermediate was present after the TMA exposures.

The Al_2O_3/aluminosilicate intermediate is consistent with a "conversion-etch" mechanism where SiO_2 is converted by TMA to Al_2O_3, aluminosilicates and reduced silicon species. *Ex situ* x-ray photoelectron spectroscopy (XPS) studies confirmed the reduction of silicon species after TMA exposures. Following the conversion reaction, HF can fluorinate the Al_2O_3 and aluminosilicates to species such as AlF_3 and SiO_xF_y. Subsequently, TMA can remove the AlF_3 and SiO_xF_y species by ligand-exchange reactions and then convert additional SiO_2 to Al_2O_3. Other conversion reactions may be helpful to transform various materials that cannot be directly etched to different materials that can be etched using thermal ALE.

[1] D. Metzler, R.L. Bruce, S. Englemann, E.A. Joseph and G.S. Oehrlein, "Fluorocarbon Assisted Atomic Layer Etching of SiO_2 Using Cyclic Ar/C_4F_8 Plasma", *J. Vac. Sci. Technol. A* **32**, 020603 (2014).

[2] Y. Lee, J.W. DuMont and S.M. George, "Trimethylaluminum as the Metal Precursor for the Atomic Layer Etching of Al_2O_3 Using Sequential, Self-Limiting Thermal Reactions", *Chem. Mater.* **28**, 2994 (2016).

2:15pm **ALE-SuA-4 The Challenges and Opportunities in Plasma Etching of Functionally Enhanced Complex Material Systems***, **Jane Chang**,* UCLA **INVITED**

The introduction of new and functionally improved materials into silicon based integrated circuits is a major driver to enable the continued down-scaling of circuit density and performance enhancement in analog, logic, and memory devices. The top-down plasma enhanced reactive ion etching has enabled the advances in integrated circuits over the past five decades; however, as more etch-resistive materials are being introduced into these devices with more complex structures and smaller features, atomic level control and precision is needed in selective removal of these materials. These challenges point to the growing needs of identifying and developing viable etch chemicals and processes that are more effective in patterning complex materials and material systems such as multiferroics, magnetic materials and phase change materials.

In this talk, a generalized approach based on combined thermodynamic assessment and kinetic validation is presented to identify and validate the efficacy of various plasma chemsitries. Specifically, potential reactions between the dominant vapor phase/condensed species at the surface are considered at various temperatures and reactant partial pressures. The volatility of etch product was determined to aid the selection of viable etch chemistry leading to improved etch rate of reactive ion etching process. Based on the thermodynamic screening, viable chemistries are tested experimentally to corroborate the theoretical prediction. Some of the above mentioned material systems such as magnetic materials used in non-volatile memory devices are used as examples to demonstrate the broad applicability of this approach.

2:45pm **ALE-SuA-6 A Novel Process for Atomic Layer Etching of ZnO using Acetylacetone and Remote O_2 Plasma***, **Alfredo Mameli**, M Verheijen, A Mackus, W Kessels, F Roozeboom,* Eindhoven University of Technology, Netherlands

Along with the drive for anisotropic processes of Atomic Layer Etching (ALE) there is interest in isotropic counterparts.[1] Therefore, in this work, we demonstrate a novel plasma-assisted ALE process for ZnO which is driven by radicals and therefore anticipated to be isotropic. The process consists of alternating doses of acetylacetone (Hacac) and O_2 plasma, interleaved by Ar purges steps. It is expected that Hacac forms volatile complexes by metal oxide surface chelation (e.g. $Zn(acac)_2$), whereas the O_2 plasma is used as a cleaning step to remove unreactive precursor fragments and to reset the surface for the next etching cycle[2]. This hypothesis is supported by a synergy test of the ALE process, which proved that only the alternated doses of Hacac and O_2 plasma led to etching, whereas neither Hacac, nor O_2 plasma alone resulted in ZnO etching.

The ZnO layer thickness measured by *in-situ* and *ex-situ* ellipsometry was found to decrease linearly with the number of cycles with an etch per cycle (EPC) of ~0.08 nm/cycle. This was corroborated by *ex-situ* FTIR and X-ray diffraction measurements. The ALE process was tested over a range of temperatures between 150 and 300°C. X-ray photoelectron spectroscopy demonstrates that the ZnO stoichiometry is preserved throughout the etching process, without any contamination of the film. The same ALE process was also used for etching other metal oxides such as CuO_x, Al_2O_3 and In_2O_3 yielding EPC values in a range between 0.01 and 0.08 nm/cycle. Furthermore, we demonstrate that this ALE process is selective over SiO_2. This was demonstrated by locally depositing SiO_2 on top of the ZnO to serve as a hard mask for the etching. The selectivity stems from the fact that Hacac does not chemisorb on SiO_2 as demonstrated by independent wet chemistry experiments and FTIR measurements conducted on the ZnO and SiO_2 powders. Finally, we will discuss the influence of the starting material properties, as preliminary investigations indicated that the crystallinity of the material to be etched can affect the EPC.

We believe that this novel plasma assisted-ALE process can be extended to other materials. This chemistry does not involve halogens or halides, which minimizes potential contamination issues. It is important to realize that this ALE chemistry gives selectivity for a different set of materials as compared to halide-based isotropic ALE processes, and therefore represents a valuable addition to the ALE toolbox.

[1] Zywotko, D. R. *et al.*, Chem. Mater. **29**, 1183 (2017)

[2] George, M. A.,*J. Electrochem. Soc.*,**143**, 3257 (1996)

3:00pm **ALE-SuA-7 Determining the Benefits and Limitations of Atomic Layer Etching: A Modeling Investigation***, C Huard,* University of Michigan*; Y Zhang, S Sriraman, A Paterson,* Lam Research Corp.*; **Mark Kushner**,* University of Michigan **INVITED**

Atomic layer etching (ALE) techniques are providing several benefits over conventional etching in maintaining critical dimensions, reducing damage and improving selectivity. During conventional etching, simultaneous synergistic reactions between neutral radicals and ions produce continuous etching. Obtaining the benefits of ALE requires sub-cycles separately consisting of self-limiting reactions – typically passivation and etching. In the ideal case, etching results from a synergy between the ALE sub-cycles, with there being no continuous etching due to simultaneous fluxes of radicals and ions during either cycle. In practice, it is difficult to produce conditions that result in this ideal, self-limited reaction sequence.

In this presentation, results will be discussed from a computational investigation of ALE of silicon in Ar/Cl_2 plasmas and SiO_2 in $Ar/C_4F_8/O_2$ plasmas. Reactor scale simulations using the Hybrid Plasma Equipment Model provide the magnitude, energy and angular distributions of reactant fluxes to a wafer. Feature scale modeling was performed using the 3-dimensional Monte-Carlo Feature Profile Model (MCFPM). An important aspect of modeling ALE is representing the finite thickness of the mixing layer formed by ion bombardment. By tracking particles as they penetrate the solid surface, surface mixing and damage are stochastically modeled in the MCFPM.

Investigations were performed of ALE using ideal and non-ideal conditions to determine the possible benefits and limitations of the ALE process. For ideal conditions, aspect ratio dependent etching (ARDE) could be essentially eliminated and surfaces retained their initial smoothness. Introducing continuous etching pathways during ALE of silicon gave rise to ARDE and increased (or introduced) surface roughness. The impact of these non-idealities were investigated in the ability of ALE to clear the poly-silicon gate etch step in 3D finFETs with varying aspect ratios. Results indicate that the ALE process requires less over-etch time than a similar continuous etch, in spite of the non-ideal reaction pathways that result from using realistic reactant fluxes. The impact of reactor scale non-uniformity of fluxes and ion energy distributions was studied for silicon trench etching, demonstrating the limits of flux and energy non-uniformities that can be remediated by the ALE process. The damage induced by ions during over-etch was studied in silicon and SiO_2 when using ALE to clear 3D contacts after a continuous main etch.

Work was supported by Lam Research Corp., DOE Office of Fusion Energy Science and the National Science Foundation.

4:00pm **ALE-SuA-11 ALE TBD 2***, **Nitin Ingle**,* Applied Materials **INVITED**

Please submit your abstract to Della Miller, della@avs.org, immediately for inclusion in the program.

4:30pm **ALE-SuA-13 Significant Improvements of CD Uniformity and ARDE in ODL Mask Etching using a Self-limiting Cyclic Etch Approach***, **Barton Lane**, P Ventzek,* Tokyo Electron America*; A Ranjan, V Rastogi,* TEL Technology Center, America, LLC

Critical dimension global and local uniformity nearing a few atom widths in carbon based hard masks is critical for < 7 nm device fabrication. This is very challenging for continuous and pulsed plasma etch processes. We show that a cyclic etching approach leads to striking improvements in both global and local uniformity. The global uniformity refers to uniformity on the scale length of cm and is typically due to variations in plasma and/or radical densities across the wafer; it is measured by the variation in the critical dimension (CD) and is often termed CD uniformity (CDU). Local uniformity refers to the uniformity between nearby features which have different local geometries for example nested versus isolated features and is often termed aspect ratio dependent etching (ARDE). We consider the etch of a patterned hydrocarbon spin cast film (ODL) using an argon/oxygen chemistry. Such films are used as part of a trilayer mask system and are common in patterning applications. The cyclic scheme breaks the etch into its two fundamental steps: an oxidation step in which oxygen moieties are introduced into the polymer matrix; and a volatilization step in which the oxidized moieties are detached from the polymer matrix. Using pairs of coupons placed in regions of a test bed reactor with significantly different plasma and neutral species densities, we show that using the cyclic scheme relative to a continuous process, that the CDU can be improved significantly. The underlying reasons for the improvement are the self-limiting nature of both the oxidation and the volatilization steps in the etch process. We show by "*in situ* OES SIMS" experiments how this self-limitation process occurs in the case of the argon and oxygen chemistry. In brief, the oxygen containing step leads to an oxidized layer; the argon only sputter step volatilizes this oxidized layer and then rapidly creates a carbonized, hydrogen depleted layer which has a low etch rate following its initial formation. The self-limitation in the argon sputter step is due to the low etch rate of this carbonized layer. In the oxygen step the high density of the carbonized layer prevents the diffusion of oxidizing species into the polymer interior after an initial saturation of the surface with oxidized moieties. This leads to a self-limiting process for a lean chemistry (low oxidizing species density).

4:45pm **ALE-SuA-14 Nanometer-Scale III-V 3D MOSFETs***, **Jesus del Alamo**, W Lu, X Zhao, D Choi, A Vardi,* MIT **INVITED**

In the last few years, as Si electronics faces mounting difficulties to maintain its historical scaling path, transistors based on III-V compound semiconductors have emerged as a credible alternative. To get to this point, fundamental technical problems had to be solved though there are still many challenges that need to be addressed before the first non-Si CMOS technology becomes a reality. Among them, harnessing the outstanding electron transport properties of InGaAs, the leading n-channel material candidate, towards a high-performance nanoscale MOSFET has proven difficult. Introducing a new material system is not the only challenge, scalability to sub-10 nm gate dimensions also demands a new 3D transistor geometry. InGaAs FinFETs, Trigate MOSFETs and Nanowire MOSFETs have all been demonstrated but their performance is still lagging Si. At MIT, we have focused in the last few years in developing etching technology for high aspect ratio III-V fins and nanowire to support the development of sub-10 nm 3D MOSFETs. We have demonstrated fins as narrow as 15 nm with an aspect ratio of ~10 and nanowires with a diameter of 20 nm and an aspect ratio of ~11. Following RIE, our nanowires and fins are trimmed using digital etch. This consists of an oxidation step in O2 plasma and an oxide removal step in a diluted acid. By separating both steps, the process is self-limiting and yields a very precise etching rate (in our case, about ~1 nm/cycle). We have also shown that digital etch improves the sidewall electrical characteristics. Using digital etch, we have been able to demonstrate InGaAs FinFETs with 7 nm wide fins and record transconductance characteristics. Regarding nanowires, the high surface tension of water-based acid makes it impossible to reduce their diameter below ~12 nm. Beyond this dimension, the nanowires collapse due to strong mechanical forces during digital etch and the yield of the process quickly drops to zero. We have recently solved this problem by using alcohol-based acids with a much lower surface tension. Using the same oxidation step, the new technique shows an etch rate of 1 nm/cycle, identical to the conventional approach. Sub-10 nm fins and nanowires with a high yield and mechanical stability have been achieved. InGaAs nanowires with diameter of 5 nm and an aspect ratio > 40 have been demonstrated. The new technique has also been successfully applied to InGaSb-based heterostructures, the first demonstration of digital etch in this material system. Vertical InGaAs nanowire gate-all-around MOSFETs with a subthreshold swing of 70 mV/dec at V_{DS} = 50 mV have been obtained demonstrating the good interfacial quality that the new technique provides.

5:15pm **ALE-SuA-16 Atomic Layer Etch Processes Developed in an ICP/RIE Etching System for Etching III-V Compound Semiconductor Materials***, **Xu Li**, Y Fu, S Peralagu, S Cho, K Floros, D Hemakumara, M Smith,* University of Glasgow, UK*; I Guiney,* University of Cambridge, UK*; D Moran,* University of Glasgow, UK*; C Humphreys,* University of Cambridge, UK*; I Thayne,* University of Glasgow, UK

In this work, we compare several atomic layer etch (ALE) processes developed in an ICP/RIE etching system based on Cl_2/Ar and HBr/Ar chemistries for etching GaN, AlGaN, InAlN, InGaAs, and InGaSb. These processes will be very important in the realisation of various energy efficient electronic devices including gate recess etching of GaN power transistors, and controlled sidewall cleaning in InGaAs and GaInSb finfets and nanowires for continued logic scaling.

Investigations were carried out in an Oxford Instrument PlasmaLab Inductively Coupled Plasma (ICP) etching system with repeat loop function. The etching chemistry is based on the self-limited formation of Al, Ga, In, Sb chlorides or bromides on the semiconductor surface as a consequence of exposure in Cl_2 or HBr gases or plasmas during the sample surface modification step of the ALE cycle. This is followed by an Ar plasma selective surface layer removal step at an optimized RF power level at which the Ar plasma only removes the surface chlorides or bromides. Reducing the power of the Ar plasma process is vital to minimizing damage to the underlying III-V materials.

A parametric exploration of the process space showed that an ALE window can be established for both the Cl_2 and HBr based processes by simply flowing the reactive gas across the sample surface – it is not necessary to establish a plasma of the reactive gases. Further, that given the response time of mass flow controllers on the etch tool, a minimum gas flow time of 2s was required to ensure process stability and repeatability. This relatively long dwell time meant that the reactive gases had to be diluted with Ar – optimal dilution ratios were found to be 8:42 Cl_2:Ar and 6:44 HBr:Ar; all at chamber pressures of 50 mTorr, total gas flow of 50 sccm, and platform temperature of 20°C. Ultimately, processes to produce repeatable removal rates of 0.13 nm/cycle were obtained in this way. Experiments also showed that the Cl_2 and HBr processes modified the III-V surface layers differently, due to the relative volatilities of the chlorine and bromine compounds formed on the III-V material surfaces. The Cl-based chemistry required an Ar plasma RF power of 33 W for surface layer removal, whereas this could be reduced to 20 W for the HBr-based chemistry. This is very important in reducing process induced damage. Experiments showed that there no observable change in either the electron mobility or channel carrier concentration in an AlGaN/GaN HEMT for RF power levels for the Ar plasma of less than 25 W at a chamber pressure of 50 mTorr; therefore an HBr-based ALE process is most appropriate for use in the realization of III-V devices.

5:30pm **ALE-SuA-17 Enhanced Thermal ALE of Aluminum Oxide Combined with ALD for UV Optical Applications***, **John Hennessy**,* Jet Propulsion Laboratory, California Institute of Technology*; C Moore,* University of Colorado - Boulder*; K Balasubramanian, A Jewell,* Jet Propulsion Laboratory, California Institute of Technology*; K France,* University of Colorado - Boulder*; S Nikzad,* Jet Propulsion Laboratory, California Institute of Technology

This work demonstrates the development of a thermal atomic layer etching procedure using alternating exposures of trimethylaluminum and anhydrous hydrogen fluoride that is used to controllably etch aluminum oxide. This ALE process is modified relative to existing HF-based methods through the use of an intermediate reaction during TMA exposure with a conditioning film of lithium fluoride. This is shown to enhance the loss of fluorine surface species and results in conformal layer-by-layer etching of deposited aluminum oxide films. The Al_2O_3 etch rate was measured over a temperature range of 225 to 300 °C, and was observed to increase from 0.8 to 1.2 Å per ALE cycle at a fixed HF exposure. The variation in etch rate is the result of increased surface fluorination during HF exposure, and the extent of this fluorination has a clear dependence on the total effective HF dose delivered per ALE cycle. Nevertheless, the process is shown to be scalable to large area substrates with a post-etch uniformity of better than 2% measured on 125 mm diameter wafers.

This ALE process utilizes the same chemistry previously demonstrated in the ALD of AlF_3 thin films, and can therefore be used to remove the surface oxide from metallic aluminum and replace it with thin fluoride layers in order to improve the performance of ultraviolet aluminum optical components by reducing the loss associated with the oxide layer. We will discuss how this approach has applications in the development of vacuum UV instruments, in next-generation UV mirrors for JPL-NASA astrophysics missions, and in enhancing the performance of nanostructured metallic Al for UV plasmonic applications. The efficacy of the technique is demonstrated by measurements of UV reflectance on evaporated aluminum films undergoing the described ALE + ALD procedure. We will present material characterization by x-ray photoelectron spectroscopy, ellipsometry, and atomic force microscopy; and we will discuss the mechanism associated with the etch enhancement produced by co-reaction with LiF.

Area Selective ALD
Room Plaza F - Session AS-SuA

Area Selective Deposition I: Deactivation (1:30-3:30 pm)/Inherent Selectivity, Activation, Deactivation (4:00-5:30 pm)

Moderators: Suvi Haukka, ASM Microchemistry Ltd., Finland, David Thompson, Applied Materials, Erwin Kessels, Eindhoven University of Technology, the Netherlands, Adrie Mackus, Eindhoven University, Netherlands

1:30pm **AS-SuA-1 Area Selective Deposition Using Spatial ALD and Polymer Patterns***, **Carolyn Ellinger**,* Eastman Kodak Company **INVITED**

In our laboratory, we use polymers in combination with inorganic metal oxides deposited by spatial atomic layer deposition (Spatial ALD, SALD) in the fabrication of electronic devices and circuits. This presentation will focus on the interaction between Spatial ALD metal oxide film growth and the properties of polymer thin films. We have previously presented on the process space of spatial ALD and selective area deposition in the context of our "patterned-by-printing" approach to printed electronics. In contrast, this presentation will provide a more general overview of the interaction-space and the resultant patterns and structures (and associated potential applications). Where possible, comparisons will be made to the more common processes of temporal ALD and selective area deposition using self-assembled monolayers (SAMs).

We will begin with a brief overview of SALD and the characteristics that distinguish it from chamber-based temporal ALD. Building on that understanding, we will review the range of potential interactions between polymer thin films and the SALD precursor chemistries (specifically TMA, DEZ, DMAI, and H_2O) and process conditions. The conversation will then move to the discussion of useful polymers for selective area deposition – reviewing both specific polymers as well as more generalized polymer properties. A range of patterning techniques and resultant patterns and structures will also be reviewed.

The implementation of SALD used in our laboratory operates at atmospheric pressure conditions, and is capable of coating a wide range of substrates – from rigid wafers and flat panels to flexible substrates that are either singulated or a continuous web. By using polymer deposition techniques (such as printing methods) that are similarly compatible with a broad range of substrates, the patterns and structures reviewed can be translated to nearly any substrate. There is promise for implementing these techniques (or their analogs) in existing manufacturing environments, as well as for using them as a basis for the development of alternative manufacturing lines.

2:00pm **AS-SuA-3 Area-selective ALD of Silicon Oxide using Acetylacetone as Inhibitor in a Three-step Cycle***, **Adrie Mackus**, A Mameli, M Merkx, B Karasulu, W Kessels,* Eindhoven University of Technology, Netherlands

Area-selective ALD is attracting renewed attention in the last few years because of its envisioned application in self-aligned fabrication schemes for future nanoelectronics. In this contribution, a new approach for achieving area-selective ALD will be introduced, based on the use of inhibitor molecules in a three-step (ABC) ALD process. This approach is inspired by previous work in which similar inhibitor molecules were used to enhance the doping efficiency of ALD-grown films by blocking adsorption sites.[1] Area-selective ALD can be obtained using such an ABC ALD process, in the case where the inhibitor molecule selectively adsorbs on specific materials (in step A), and blocks the precursor adsorption in the subsequent pulse (in step B).

Area-selective ALD of SiO_2 has been demonstrated for an ALD process consisting of acetylacetone (Hacac) inhibitor (A), $H_2Si[N(C_2H_5)_2]_2$ precursor (B), and O_2 plasma (C) pulses. This process results in immediate growth with a growth rate of 0.09 nm/cycle on GeO_2 and SiO_2, and significant nucleation delays on Al_2O_3, HfO_2, and TiO_2, as determined from *in-situ* spectroscopic ellipsometry measurements. The nucleation behavior of this SiO_2 process on GeO_2 and Al_2O_3 was corroborated by X-ray photoelectron spectroscopy (XPS). In addition, the selectivity of the ALD growth was demonstrated on samples with patterned Al_2O_3 on GeO_2. Density functional theory (DFT) simulations suggest that Hacac adsorbs readily on Al_2O_3, while the adsorption on SiO_2 itself is an endothermic reaction with a high activation barrier. *In-situ* Fourier transform infrared spectroscopy (FTIR) studies confirmed that Hacac chemisorbs on Al_2O_3 and blocks $H_2Si[N(C_2H_5)_2]_2$ precursor adsorption. Conversely, only a small amount of Hacac adsorption was detected on SiO_2.

A unique feature of this new approach for area-selective ALD is that it distinguishes between the growth on different metal oxide surfaces (e.g. GeO_2/SiO_2 versus $Al_2O_3/HfO_2/TiO_2$). Moreover, in contrast to most other area-selective ALD approaches, it is compatible with plasma-assisted or ozone-based ALD. Both of these features open up new application opportunities for area-selective ALD. It is expected that the approach can be extended to other materials, and potentially allows for tuning the selectivity by selecting the inhibitor molecule.

[1] A. Yanguas-Gil, J.A. Libera, and J.W. Elam, Chem. Mater. **25**, 4849 (2013).

2:15pm **AS-SuA-4 Evaluation of Different Nanoimprint Resists for a use in Area-selective Atomic Layer Deposition of Selected Materials***, R Ritasalo,* Picosun Oy, Finland*; M Messerschmidt,* Micro Resist Technology GmbH*; K Grigoras,* VTT, Finland*; S Ek,* Picosun Oy, Finland*; E Østreng,* Picosun Oy*; M Prunnila,* VTT*; **Tero Pilvi,*** Picosun Oy

Nanopatterns of diverse materials are of much interest and have great relevance as a means of enhancing performance, enabling miniaturization, or as determining components of functional devices or interfaces. Several top-down and bottom-up techniques have been attempted to meet these goals, however with varying degrees of success [1]. In this study we employ a combination of nanoimprint lithography (NIL) and area-selective atomic-layer deposition (ALD); in which NIL is used to produce suitable patterned polymeric templates for area-selective ALD enabling thus a patterned ALD growth.

ALD requires typically the presence of OH-groups on the sample surface in order to get growth initiated. The lack of active surface sites e.g. in the case of hydrophobic polymer layers inhibits the nucleation process. This method would enable growth of patterned ALD wafers and would therefore eliminate one costly mask layer step in the fabrication process.

The main goal of this study is to evaluate and to identify those NIL resists that feature effective ALD growth inhibition properties and to test the concept with NIL-patterned templates and using PICOSUN™ ALD technology. For these investigations in total four NIL resists with different chemical compositions were chosen. The selection of ALD materials included oxides of ZnO, HfO_2, ZrO_2, Ta_2O_5, TiO_2 and Al_2O_3, as well as Pt as a metallic candidate. After the ALD step the samples were treated by oxygen plasma to evaluate their performance in terms of the area selectivity. Examples of this empirical approach are presented in Fig 1. In those cases in which a compact ALD coating layer is formed onto to the organic NIL resist, the oxide layer acts as an etch barrier for the oxygen plasma, so that no NIL resist is removed (Fig. 1b,c) while in those cases where no compact oxide layer is deposited, the oxygen plasma will attack and remove the organic NIL resist (Fig. 1a).

The results revealed that the type of applied NIL resist, the type of investigated ALD material and also the applied ALD parameters had all significant effects on the ALD growth inhibition capability. Usually the selectivity was few tens of cycles but at best it reached over 200 cycles. The most promising candidates for a use in area-selective materials by ALD were ZnO, HfO_2, ZrO_2 and one of the two studied TiO_2 and Al_2O_3 processes. We also found, that in such cases where only a limited area-selectivity of the NIL resist toward the ALD process is observed, nanopatterns can also be effectively fabricated (Fig. 2).

[1] Suresh et al., J. Phys. Chem. C116 (2012) 23729−23734.

Acknowledgements:The research has received funding from the EU FP7 project QUANTIHEAT (604668)

2:30pm **AS-SuA-5 Developing a Full Wafer-scale Approach Towards High ALD Selectivity on Copper vs Low-K (and Oxides) using a Single ALD/SAMS Platform***, **Laurent Lecordier,*** Ultratech*; S Armini, S Herregods,* IMEC, Belgium

Implementation of robust production-scalable methodologies for area-selective deposition (ASD) could have a significant impact on simplifying process flows during device fabrication. However process integration at the wafer scale (i.e., 200-300 mm diam.), including surface pre-treatment, surface de-activation followed by selective ALD has remained elusive. In this work, we present our results towards achieving excellent selectivity of HfN_x ALD on copper vs. low-K (and oxides) using C18 octadecanethiol (ODT) as a blocking layer.

SAMS and ALD depositions were performed in a commercial Ultratech CNT Savannah platform equipped with a SAMS kit optimized for delivery of large C18 molecules in gas phase. *In-situ* spectroscopic ellipsometry (SE) was used to optimize the process performance during the different steps including reduction of the native copper oxide, ODT passivation and selective ALD growth. Results were validated with *ex-situ* XPS, RBS and SEM characterization.

Several methods were investigated to rapidly reduce the native copper oxide including exposures to ethanol as well as TMA and TDMAHf. ALD-inhibiting films were deposited in gas phase with short (<900s) ODT exposures. Temperature and reduction methods were shown to have a significant impact on ODT growth varying from saturating single monolayer growth to non-self limited growth with thicknesses varying from 30 to 80Å.

In-situ SE measurements during HfN_x ALD on ODT-treated copper and low-K showed a high degree of selectivity with HfN_x growth delayed for up to 480 ALD cycles on copper, while no growth inhibition was detected on ODT-treated low-K and oxides. Interestingly the non self-limited ODT films were shown to be the best ALD-growth inhibitors.

The authors will discuss the benefits and challenges associated with this rapid gas-phase methodology, emphasizing process time and wafer scalability to 300 mm, dose control challenges associated with delivery of large C18 SAMS molecules, and the significant impact of self-limited vs. non self-limited ODT growth on ASD performances.

2:45pm **AS-SuA-6 Fabrication of Large-area Nanolines by Area-selective Atomic Layer Deposition***, J Ekerdt, **Zizhuo Zhang,*** University of Texas at Austin

Metal lines are common in semiconductor applications, such as interconnect lines and advanced memory word/bit lines. As the device features scale down, fabrication of large-area uniform nanolines becomes harder. Photolithography followed by etching is the usual patterning method for nanolines but the 100-nm pitch has introduced lithographic challenges when applied across large areas. Furthermore, subtractive etching of metal films typically relies on plasma processes that can generate side products detrimental to device performance.

We offer an alternative to patterning large-area nanolines through a sequence of nanoimprint-lithography, area-selective atomic layer deposition (A-SALD) of a metal oxide film and oxide reduction to the metal. The nanoimprint process can create wafer-scale nanoscale patterns with low cost, high throughput and high resolution. A-SALD is a process by which the chemical nature/reactivity of a surface can be manipulated such that ALD nucleation occurs only in desired regions.

In this work, Co is taken as the exemplary metal; however the process works for other transition metals, including Fe, and Ni. Previous efforts to deposit Co metal using bis(N-tert butyl, N'ethylpropionamidnato) cobalt (II) and H_2 in ALD have suffered from carbon and nitrogen incorporation into the film and nucleation on polymer- and alkylsilane-coated surfaces. Therefore a route to impurity-free CoO deposition in the defined areas followed by reduction from CoO to Co is selected. The approach is illustrated with a 110-nm pitch nanoline pattern of 40 nm-wide trenches and 120 nm-high cured-imprint polymer lines created by nanoimprinting. After O_2/Ar plasma-etching to remove a 10 nm residual layer at the trench bottom, CoO ALD occurs only at the bottom of the trenches. Following deposition at 180 °C and removal of the polymer lines with etching, the CoO can be reduced to form Co metal using a reducing gas at elevated temperature or an oxygen-scavenger layer, such as Al, near ambient temperature. With this A-SALD approach, we are able to pattern large-area uniform and parallel Co metal nanolines with a 110-nm pitch. The nanoline width can be tuned by the O_2/Ar treatment of imprinted pattern and the height of nanolines can be adjusted by the number of ALD cycles. X-ray photoelectron spectroscopy is used to determine the composition and oxidation state of nanolines at various steps in the process. Scanning electron microscope and atomic force microscope are used to determine the pitch, width and height of the nanolines. Using I-V measurement and vibrating sample magnetometer, we explore the electrical and magnetic properties of the Co nanolines.

3:00pm **AS-SuA-7 Nanoscale Selective Deposition of TiO_2 using e-beam Patterned Polymeric Inhibition Layers and TDMAT Precursor***, A Haider, M Yilmaz, P Deminskyi,* Bilkent University, Turkey*; **Hamit Eren**,* Delft University of Technology, Netherlands*; N Biyikli,* Utah State University

Controlling the lateral dimensions of thin films by patterning is an essential requirement for microelectronics industry towards continuous device miniaturization. Conventionally, thin film patterning is achieved by photolithography which includes several processing steps. During the atomic layer deposition (ALD) process, film nucleation is critically dependent on the surface chemistry of the substrate which makes it possible to achieve area-selective ALD (AS-ALD) by chemically modifying the substrate surface. Local modification of substrate surface opens up possibilities to achieve lateral control over film growth in addition to robust thickness control during ALD process. AS-ALD offers numerous advantages in device fabrication such as reduction of the lithography steps required, elimination of complicated etching processes, and minimization of expensive and poisonous reagent use.

In this work, we report a detailed investigation to select the most compatible polymer blocking layer among poly(methyl methacrylate) (PMMA), polyvinylpyrrolidone (PVP), and inductively coupled plasma (ICP) polymerized fluorocarbon (CF_x) for AS-ALD of TiO_2. TiO_2 was grown at 150 °C using tetrakis(dimethylamido) titanium (TDMAT) and H_2O as titanium and oxygen precursors, respectively. PMMA and PVP were deposited using spin coating and C_4F_8 was grown using inductively coupled plasma (ICP) etch reactor. Contact angle, scanning electron microscope (SEM), spectroscopic ellipsometer, and X-ray photoelectron spectroscopy (XPS) measurements were performed to investigate the effectiveness of polymer layers for AS-ALD process of TiO_2. TiO_2 was grown with different number of growth cycles (maximum = 1200 cycles) on PMMA, PVP and CF_x. PMMA revealed successful growth inhibition upto the maximum inspected growth cycles. PVP was able to block TiO_2 growth upto 300 growth cycles, while CF_x revealed no inhibition capability. Finally, mm, µm, and nm-scale self-aligned deposition of TiO_2 is demonstrated using a PMMA masking layer that has been patterned using e-beam lithography. Additionally, we used the selectively grown TiO_2 layers as an etch mask layer to create deep trench structures inside Si. SEM, EDX line scan, EDX elemental mapping, and XPS elemental mapping measurements revealed successful patterning of TiO_2 features. AS-ALD of TiO_2 demonstrated in the present work offers a novel approach to fabricate close packed nanopatterns for various device architectures without any complex etching or lift-off processes.

3:15pm **AS-SuA-8 Area-selective Atomic Layer Deposition using Inductively Coupled Plasma Polymerized Fluorocarbon Layer: A Case Study for Metal-Oxides and Metals***, **Ali Haider**, P Deminskyi, T Khan,* Bilkent University, Turkey*; H Eren,* Delft University of Technology, Netherlands*; N Biyikli,* Utah State University

Nanoscale process integration demands novel nano-patterning techniques in compliance with the requirements of next generation devices. Conventionally, top-down subtractive (etch) or additive (deposition/lift-off) processes in conjunction with various lithography techniques is employed to achieve film patterning, which become increasingly challenging due to the ever-shrinking misalignment requirements. To reduce the complexity burden of lithographic alignment in critical fabrication steps, self-aligned processes such as selective deposition and selective etching might provide attractive solutions.

Here, we demonstrate a methodology to achieve area-selective ALD (AS-ALD) by using inductively couple plasma (ICP) grown fluorocarbonpolymer film as growth inhibition layer. The fluorocarbon layer was grown using C_4F_8 feed gas in a conventional ICP-etch reactor. Our approach has been tested for metal-oxides and metals including ZnO, Al_2O_3, HfO_2, Pt, and Pd. Contact angle, X-ray photoelectron spectroscopy, spectroscopic ellipsometer, and scanning electron microscopy measurements were performed to investigate the blocking ability of plasma polymerized fluorocarbon layers against ALD-grown films. Characterizations carried out revealed that effective blocking on fluorocarbon layer is achieved for ZnO, Pt, and Pd films with different blocking cycle numbers before nucleation initiates. On the other hand, a rather slow nucleation has been observed for HfO_2 growth on fluorocarbon coated surfaces, while Al_2O_3 growth showed almost no delay with a growth rate equal to the ones on conventional substrate surfaces. By exploiting this inhibition feature, thin film patterning has been demonstrated by growing ZnO, Pt, and Pd films on photolithographically patterned fluorocarbon/Si samples. The robust albeit rather simple and straightforward technique presented in this work overcomes various challenges associated with previous methods of AS-ALD and provides an alternative route towards nano-patterning using selective deposition.

4:00pm **AS-SuA-11 Adventures and Advances in Selective Deposition***, **David Thompson**,* Applied Materials **INVITED**

Please submit your abstract to Della Miller, della@avs.org, immediately for inclusion in the program.

4:30pm **AS-SuA-13 Direct-write ALD of Transparent Conductive Oxides: Micro- and Nanoscale Patterned In_2O_3:H and ZnO***, **Alfredo Mameli**, B Karasulu, B Barcones Campo, M Verheijen, A Mackus, W Kessels, F Roozeboom,* Eindhoven University of Technology, Netherlands

Area-Selective Atomic Layer Deposition (AS-ALD) can push device manufacturing towards new frontiers. To date, several approaches have been developed for achieving area-selective deposition that can be classified as either area-activation[1] or area-deactivation.[2] The former is referred to as *direct-write* ALD when no subtractive steps are employed. In this work, we report on *direct-write* ALD of two transparent conductive oxides, In_2O_3:H and ZnO. The method exploits the selective precursor adsorption on OH-terminated versus H-terminated Si surfaces and the resulting differences in nucleation delay.

Previously we have demonstrated that microscale In_2O_3:H patterns can be fabricated by local activation of the surface using a micro-plasma printer, followed by a second step in which AS-ALD takes place on the activated surface only.[3] Similar chemistry is now explored for ZnO AS-ALD, while aiming at nanoscale dimensions. In this case an ultra-thin SiO_2 seed layer was deposited to activate the H-terminated surface (i.e., a-Si:H) for ALD growth. 500-by-500 nm² SiO_2 seed layers were deposited by electron beam induced deposition (EBID) using tetraethyl orthosilicate (TEOS) and H_2O as the precursors. For the ALD of ZnO, diethylzinc (DEZ) and H_2O were used as the precursor and the co-reactant, respectively, in a thermal ALD process at substrate temperatures ranging from 100 to 250°C. Selective deposition of ZnO was obtained upon 80 ALD cycles, with good selectivity as demonstrated by *in-situ* ellipsometry, SEM, cross-sectional TEM and energy dispersive X-ray spectroscopy (EDX) analysis. The influence of the ALD process temperature and EBID patterning parameters on the extent of selectivity have been investigated in detail. First principle density functional theory calculations corroborate the selectivity of the ALD process by revealing a kinetically hindered surface reaction between DEZ and H-terminated Si surfaces.

References

[1] A. J. M. Mackus *et al.*, J. Phys Chem. C, **117**, 10788-10798 (2013)

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4:45pm **AS-SuA-14 Inherent Substrate-Selective Growth of Cobalt and Nickel Metal Films by Atomic Layer Deposition***, **Marissa M. Kerrigan**, C Winter,* Wayne State University

Atomic layer deposition (ALD) affords thin films with high conformality and precise thickness control due to its self-limited growth mechanism, and enables the increasing demands for smaller feature sizes in microelectronics devices to be met.[1] Area-selective ALD (ASALD) growth is receiving attention in the fabrication of microelectronic devices, since it can eliminate complicated etching steps from the fabrication process and minimizes expensive and toxic reagent use.[2] To date, few ASALD processes for metals have been reported, driving a need for new processes to be developed.[2] Thin films of cobalt metal grown by ASALD are of considerable interest for use in microelectronics devices, specifically as a metallization liner and cap for copper features in sub-10 nm logic nodes.[3] Our laboratory has recently reported an ALD process for the inherent selective deposition of cobalt metal thin films using bis(1,4-di-*tert*-butyl-1,3-diazabutadienyl)cobalt(II), Co(^{tBu2}DAD)$_2$, and formic acid.[4-5] This process affords high-purity, low-resistivity cobalt films, with a growth rate of 0.95 Å/cycle. Importantly, growth occurs preferentially on metal substrates over dielectric substrates. However, the use of formic acid as a co-reactant is undesirable for industrial applications. In this work, we will describe the development of a new ASALD process for high-purity, low-resistivity (~13 μΩcm) cobalt metal films from Co(^{tBu2}DAD)$_2$ and alkyl amines, with a growth rate of 0.98 Å/cycle on metal substrates. No cobalt metal growth is observed on dielectric substrates. We will also report a new ASALD process for high-purity, low-resistivity (~20 μΩcm) nickel metal films from Ni(^{tBu2}DAD)$_2$ and alkylamines, with a GR of 0.60 Å/cycle on metal substrates. No nickel metal growth is observed on dielectric substrates. We will also discuss extending M(^{tBu2}DAD)$_2$ and alkyl amines as a general process for the low temperature ALD growth of other first row transition metal films.

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5:00pm **AS-SuA-15 Delayed Nucleation of HfO$_2$ and TiO$_2$ ALD on Carbon via Cyclic Plasma Treatments for Application in Selective-Area Deposition***,* ***Eric Stevens,*** North Carolina State University, USA*; Y Tomczak, B Chan, E Altamirano-Sanchez,* IMEC, Belgium*; G Parsons,* North Carolina State University, USA*; A Delabie,* IMEC, Belgium

Fabrication of future nanoelectronic devices will require innovative and scalable patterning techniques. The use of a sacrificial patterning layer, such as Advanced Patterning Film (APF), would allow metal oxide materials to be deposited in a trench-fill approach, assuming growth inhibition on APF selective to the growth substrate. This work seeks an in-depth understanding of the nucleation and growth behavior of metal oxide ALD on APF, and the effects of surface pre-treatments on the surface functionalization for use in TiO$_2$ and HfO$_2$ patterning.

A high density APF film was deposited on 300mm Si wafers using plasma enhanced CVD of C_2H_2 at 400°C, yielding an amorphous carbon composed of mostly sp^2 and sp^3 hybridized carbon. The inherent selectivity of the as-deposited APF films was probed by depositing HfO$_2$ (HfCl$_4$ + H$_2$O at 300°C) and TiO$_2$ (Ti(OCH$_3$)$_4$ + H$_2$O at 250°C) by ALD. These water-based ALD processes are anticipated to proceed via island growth on C-C and C-H surfaces. Interestingly, uninhibited ALD growth of both TiO$_2$ and HfO$_2$ was observed for as-deposited APF substrates, presumably due to ~5% oxygen present at the surface (X-ray Photoelectron Spectroscopy, XPS) and an RMS value of 0.55 nm.

In order to remove oxygen and impede nucleation of metal oxide ALD, an in situ, direct H$_2$ plasma pre-treatment was investigated. XPS depth profiling revealed that for both treated and untreated APF, the oxygen content converged to ~1% after 2-3 nm Ar sputtering, implying a partial oxidation of the APF surface when exposed to air. A plasma pretreatment of 100W for 10s was sufficient to reduce the surface oxygen from 5% to 3%, with ~3 nm of APF etching observed (spectroscopic ellipsometry). The combination of high power and cyclic treatments are believed to etch the partially oxidized top few nanometers and reduce the amount of sites available for re-oxidation, resulting in mostly C-H and C-C surface termination.

The effect of plasma power was screened by subjecting APF substrates to in situ plasma treatments followed by 30 cycles of TiO$_2$ ALD (Figure 1). Low power treatments (e.g., 50W) had minimal effect, whereas using 400W and repeated cycling within the ALD sequence (e.g., (400Wx2 + 15cy)x2) yielded growth below the RBS detection limit on the APF, corresponding to 1.3 nm of TiO$_2$ on receptive silicon nitride. Furthermore, a cyclic H$_2$ plasma treatment of 400Wx2 allowed for up to 60 cycles of TiO$_2$ and HfO$_2$ ALD on APF without film closure (Figures 2, 3). These insights can aid the design of patterned substrates which incorporate area selective ALD of TiO$_2$ and HfO$_2$ on SiN, while delaying film closure on APF.

5:15pm **AS-SuA-16 Selective Deposition Process Combining PEALD and ALE***,* ***Christophe Vallée,*** Univ. Grenoble Alpes, CNRS, France*; R Gassilloud,* CEA-Leti, France*; R Vallat,* Univ. Grenoble Alpes, CNRS, France*; C Mannequin,* University of Tsukuba*; A Uedono,* University of Tsukuba, Japan*; V Pesce,* Univ. Grenoble Alpes, CNRS, France*; N Posseme,* CEA-Leti, France*; P Gonon, A Bsiesy,* Univ. Grenoble Alpes, CNRS, France **INVITED**

At advanced nodes, lithography starts to dominate the CMOS technology cost and alternative approaches are needed to continue 2D scaling and extend Moore's law. Selective deposition process, is a very promising path to enhance patterning capabilities and control its cost. From all the different deposition processes, Atomic Layer Deposition (ALD) is probably the more suitable tool to develop a selective deposition due to its high surface sensitivity. The first part of this paper will be an overview of different existing ALD selective deposition processes:

- Selective ALD using self-assembled monolayers (Selective-Area or Area-Selective ALD)
- Selective ALD using block copolymer
- Selective ALD using temperature
- Selective ALD using spatial ALD (Atomic Layer Printer)

In the second part, we will focus on plasma-based selective ALD process. Cold plasmas used for ALD assistance contain many energetic species such as ions and radicals that can be used to design a selective deposition process. For example, it has been proposed to use an ion implantation assistance to perform topography selective deposition on 3D structures. In our group, we are developing a plasma ALD selective deposition process by adding a plasma etching step. For this process, easy to use and compatible with high throughput manufacturing, three waypoints are needed:

- First a different nucleation delay between two substrates. Here we take advantage of the inherent substrate-dependent growth initiation of ALD;
- Second an etching step is needed with an etch rate controlled at the nm scale in order to remove the deposited material on one substrate;
- A plasma-induced surface modification of the substrate where the material has been removed is needed. Idea here is to add after each etching step an additional nucleation delay before starting the growth again.

This process that has been developed in a 300 mm plasma deposition tool from Kobus will be more detailed and examples of selective deposition processes combining PEALD and etching steps for Ta$_2$O$_5$ and TiO$_2$ will be given. The impact of the process on the chemical and electrical properties of the oxides will also be discussed thanks to XPS, XRR, ellipsometry and positron annihilation spectroscopy as well as C(V) and I(V) characterizations. Enhancing the performance of this process needs to optimize the etching step. For this purpose, we are currently trying to develop specific atomic layer etching processes in the PEALD tool by adding a RF substrate bias waveform developed by Oxford in a FLEXAL tool. This specific experimental set up and first results will also be addressed.

Nanostructure Synthesis and Fabrication
Room Plaza ABC - Session NS+EM-SuA

2D Materials (1:30-3:30 pm)/Laminate, Multicomponent, and Emerging Materials (4:00-5:30 pm)

Moderators: Jiyoung Kim, University of Texas at Dallas, Dennis Hausmann, Lam Research, Sumit Agarwal, Colorado School of Mines

1:30pm **NS+EM-SuA-1 Plasma-enhanced Atomic Layer Deposition of Large-area MoS$_2$: From 2-D Monolayers to 3-D Vertical Fins***,* ***Akhil Sharma,*** *S Karwal, V Vandalon, M Verheijen,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, UK*; R Sundaram,* Oxford Instruments Plasma Technology*; W Kessels, A Bol,* Eindhoven University of Technology, Netherlands

Atomic layer deposition (ALD) might prove as a key enabler for tackling the current challenge of large-area growth of 2-D materials with wafer-level uniformity and digital thickness controllability. In this contribution, we have implemented plasma-enhanced ALD to synthesize large-area MoS$_2$ thin films with tuneable morphologies i.e. in-plane and vertically standing nano-scale architectures on CMOS compatible SiO$_2$/Si substrates. The large scale 2D in-plane morphology has potential applications in nanoelectronics, while the 3D fin structures could be ideal for catalysis applications such as water splitting.

The ALD process was characterized over a wide temperature range between 150°C - 450°C by using a combination of a metal organic precursor $[(NtBu)_2(NMe_2)_2Mo]$as Mo source and a H_2S based plasma as the co-reactant. A saturated growth rate of ~0.9 Å/cycle was observed within the parameter space investigated. The number of layers in the MoS_2 film could be controlled down to a mono-layer by tuning the number of ALD cycles. The precise variation in thickness was confirmed by Raman spectroscopy which showed a monotonic decrease in the frequency difference between the two characteristic modes for MoS_2 with decreasing layer thickness down to 21 cm^{-1} which corresponds to a monolayer. The photoluminescence spectroscopy data was in line with these results, showing a strong peak at ~1.9 eV corresponding to the direct band gap transition for the mono-to-few layered MoS_2. XPS showed that the films were pure and stoichiometric in nature with negligible trace amounts of carbon and oxygen contaminants. The HAADF TEM analysis of the films grown at 450°C showed that during the initial ALD cycles, MoS_2 islands extended in the lateral direction and merged to form a film which continued to grow in a layer-by-layer fashion until a certain thickness. Thereafter, an out-of-plane vertical growth mode started to dominate as shown by cross-sectional TEM analysis. The origin of this transition from in-plane to out-of-plane growth mode might be attributed to the enhanced precursor adsorption on high surface energy locations such as grain boundaries, kinks or ledges. Due to the crowding effects at these favourable adsorption sites, vertical growth of MoS_2 is observed.

These results show that ALD might be instrumental in realizing not only the large area growth of high-quality 2-D materials but can also be applied as a tool to control the morphology of thin films which might yield into interesting structures (including heterostructures) for various opto-electronics and catalysis applications.

1:45pm **NS+EM-SuA-2 Low-Temperature Atomic Layer Deposition of MoS_2 Films*, Michael Moody*,** *T Jurca, A Henning, J Emery, B Wang, J Tan, T Lohr, T Marks, L Lauhon,* Northwestern University

Molybdenum disulfide (MoS_2) is a widely-studied layered semiconductor with interesting fundamental optoelectronic properties and promising applications in the two-dimensional limit. If a suitable metal-organic precursor and reaction chemistry were available, atomic layer deposition (ALD) could extend the impact of fundamental work on this system by enabling growth of consistent, large-area films. Here we report the use of the volatile molybdenum complex, tetrakis(dimethylamido)molybdenum (MoTDMA) and H_2S for direct low-temperature ALD of MoS_2 films. Preliminary wet chemical screening revealed a high reactivity of MoTDMA with H_2S , suggesting suitable chemistry for MoS_2 ALD under mild conditions. Indeed, ALD growth of amorphous MoS_2 was subsequently achieved at temperatures as low as 60°C, a temperature compatible with polymer substrates and photolithographic patterning over multiple length scales. Associated with the high reactivity of this system is robust nucleation , even on layered materials with interlayer van der Waals bonding such as graphene and exfoliated MoS_2. Annealing of amorphous MoS_2 films results in continuous, semiconducting nanocrystalline films, as characterized by multiple structural techniques including GIXRD and HRTEM. This work provides a route to 2D materials via ALD and post-processing, and exploration of related compounds to further tailor reactivity and ALD window is in progress.

2:00pm **NS+EM-SuA-3 Dielectric-MoS_2 Interfaces Grown by Atomic Layer Deposition*, Steven Letourneau,*** Boise State University*; A Mane, J Elam,* Argonne National Laboratory*; E Graungard,* Boise State University

Molybdenum disulfide (MoS_2) has become a prototypical transition metal dichalcogenide (TMDC) atomic-layered material because of its unique materials properties. For example, bulk MoS_2 exhibits an indirect band-gap of 1.3 eV, while a single monolayer has a direct band-gap of 1.8 eV. Recently, nanometer scale transistor devices have been made with MoS_2 and graphene, yet much of this work relies on layered materials prepared using chemical vapor deposition (CVD) and mechanically exfoliation. Multiple reports have demonstrated the growth of MoS_2 via CVD, but only a few studies have reported MoS_2 growth using atomic layer deposition (ALD), which offers potential advantages for high volume semiconductor manufacturing. Here, we report the ALD of few-layer MoS_2 films using MoF_6 and H_2S on various ALD-grown dielectric surfaces and the ALD of metal oxides on the ALD MoS_2 films at temperatures between 100-300 °C. In particular, we used in-situ quartz crystal microbalance measurements to investigate the nucleation of MoS_2 ALD on oxide surfaces and vice versa. In general, self-limiting growth of MoS_2 was observed on a wide range of dielectric surfaces including alumina, magnesia, and hafnia. The ALD MoS_2 films were amorphous as-deposited, but crystallized into a layered atomic structure upon annealing at 800 °C. Using in-situ spectroscopy and electrical measurements, growth inhibition of MoS_2 was seen depending on the growth substrate. These studies provide insight into the low-temperature ALD of MoS_2 and provide guidance for the ALD of additional TMDC films.

2:15pm **NS+EM-SuA-4 Plasma-Enhanced Atomic Layer Deposition of sub-5 nm high- k Dielectrics on 2D Crystals*, Katherine Price,*** *F McGuire, A Franklin,* Duke University

Recently, 2D crystals have been targeted as the basis for enabling many exciting nanoelectronic and optoelectronic applications. One of the main challenges inhibiting the integration of 2D crystals is uniform deposition of a scalable, high-quality dielectric, which serves as an integral aspect of some devices (as with top-gated field-effect transistors (FETs)) or as a protection from ambient conditions for other devices. This problem arises from the chemically inert surface of 2D crystals, which prevents uniform growth of a dielectric film using atomic layer deposition (ALD). While thick ALD high-k films can be obtained on transition metal dichalcogenides (TMDs) through island growth, ultrathin films (< 5 nm) have not been possible without additional surface modification steps or the addition of a buffer layer. In this work, we show that a plasma-enhanced ALD (PEALD) process, compared to traditional thermal ALD, substantially improves nucleation on TMDs, such as MoS_2 and WSe_2, without hampering their electrical performance, and enables uniform growth of high-k dielectrics to sub-5 nm thicknesses. A custom-designed PEALD system (from Kurt J. Lesker Company) with a remote plasma sustained by Ar carrier gas was used for this study. Ultrathin high-k films, including Al_2O_3 and HfO_2, were successfully grown on mechanically exfoliated 2D crystals. A systematic comparison between PEALD (using O_2 precursor) and ALD (using H_2O precursor) revealed significant improvement in overall surface coverage and rugosity using PEALD. Back-gated FETs were used to study the electrical properties of the TMDs before/after ALD or PEALD. Interestingly, PEALD of HfO_2 resulted in an greater overall improvement in performance based on hysteresis and on-current compared to ALD of HfO_2. Mechanisms for the dramatic nucleation improvement and impact of PEALD on the 2D crystal structure were studied by x-ray photoelectron spectroscopy (XPS). XPS showed no evidence of oxidation that would adversely impact the electrical properties of the TMDs. To demonstrate the utility of the PEALD-enhanced nucleation, HfO_2 films as thin as ~3 nm were realized on MoS_2 and used in the gate stack of top-gated FETs, yielding robust performance for key metrics such as leakage current and gate control. In addition to providing a detailed analysis of the benefits of PEALD vs ALD on 2D crystals, this work reveals a straightforward approach for realizing ultrathin films of device-quality high-k dielectrics on 2D crystals without the use of additional nucleation layers or damage to the electrical performance.

2:30pm **NS+EM-SuA-5 Novel *in-situ* Electrical Characterization of the Atomic Layer Deposition Process on 2D Transition Metal Dichalcogenides Transistors*, Antonio Lucero,*** *J Lee, L Cheng, H Kim, J Lee, S Kim, J Kim,* University of Texas at Dallas

Two-dimensional transition metal dichalcogenide (TMD) materials are promising candidates for future, low-power semiconducting applications[1]. In spite of their numerous desirable characteristics, there are a number of challenges facing the implementation 2D TMDs into high performance transistors. Key among these problems is the development of a scalable gate dielectric deposition process due to the chemical inertness of the TMD surface[2]. In this report four deposition processes are studied using a novel, *in-situ* electrical characterization system.

Exfoliated MoS_2 backgated devices are loaded into an ultra-high vacuum (UHV) cluster tool which integrates a thermal ALD, a plasma enhanced ALD, and a plasma enhanced chemical vapor deposition with a UHV electrical probe station (Fig. 1). Thermal ALD of Al_2O_3, both alone and combined with nitrogen radical surface functionalization, hollow cathode nitrogen plasma surface functionalization, and ozone surface functionalization are studied. Samples are transferred between deposition and characterization chambers under UHV conditions, allowing “half-cycle” studies to be performed (Fig. 2). Common to all results, as well as *ex-situ* studies, the ALD process results in a reduction of the on-off ratio, an increase in drive current, and a large negative shift in the threshold voltage (V_{th}). The shift in V_{th} can be seen immediately after the functionalization step or from the first ALD pulse if no functionalization is performed. In the case of functionalization, the shift in V_{th} is attributed to the oxidation of the MoS_2 surface, a result of oxygen contamination during radical functionalization. The effect of surface dipoles, precursor adsorption and coverage, and nucleation during the ALD process will be discussed as they relate to the electrical characteristics of the device.

This work was supported by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST, and by NRF (No. 2015M3D1A1068061) in Korea. We thank TMEIC for providing the ozone generator and nitrogen radical generator used in this work.

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2:45pm **NS+EM-SuA-6 Deposition of MoS$_2$ and WS$_2$ from bis(tert-butylimido)-bis(dialkylamido) Compounds and 1-Propanethiol**, ***Berc Kalanyan***, *J Maslar, W Kimes, B Sperling,* National Institute of Standards and Technology*; R Kanjolia,* EMD Performance Materials

Layered two dimensional (2D) transition-metal dichalcogenides (TMDs) are finding use in nanoelectronic and optoelectronic applications due to their thickness dependent optical and electrical properties. Scalable fabrication of TMD-based devices requires deposition routes that can produce continuous and uniform films with sub-nanometer thickness control. Atomic layer deposition (ALD) is a highly promising route for the synthesis of 2D TMDs and heterostructures due to digital thickness control achieved by sequential self-limiting chemistry. Another advantage of ALD is that thickness control and the structural development of the films can be decoupled by separating the deposition and crystallization steps. Existing ALD-like chemistries for TMD growth use metal halide and hydrogen sulfide sources. We report on the development of MoS$_2$ and WS$_2$ growth processes from metalorganic and thiol precursors, which offer halide-free chemistry and eliminate the safety hazards associated with H$_2$S.

We deposited thin films using (N^{t}Bu)$_2$(Nme$_2$)$_2$M and 1-propanethiol, where M={Mo,W}, at wafer temperatures of 200°C to 400°C on SiO$_2$/Si substrates. The amount of precursor injected was directly measured using inline non-dispersive infrared optical flow meters. Precursor saturation conditions were evaluated using optical flow measurements and X-ray photoelectron spectroscopy (XPS). As-deposited and sulfur annealed films were further evaluated using X-ray diffraction (XRD) and Raman spectroscopy. As-grown films were amorphous and included a mixture of a sulfide and a conductive phase, likely a nitride. For the Mo precursor, the onset of sulfur incorporation occurred around 300°C, similar to values reported for Mo$_2$N produced using ammonia1. Below 300°C, deposition was limited to a thin surface oxide. Higher temperatures resulted in an increase in growth rate, which also introduced a weak CVD component to the growth. Deposition rates were <0.5 Å/cycle at 350°C. Exposure studies revealed that relatively long saturation times for thiol were required to incorporate sulfur into the film, analogous to the NH$_3$ reaction for WN^2. As-deposited films were successfully annealed to 2H-MoS$_2$ under a sulfur atmosphere, which also removed residual ligands, including nitrogen-containing groups. In this paper, we will also present similar results and process characteristics for the WS$_2$ route and discuss initial results from MoS$_2$/WS$_2$ nanolaminates.

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3:00pm **NS+EM-SuA-7 Direct Growth of Layered Boron Nitride Films on MoS$_2$ using Atomic Layer Deposition for 2D Based Nano-electronics**, ***Jaebeom Lee***, *L Cheng, H Zhu, A Ravichandran, A Lucero, M Catalano, M Kim, R Wallace, L Colombo, J Kim,* University of Texas at Dallas*; Z Che,* The University of Texas at Dallas

Hexagonal boron nitride (h-BN), a graphene analogue with strong covalent bonding of boron and nitrogen, is an atomically thin two-dimensional (2D) dielectric material having interesting properties, such as atomic flatness, high stiffness, near lattice matching with graphene, and low surface energy. These unique properties have made h-BN a widely-studied dielectric as a substrate material and a gate dielectric for graphene based device. However, direct integration of h-BN with other 2D semiconductors, such as graphene and MoS$_2$, remains a major challenge because of their low surface reactivity which leads to poor surface nucleation of h-BN, thus preventing the synthesis of large area films with controllable thickness and grain size.

We used atomic layer deposition (ALD) using BCl$_3$ and NH$_3$ as precursors in the temperature range of 600~800 ℃ as shown in figure S1 to grow h-BN thin films. We evaluated the growth of layered BN on different substrates, such as Co, SiO$_2$, HOPG and MoS$_2$ and found that the nucleation mechanism depends on substrates. The distinct nucleation mechanisms of layered BN are likely attributed to the unique surface reactivities of the various substrates. Both Co and SiO$_2$ shows uniform nucleation sites, while growth on HOPG and MoS$_2$ showed growth mostly at the step edges due to the presence of dangling bonds and the inert nature of the basal plane. In order to increase the nucleation density we used O$_3$ pretreatment to functionalize the surface of MoS$_2$. The AFM images revealed enhanced nucleation of BN with an average grain size of ~ 20nm at a growth rate of ~ 0.22 Å/cycle. We also performed XPS measurements of the B 1s and N 1s peaks at 190.66 and 398.07 eV respectively, and the B:N ratio was estimated to be close to 1. The formation of layered BN was also verified further with the identification of satellite features at the higher binding energy shoulders of the XPS peaks, which is in good agreement with the layered BN structure observed in our HR-TEM images that show an interlayer spacing of 0.34nm (Fig S2). The band-gap of ALD grown BN was also estimated to be around 5.1 eV based on the analysis of N 1s XPS loss feature, and the dielectric constant was estimated to be about 3.8 from capacitor measurements. Our results suggest that polycrystalline layered BN can be grown by ALD on Co, SiO$_2$, HOPG and MoS$_2$. Further studies will have to be performed to improve the crystalline quality of the films.

We acknowledge partial financial support from the Southwest Academy on Nanoelectronics (SWAN) sponsored by the Nanoelectronic Research Initiative (NRI) and NIST and we thank TMEIC for providing the ozone generator.

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3:15pm **NS+EM-SuA-8 Fabrication of Functional Complex Nanostructures Based on Novel Atomic Layer Deposition Approach of Boron Nitride**, ***Wenjun Hao***, *C Marichy, C Journet, A Brioude,* Univ Lyon, France **INVITED**

Renewal clean energy and environment are two of the most important concerns for the coming decades. Carbon-based nanostructures are leading nanomaterials due to their outstanding properties. Less investigated, hexagonal BN nanostructures such as nanotubes and nanosheets, which can be seen as the structural analogues to their carbon counterparts[1], are very attractive materials with various applications such as energy[2] and environmental domains[3]. Atomic Layer Deposition (ALD) technique is an effective approach for surface modification and fabrication of complex nanostructured materials.[4] However, few ALD processes of BN were reported so far and they are mostly based on ammonia and/or halide precursors and no high crystalline quality was yet achieved[5–8]. Based on Polymer Derived Ceramic (PDC) chemistry[9], a new low temperature ALD process of BN, that permits access to various h-BN complex nano- and hetero-structures, was developed.

In the present communication, we report for the first time the fabrication of h-BN complex nano- and hetero-structures by a two-step ALD approach using trichloroborazine reacting with hexamethyldisilazane. This two-step process consists first of the growth layer by layer of a preceramic BN films at low temperature, and then to its densification into pure h-BN by annealing process. h-BN thin films were successfully deposited onto various substrates/templates, such as carbon nanotubes, SiO$_2$ nanoparticles, polycarbonate membrane, sapphire, etc. The obtained h-BN materials were characterized by TEM, SEM, EDS, XPS and Raman. The present low deposition temperature ALD approach provides a versatile ammonia free method to fabricate high quality h-BN nano- and hetero-structures.

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4:00pm **NS+EM-SuA-11 When There is no Bulk: Growth and Structure of Dielectric and Semiconductor Oxide Nanolaminates***, Angel Yanguas-Gil,* Argonne National Laboratory **INVITED**

Nanolaminates represent the first-order generalization of a conventional ALD process, one in which the traditional ABABAB sequence is replaced by a more general $(AB)_n(CD)_m$ combination of two different processes. In this talk I will focus on the growth, properties, and stability of oxide semiconductor and dielectric laminates. These materials are key for a wide range of applications, including photovoltaics, memory, logic, and power electronic devices. However, in addition to their applied interest, nanolaminates constitute a fantastic model system to explore the structure and properties of sub-nm materials whose structure and coordination environment are different from the bulk. Being intrinsically metastable, the stability of these structures also provides us with a way of probing the mobility of atoms at the nanoscale, an important factor in the long-term reliability of nanomaterials.

Through a combination of in-situ characterization, synchrotron characterization techniques, and simulations we have probed the structure and stability of nanolaminate materials as the thickness of its constituents evolve from a bulk like structure down to isolated clusters in a foreign host, focusing primarily on three different subsystems: Al_2O_3/ZnO, In_2O_3/SnO_2, and MO_2/Al_2O_3, where M=Ti, Hf. Changes in microstructure as determined using X-ray absorption spectroscopy correlate with changes in the chemical and electronic properties of the material. This is the case of the Al_2O_3/ZnO system, for which the departure from a wurzite-like coordination environment in ZnO below 10 ALD cycles correlates with an increase in the etching of the ZnO layer by TMA.

I will also focus on how to control the synthesis of doped and nanolaminate materials to tune the microstructure of amorphous materials. I will show how by adding an in-situ surface functionalization step to the conventional AB ALD cycle we can tune the reactivity and the growth per cycle of a wide range of ALD processes. We can leverage this approach to tune the composition of binary and ternary laminate materials, for instance to control the doping efficiency in transparent conductors or the isotropic mixing of components in as-deposited dielectric laminates. In addition to the modification of the structure of the laminate materials, this technique also allows us to probe the precursor-surface interaction during the first CD cycle of a laminate growth by comparing the growth inhibition observed in the laminate and in each of the individual constituents.

4:30pm **NS+EM-SuA-13 Perfecting Single-Crystal Ternary Perovskite $YAlO_3$ Epitaxial Growth on GaAs(111)A Utilizing Atomic Layer Deposited Sub-Nano-Laminated Y_2O_3/Al_2O_3***, **Lawrence Boyu Young**, C Cheng, K Lin, Y Lin, H Wan,* National Taiwan University, Republic of China*; M Li,* National Nano Device Laboratories, Republic of China*; R Cai, S Lo,* Industrial Technology Research Institute, Republic of China*; C Hsu,* National Synchrotron Radiation Research Center, Republic of China*; J Kwo,* National Tsing Hua University, Republic of China*; M Hong,* National Taiwan University, Republic of China

Hetero-epitaxial growth of functional oxides on commercial semiconductor Si and GaAs wafers enables new technological applications, taking advantages of the advanced CMOS ICs and high-speed opto-electronic devices. Moreover, the hetero-growth between distinctly different chemical bonding and lattice constants is scientifically exciting and technologically challenging. In this work, we have perfected single crystal hexagonal perovskite $YAlO_3$ on GaAs(111)A using atomic layer deposited (ALD) sub-nano-laminated (snl) Y_2O_3/Al_2O_3 multi-layers (super-cycles) through post-deposition rapid thermal annealing (RTA) with temperatures above 900^{o}C. We have studied the crystallography of single crystal hexagonal perovskite $YAlO_3$ (YAP) using synchrotron radiation x-ray diffraction (SR-XRD) and scanning transmission electron microscopy (STEM). The epitaxial relationship between $YAlO_3$ and GaAs is $YAlO_3$GaAs, as determined from the XRD radial scan along the in-plane direction. Comparing the YAP crystallinity of snl (super-cycles) and nl Y_2O_3/Al_2O_3 multi-layers, the cross-sectional STEM image for the former (Fig. 1(a)) reveals a more ordered atomic image, smoother crystalline $YAlO_3$/GaAs(111) interface, and continuous crystalline domain over 100-nm along substrate in-plane direction than that for the latter (Fig. 1(b)). Moreover, Pendellösung fringes from the XRD normal scans were observed for the super-cycled samples, much more so than those of nano-laminated samples (Fig. 2), [1] again indicating better crystallinity and smoother interfacial roughness. We have also attained very narrow FWHM of $YAlO_3$(0004) θ-rocking scan ~ 0.026^{o} from the snl samples, compared favorably with 0.27^{o} from the nl samples (Fig. 3). We have studied the surface morphology of the samples using atomic force microscopy (AFM). The smoother surface root mean square roughness of ~ 0.13 nm was observed in the snl super-cycled sample, which is 6 times smaller than that of our previous nl sample, and was close to the surface roughness of GaAs(111)A substrate ~ 0.13 nm as measured using an in-situ scanning tunneling microscope. Finally, the time-evolutions of surface normal radial scans of snl and nl samples were presented. After the 900^{o}C anneal, the formation of $YAlO_3$ was much quicker ~ 2s to reach the saturation thickness than that of our previous sample ~ 60s, indicating that only 1/30 thermal budget was needed to form YAP by using sub-nano-laminated Y_2O_3/Al_2O_3 super-cycles.

[#]LBY, CKC, and KYL have contributed equally to this work.

*CHH, JK, and MH are the corresponding authors.

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4:45pm **NS+EM-SuA-14 Thermal Coefficient of Resistance (TCR) Measurements for Atomic Layer Deposited Metal-Metal Oxide Nanocomposites***, **Anil Mane**, J Avila, Y Zhang, J Elam,* Argonne National Laboratory

Precisely controlled metal-metal oxide nanocomposite layers prepared by atomic layer deposition (ALD) exhibit material properties that can be tuned over a broad range by adjusting the metal content such as band gap, absorption coefficient, resistivity, and electrochemical corrosion resistance. Consequently, these metal-metal oxide nanocomposites are well suited in a variety of applications including resistive layers in microchannel plates (MCPs), protective coatings for lithium ion battery cathodes, charge drain layers for MEMS devices, and selective absorber coatings for concentrated solar power.

For resistive layers in MCPs, the thermal coefficient of resistance (TCR) is a critical materials property because it dictates the range of allowable operating temperatures for devices (e.g. photon, neutron, or particle detectors) that incorporate the MCP for electron amplification. The ability to control the TCR will enable new applications such as cryogenic detectors or detectors that must endure large temperature changes during operation. To address this need, we have synthesized a variety of ALD metal-metal oxide nanocomposite layers by combining different metals (W, Mo, Ta, and Nb) and metal oxides (Al_2O_3, ZrO_2, TiO_2, Ta_2O_5, Nb_2O_5, and HfO_2). We studied the electrical transport properties of these ALD films and focused on their temperature dependence in order to extract the TCR. In all cases, the TCR is negative, so that the resistance drops with increasing temperature as expected for a semiconducting material. In addition, the magnitude of the TCR increases with the film resistivity, and depends on both the metal and the metal oxide components of the composite (Fig. 1). This presentation will expound on these findings and explain the implications for MCP detectors.

5:00pm **NS+EM-SuA-15 Phase Control of Ga_2O_3 Films Deposited by Atomic Layer Epitaxy***, **Virginia Wheeler**, N Nepal, D Meyer, C Eddy, Jr.,* U.S. Naval Research Laboratory

Ga_2O_3 has attracted significant interest as a promising ultra-wide bandgap material for next generation high-power, high-temperature electronic and UV detector applications. While there are five polymorphs of Ga_2O_3, the β-Ga_2O_3 (monoclinic) is the most stable and thus the most widely studied to-date. By comparison, the ε-Ga_2O_3 phase is slightly less energetically favorable but has a similar bandgap (4.9 eV) and a hexagonal wurtzite crystal structure that results in a polar phase. The calculated polarization strength of ε-Ga_2O_3 is 10 and 3 times larger than that of GaN and AlN, respectively. Like the III-N system, polarization induced charges can lead to higher charge densities and mobilities in two-dimensional electron gases formed at heterojunctions, which would improve the viability of Ga_2O_3 electronic devices. However, experimental data on attaining the ε-Ga_2O_3 phase is extremely limited and homo- or heteroepitaxial films currently demonstrated are of very poor quality. In this work, we use atomic layer epitaxy (ALE) to produce high-quality heteroepitaxial Ga_2O_3 films and demonstrate phase selectivity with a variation in growth temperature, plasma gas chemistry and plasma pressure.

ALE Ga_2O_3 films were deposited on c-plane sapphire substrates in an Ultratech Fiji 200 reactor equipped with a load lock and turbo pump. All films were produced using trimethylgallium and O_2 plasma precursors with pulse/purge times of 0.015s/10s and 10s/10s, respectively. The growth temperature, plasma gas flow, and pressure were varied to determine their impact on resulting film crystallinity and phase composition. Independent of growth conditions, all films were crystalline, high resistivity films with Ga/O ratios between 0.68-0.70 and no indication of C contamination by XPS.

Decreasing chamber pressure an order of magnitude drastically effected the resulting phase, yielding pure β-Ga_2O_3 at high pressure and pure ε-Ga_2O_3 at low pressures. Additionally, at low pressures, as the growth temperature was increased from 300 to 500°C, subsequent films went from mixed phase, to purely ε-Ga_2O_3 at 350°C, to purely β-Ga_2O_3 at 500°C. Alternatively, at 350°C and low pressure, the phase could be altered by a change in O_2 plasma flow. High-quality β-Ga_2O_3 films were produced at 5sccm O_2 that had an RMS roughness of 0.38nm and XRD FWHM of 268 arcsec for a 30nm film. At 40sccm, high-quality ε-Ga_2O_3 films were obtained with an RMS roughness of 0.15nm and XRD FWHM of 250 arcsec for a 30nm film. Thus, using ALE high-quality, phase selective films can be achieved to satisfy application requirements.

5:15pm **NS+EM-SuA-16 High Quality SiN and SiO₂ Films Produced by PEALD with Microwave ECR Plasma Below 200 ºC**, ***Jesse Kalliomaki**, V Kilpi,* Picosun Oy, Finland*; T Maline,* Picosun Oy*; H Enami, N Mise,* Hitachi High-Technologies Corp., Japan*; H Hamamura, T Usui,* Hitachi R&D Group

Due to continuous feature size scaling down and change to the 3D structures, currently new process innovations are required more strongly than the previous. Conformal film formation of Si compounds like SiO_2 and SiN is the key technologies and is widely used for double patterning, spacer and liner applications. PEALD at low temperature is one of the suitable solutions for these applications. We reported the superiority of low pressure microwave ECR(M-ECR) plasma for Si substrate nitridation at low temperature [1].

In this study, SiN and SiO_2 film properties were evaluated for demonstrating the advantage of the newly combined tool with the M-ECR plasma and the leading ALD system from Picosun. BDEAS (Bis(Diethylamino)Silane) was used as Si precursor. N_2 and O_2 gas were introduced into M-ECR plasma to form SiN and SiO_2, respectively. Process pressure was set lower than 1Pa. Film density and WER (wet etching rate) were measured by XRR and DHF (0.5%), respectively. Composition of film was analyzed by XPS with Ar sputter.

SiN film density obtained in this study was investigated as a function of deposition temperature and compared with that of the conventional PEALD SiN [2,3] as shown in Fig. 1. The film density slightly increases with rise in deposition temperature and the value is about 2.9 g/cm^3 at low temperature below 200 ºC. This value is much higher than that of the conventional PEALD SiN and nearly equal to that of LPCVD SiN at 850 ºC. WER obtained in this study is extremely low compared to that of the conventional PEALD SiN as shown in Fig. 2. This low WER is advantageous for device fabrication. XPS analyses reveal that residual C in the film is less than 3 %. Longer exposure time of N_2 plasma could reduce the C content and WER. Efficient generation of the radicals and ions by M-ECR plasma at low pressure [4] is supposed to improve the film properties.

SiO_2 film properties deposited at 150 ºC were also investigated. Film density is 2.2 g/cm^3, this value is nearly equal to that of thermal SiO_2. WER is 4.5 nm/min and this value is smaller than that of the conventional LPCVD SiO_2 formed at 750 ºC (6.0 nm/min). O/Si ratio of the film is 2.1 and residual C is less than 1 %.

From these results, PEALD with M-ECR plasma can be one of the most advantageous solutions for next-generation leading edge devices and other novel devices.

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5:30pm **NS+EM-SuA-17 Tertiary Butyl Hydrazine as a Reducing Agent for Low-Temperature Atomic Layer Deposition of Low-Resistivity Copper Thin Films**, ***Katja Väyrynen**, K Mizohata, J Räisänen,* University of Helsinki, Finland*; D Peeters, A Devi,* Ruhr-University Bochum, Germany*; M Ritala, M Leskelä,* University of Helsinki, Finland

Copper plays an important role in the development of microelectronics as it is the primary interconnect material. The manufacturing procedure of the Cu interconnects is typically two-fold: first, a Cu seed layer is deposited by PVD followed by a Cu fill process carried out by electrochemical deposition. In order to reduce component sizes, and thus increase device efficiency, thin yet continuous Cu films are desired. This can be accomplished by replacing the existing course of action, or at least the PVD step, with more accurate deposition methods such as ALD. The Cu ALD processes known to date, however, exhibit limited applicability due to issues ranging from agglomeration caused by high temperatures to Zn incorporation and strong substrate sensitivity.

Tertiary butyl hydrazine (TBH) was recently introduced as an ALD reactant for the reduction of silver thin films.[1] Otherwise, the use of hydrazine or its alkyl derivatives in metal ALD has been scarce.[2,3] In this work, Cu thin films were deposited via reduction of $Cu(dmap)_2$ (dmap = dimethylamino-2-propoxide) by TBH. The process was investigated between temperatures of 80 and 140 °C. A saturating growth mechanism was observed with respect to both precursors at 120°C. Both the growth characteristics and the film properties were found to vary depending on the substrate, but deposition was not limited only on certain starting surfaces. The films were identified as crystalline cubic Cu with a minor preference towards (111) orientation. The films were relatively smooth and showed uniform thickness across the 5 x 5 cm^2 substrates. At the lowest, a resistivity of 1.9 µΩcm was measured from a 54 nm film exhibiting a Cu content of 97.2 at.%. Oxygen was identified as the main impurity (1.7 at.%) but it was limited almost entirely to the film surface indicating oxidation upon exposure to air (Figure 1).

The films were deposited in a hot-wall flow-type F-120 ALD reactor (ASM Microchemistry). Thorough film characterization was carried out by energy-dispersive X-ray spectrometry, scanning electron microscopy, X-ray diffraction, four-point probe, and time-of-flight elastic recoil detection analysis.

[1] Z. Golrokhi et al. *Appl. Surf. Sci.***2017**, *399*, 123–131.

[2] T. J. Knisley et al. *Chem. Mater.***2011**, *23*, 4417–4419.

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ALD Applications
Room Plaza Exhibit - Session AA-SuP

ALD Applications Poster Session

AA-SuP-1 Atomic Layer Deposition Surface Functionalized Adsorbents for Adsorption of Metal Ions and Organic Pollutants*, **Xiaofeng Wang**, X Liang,* Missouri University of Science and Technology

Ultrathin TiO_2 and Al_2O_3 films were deposited on silica gel particles and biochars by atomic layer deposition (ALD), respectively. TiO_2 coated silica gel particles were used as adsorbents for adsorption of metal and metalloid ions; their adsorption ability for a mixture of 19 trace elements of heavy metals and other toxic elements, including As(V), Se (IV), Be(II), Al(III), V(V), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Ba(II), Tl(I), Sb(III), Cd(II), Ag(I), Sr(II), Mo (VI), and Pb(II), from aqueous solutions was investigated. At pH 5, the 20 and 40 cycles of TiO_2 coated samples without heat treatment removed remarkable amount of As(V), Se(IV), V(V), Mo(VI), Pb(II), Sb(III), Ag(I), Cu (II), and Ba(II) from the solution simultaneously. The micron-sized adsorbent particles were separated easily from water due to their large particle size, making it practically suitable for trace contaminant remediation in water. Al_2O_3 deposited biochars were used for removal of organic pollutants and the adsorption capacities were evaluated by adsorption of methylene blue (MB). The data fit well with the Langmuir isotherm and the maximum adsorption capacities were found to be 26.8 and 35.0 mg/g at 25 ºC for the uncoated biochar and 5 cycles of Al_2O_3 coated biochar, respectively. The improvement of adsorption capacity after Al_2O_3 ALD coating was due to its improved hydrophilia.

AA-SuP-2 Supported Ni Nanoparticle Catalysts Synthesized by Atomic Layer Deposition for Dry Reforming of Methane*, **Zeyu Shang**, X Liang,* Missouri University of Science and Technology

Due to the limited availability and high cost of noble metals, Ni nanoparticles have been widely employed as catalysts in many research areas. Conventionally, supported Ni nanoparticles catalysts were synthesized by impregnation methods, but the particles were normally relatively large (typically tens of nanometers). Lately, extremely small Ni nanoparticles (~3 nm) have been successfully synthesized by atomic layer deposition (ALD). In our study, we deposited Ni nanoparticles on high surface area γ-Al_2O_3 substrates. The catalysts were employed for dry reforming of methane (DRM). DRM is important because two main greenhouse gases (carbon dioxide and methane) could be converted to syngas in this reaction process. The main disadvantage of the Ni catalyst for DRM reaction is deactivation, due to coking and sintering of Ni metal nanoparticles. In this study, the Ni/γ-Al_2O_3 catalyst prepared by ALD showed very high activity and stability in catalyzing DRM reaction in over 300 h at temperatures that ranged from 700 °C to 850 °C. The excellent stability of the catalyst resulted from the formation of $NiAl_2O_4$ spinel. The high catalytic activity was due to the high dispersion of Ni nanoparticles deposited by ALD and the reduction of $NiAl_2O_4$ spinel to Ni during the DRM reaction at 850 °C.

AA-SuP-3 Wear Behavior of Annealed Atomic Layer Deposited Alumina Thin Films*, **Zakaria Hsain**, G Zeng, B Krick, N Strandwitz,* Lehigh University

Atomic layer deposited (ALD) alumina is a promising candidate for use as a wear-resistant and protective coatings in micro-electromechanical systems (MEMS); however, few efforts have been made to quantify and understand its wear behavior. The tribological properties of ALD alumina are affected by numerous factors related to processing, environment, and operating conditions. In this study, ALD alumina coatings of varying thicknesses are annealed at different temperatures, then subjected to tribological testing in dry nitrogen and humid air environments. Tribological properties, particularly wear rate, appear to be heavily influenced by annealing temperature. Surprisingly, wear rate dropped by more than two orders of magnitude after annealing at 1000 ºC, while coatings annealed at 900 and 1100 ºC were not as wear resistant.

This increase in wear resistance is due to crystallization and densification of the ALD coating. Other factors which are shown to contribute to wear mitigation include tribofilm formation and thermally-activated diffusion at the coating/substrate interface.

AA-SuP-4 Surface Enhanced Raman Scattering Effect on Various Pt Nanostructures by using Self-aligned Block Co-Polymer Template, Pt Atomic Layer Deposition*, **Won-Kyun Yeom**, J Shin, D Sung, J Oh, J Oh, G Yeom,* Sung Kyun Kwan University, Republic of Korea

Surface Enhanced Raman Spectroscopy(SERS) is a Raman Spectroscopic (RS) technique that provides greatly enhanced Raman signal from Raman-active molecules that have been adsorbed onto certain specially prepared metal surfaces. Theoretically, any metal would be capable of exhibiting Surface Enhance (SE), but noble metals and alkali metals satisfy calculable requirements and provide the strongest enhancement. Metals such as Pd or Pt exhibit enhancements of about 10^2~10^3 for excitation in the near ultraviolet. The SERS is applied as various bio and chemical sensors and analyzers.

In this research, SERS effect was investigated with various nanostructure and, by using self-aligned Block Co-Polymer(BCP) and Pt Atomic Layer Deposition(ALD), 40nm-scale Pt nanostructures with different shapes (nanorod, nanohole, and nanotube) and different heights (30nm, 50nm, and 90nm) were fabricated. The SERS effect investigated with rhodamine 6G on these nanostructures showed that the SERS effect is dependent on the shape of the nanostructure rather than the nanostructure.

In conclusion, using Pt ALD and BCP, different Pt nanostructures were formed on silicons substrate, and the effect of shape and size of the Pt nanostructure on the SERS effect of rhodamine 6G with the concentration of 10^{-6} mol was investigated. Among the investigated nanostructures, the Pt nanotube structure with 40nm-scale diameter / 90 height exhibited the best SERS effect.

AA-SuP-5 Effect of Post-annealing on the Performance of Ultraviolet Photodetectors with Atomic-Layer-Deposited ZnO Semiconductor*, **Jian Gao**, W Liu, S Ding,* Fudan University, China

Ultraviolet photodetectors (PDs) can be applied to various fields, such as flame alarming, missile plume detection, ultraviolet solar irradiation etc. In this work, we have investigated the effect of post-annealing on the ZnO metal-semiconductor-metal (MSM) ultraviolet photodetectors. The ZnO thin films were deposited by atomic layer deposition (ALD) on SiO_2/Si(100) substrates, and then Cr/Au bi-layers were used as interdigital electrodes. For as-fabricated ultraviolet PD, the dark current was too large and beyond our measurement range. Therefore, post-annealing in air under different temperatures and durations was performed on the ultraviolet PDs. After being annealed in air for 30 min, the dark- and photo-currents of the ultraviolet PDs reduced with increasing annealing temperature. For 250 ºC annealing temperature, the dark current was equal to 5.16×10^{-11} A, and the ultraviolet-visible rejection ratio reached to 1.4 $\times10^6$, and the responsivity was as high as 1.78×10^3 A/W at 5V. Furthermore, increasing post-annealing time at 200ºC in air can also greatly improve the performance of the ultraviolet PDs. In terms of 90 min post-annealing, the ultraviolet PD demonstrated a very low dark current of 1.42×10^{-10} A, a large ultraviolet-visible rejection ratio of 9.6×10^6, and a quite large responsivity of 1.30×10^4 A/W at 5V. This phenomenon can be attributed to the positive feedback of hole traps near the cathode. In a word, it is shown that the atomic-layer-deposited ZnO thin film is a promising candidate for high responsivity and low dark current ultraviolet PDs.

AA-SuP-6 Density and Origin of Pinhole-Defects in ALD Barrier Coatings on Steel Substrates*, **Tim Poljansek**, S Klein,* Robert Bosch GmbH, Germany*; J Bartha,* TU Dresden, Germany

ALD is capable of coating 3D substrates with a conformal, dense and defect free thin film. Because of that ALD is a promising technique to protect steel parts from corrosion [1]. However, the film growth on steel is not as good as on a silicon wafer, resulting in pinholes in the coating. The density of these pinholes is a crucial parameter, which strongly influences the barrier properties of the films. Reducing the pinhole density is a prerequisite for effective corrosion protection barriers. Therefore, the origin of the defects must be understood to eliminate the defect sources.

The goal of these investigations is to study the origin of the defects and to investigate the correlation of the pinhole density with the thickness of the coating and the surface pre-treatment.

A well-suited technique to visualize pinholes in an insulating ALD film on a conductive substrate is the copper electroplating process [2]. Thereby, copper is deposited on every part of the substrate that is not covered by the coating. This leads to copper bumps on every pinhole in the layer, without destroying the defect and its origin.

Al_2O_3 and Ta_2O_5 were deposited in a Picosun SUNALE R-200 Advanced reactor at 180 °C. The precursors for Al_2O_3 and Ta_2O_5 were trimethylaluminum and tris(ethylmethylamido)(tertbutylimido)tantalum(V), respectively, and water. For the copper deposition the electroplating solution CUPROSTAR NC from enthone was used. The substrates used in this study are grinded and lapped case hardened steel disks.

On Al_2O_3 and Ta_2O_5 coated steel samples after electroplating the defect density shows an exponential decay with increasing film thickness, until there are only few copper bumps detectable. Furthermore, thin Al_2O_3 coatings show less pinholes than Ta_2O_5 coatings, indicating a better film growth of Al_2O_3 on steel. The defect density of thin ALD coatings can be reduced if an additional surface pre-treatment with an alkaline cleaner is introduced,. To investigate the origin of the pinholes some of the copper bumps were milled with focused ion beam. At the center of some copper bumps a protrusion, most likely the origin of the pinhole, can be seen on the steel substrate. This is presumably a grain of dust.

The origin of the defects is under further investigation with secondary ion mass spectrometry. In addition, further experiments with different surface pretreatments, process parameters and ALD coatings are still in progress.

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[2] Y. Zhang, J.A. Bertrand, R. Yang, S.M. George, Y.C. Lee, Thin Solid Films 517 (2009) 3269-3272

AA-SuP-7 Room-Temperature Atomic Layer Deposition of Al_2O_3 for Anticorrosion Coatings*, **Kensaku Kanomata**, M Ishikawa, M Miura, B Ahmmad, S Kubota, F Hirose,* Yamagata University, Japan

Room temperature atomic layer deposition processes of SiO_2, TiO_2, Al_2O_3 and ZrO_2 were reported by using plasma excited humidified argon. In this work, we examine the RT-ALD deposited Al_2O_3 as an anticorrosion coating for stainless steels. Trimethylaluminum (TMA) as the aluminum precursor was introduced with mass flow controller (MFC). A remote plasma system generating excited humidified argon was installed to the ALD chamber. The source gas for the oxidizing gas is a mixture of water vapor and argon. The plasma was generated in a glass tube with an induction coil with 13.56 MHz and RF power of 100 W. For the Al_2O_3 deposition, we repeated the cycle of TMA saturation and oxidizing gas treatment at RT. The TMA exposure was set at 5.86×10^{-3} Torr× 40 sec. The saturation of TMA on the hydroxylated surface was confirmed by the IR absorption spectroscopy. The plasma excited oxidizing gas was injected for 2 min. In the conference, we show the anticorrosion test of ALD coated stainless steel in an HCl solution. We used SUS430 plates with a size of $20\times50\times0.5$ mm^3 as the sample. In this test, we used a not-diluted HCl solution with a concentration of 35 %. All the samples were immersed in the HCl solution for a certain amount of minute at room temperature and we observed its surface coloring. In the conference, we discuss the applicability of the RT-ALD to the anticorrosion coating for metal components.

AA-SuP-8 Structural and Optical Properties of SnS and SnSe Thin Films Grown by Atomic Layer Deposition for Photovoltaic Applications*, **Ji Hye Kim**, Y Tak, H Park,* ISAC Research Inc., Republic of Korea

Because of low cost and abundance in nature, SnS has recently received great attention. Tin sulfides (SnS_x) as well as Tin selenice (SnSex) have great potentials to provide high solar conversion efficiency because of an narrow optical band gap of 1.0 to 1.5eV with p-type conductivity. Although ideal conversion efficiency of SnS solar cells is 32%, existing SnS solar cells has very low efficiency. Recently, atomic layer deposited SnSx showed the highest efficiency. However, structural and optical properties of the films were not studied yet. We have prepared SnSx and SnSex films by atomic layer deposition using metal-organic at various substrate temperature. The structure, morphology and optical properties of the prepared thin films were studied using X-ray diffraction, scanning electron microscopy (SEM) and optical absorption techniques respectively and the results are discussed.

AA-SuP-9 Characterization of the Alumina-Alucone Multilayer Thin Film for a Flexible Transparent Electrode by Atomic Layer and Molecular Layer Depositions*, **Sung Tae Hwang**, S Song, G Lee, B Choi,* Korea University, Republic of Korea

To improve the mechanical reliability of the thin films deposited on a flexible display substrate, the interests in organic-inorganic hybrid systems are increasing in the related industries. In this study, the organic-inorganic hybrid thin films are deposited on polymer substrate using atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques. The combination of organic- inorganic layer can provide the improvement of the mechanical properties of thin films by interposing the organic layer between ceramic layers[1,2]. The Al_2O_3 – ZnO laminated layers were deposited using ALD and alucone layer was deposited using MLD technique on the transparent polyimide (TPI) film substrate with various thickness. All TPI specimens were treated with oxygen plasma before thin film deposition to make functional radical species on the surface of TPI[3]. The mechanical properties of the thin films were measured using a micro-tensile test, nano-scratch test and nano-indentation test. By changing the ratio of organic-inorganic layer thickness and position of organic layer, the optimal condition of the thin films was investigated.

AA-SuP-10 Investigation of Pure Antimony Films Grown by PALD*, **Bodo Kalkofen**, M Silinskas, R Balasubramanian, B Garke,* Otto von Guericke University, Germany*; H Gargouri,* Sentech Instruments, Germany*; E Burte,* Otto von Guericke University, Germany

In this work, the deposition kinetics of the growth of pure antimony thin films, the properties of such films and the applicability of Sb films as dopant sources for shallow doping of silicon, germanium, and SiGe were studied. The plasma-assisted atomic layer deposition (PALD) with remote conductively coupled plasma source was carried out for this purpose. $Sb[N(CH_3)_2]_3$ was used as antimony precursor and hydrogen as reactive and plasma gas.

Different deposition parameters, such as substrate temperature, deposition pressure, precursor injection time, plasma current, sequence and duration of each step were tested in order to find the optimal deposition conditions for stable Sb films that could be further used as antimony dopant sources.

For almost all deposition conditions, the deposited Sb films were mostly stable in the ambient air as confirmed by ellipsometric measurements but showed very thin antimony oxide layer at the top surface after transfer in air to X-ray photoelectron spectroscopy analysis (XPS) (see Fig. 1). Short Ar sputtering removed adventitious carbon contamination from the films as well as the antimony oxide, and pure antimony could be detected by XPS as shown in Fig. 2, where no trace of oxygen was found. Generally, the impurity level of contaminants was below XPS detection level after Ar sputtering. Additionally, the as-grown films were polycrystalline as shown from results of X-ray diffraction analysis in Fig. 3.

AA-SuP-11 Fabrication of Hollow Structures Using Plasma Enhanced Atomic Layer Deposition*, **Masayuki Nakamura**, T Kobayashi, T Sagawa, T Tatsuta, S Motoyama,* Samco Inc., Japan*; P Wood,* Samco Inc.*; O Tsuji,* Samco Inc., Japan

As the dimensions of MEMS and power devices shrink, the atomic-scale control of ultra-thin dielectric film over 3D structures becomes more important. ALD gets a lot of attention because of its pure surface limits reaction and excellent thickness and uniformity control. In this study, we apply conventional TMA and H_2O based ALD and N_2 plasma enhanced ALD (PEALD) process to deposit AlO_x and AlN films over 3D structures, and introduce a new dry process to make AlN hollow structures.

Firstly, we deposited AlO_x films over Si substrates. The chemically-treated Si substrates were loaded into a SAMCO AL-1 system, and AlO_x films were deposited using TMA and H_2O at 250°C. The film thickness was determined by an interference film thickness meter. The thickness increased linearly with the number of cycles at 1.2Å/cycle, which indicates precise thickness control with minimal surface roughness.

Next, we deposited AlO_x over a high aspect ratio (~40) trench structure. Trench structures 72µm deep with a scallop size of 84nm were prepared using Si deep RIE processes over a Si substrate. In the SEM cross sections, the upper and bottom film thickness are the same, and uniform step coverage of 84nm scallops can also be observed. Atomic-scale, layer-by-layer processing enables this perfect step coverage.

Finally, we fabricated an AlN dome-shaped hollow structure over a sapphire substrate. MEMS sensors with this kind of hollow structure have been fabricated via wet etching, but it generates a large amount of waste liquid[1][2]. Therefore, we applied the PEALD process, where the alternating supply of TMA and capacitively coupled N_2 plasma forms 140 nm thick AlN over the dome-shaped photoresist patterns. After the deposition, 1000°C anneal was performed using a microwave heating system. In the SEM images, there is no photoresist underneath the AlN film, and the dome shapes perfectly trace the original photoresist pattern. The thicker film required longer annealing time, which indicates that the photoresist evaporates via AlN grain boundaries or cracks. This technique enables fabrication of hollow structures with a microscale diameter and nanoscale film thickness without the use of wet processing.

Reference

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[2] R. Lanz, P. Carazzetti and P. Muralt: Proc. IEEE Ultrasonics Symposium 981 (2002).

**AA-SuP-12 PALD of Germanium Antimony Tellurium Compounds*, Mindaugas Silinskas*, *B Kalkofen, R Balasubramanian, N Harmgarth,* Otto von Guericke University, Germany*; H Gargouri,* Sentech Instruments, Germany*; E Burte,* Otto von Guericke University, Germany

In this work, the germanium, tellurium, germanium telluride, antimony, antimony telluride and germanium antimony telluride thin films were deposited by plasma-assisted atomic layer deposition (PALD) with remote conductively coupled plasma source. $Ge[N(CH_3)_2]_4$, $Sb[N(CH_3)_2]_3$, and $C_8H_{18}Te_2$ as well as other new precursors were tested as germanium, antimony, and tellurium sources. Pure hydrogen and its mixture with argon were applied as reactant gas for the plasma.

Various deposition parameters, such as substrate temperature, deposition pressure, precursor injection time, plasma current, sequence and duration of each step and number of the steps were varied in order to characterize the deposition process.

The Investigation of chemical composition shows that the chemical composition of the films can be effectively changed by the changing of the numbers of the precursor steps in the supercycles. Additionally, the impurities content is mostly related to the plasma (hydrogen) step.

X-ray diffraction analysis indicates that crystallinity of the films depends mainly on the compositions of the films but not on the deposition temperature.

**AA-SuP-13 Flexible Alucone/Al_2O_3/Alucone Hybrid Dielectric Layers using *in-situ* ALD/MLD Techniques*, Dong-Won Choi*, *S Lee,* Hanyang University, Korea*; J Lee,* Hanyang University, Korea, Republic of Korea*; J Park,* Hanyang University, Republic of Korea

Flexible electronics have spread across an expansive area such as fundamental transistors, sensing devices, and flexible Organic light-emitting diode display. One of main issues for flexible electronics is mechanically robust insulator materials to work with flexible substrates and newly emerging semiconductor materials. Most of dielectric materials are based on inorganic materials such as oxide and nitrdie due to its high capacitance, low leakage and high breakdown field property. However, most of inorganic materials are limited for flexible electronic devices because inorganic materials showed brittleness characteristics with mechanical stress. In order to overcome this problem, inorganic/organic hybrid dielectric layers are suggested owing to the its superial mechanical property. However, it is challenging to make uniform pinhole free organic dielectric layer because there is no suitable process and materials. Molecular Layer Deposition (MLD) process might be strong cadidate for uniform phinhole free organic thin film deposition because MLD process can allow accurate thickness control and conformal coverage over the substrate area, accompanied by high film quality at low temperature.

In this study, we investigated dielectric properties of single alucone organic layer using MLD technique, and Al_2O_3/Alucone/Al_2O_3 inorganic/organic/inorganic structure using *in-situ* ALD/MLD process. As a result, the uniform and well aligned inorganic/organic/inorganic structure was fabricated as shown in figure, and suggested hybrid layer exhibited excellent dielectric properties. This presentation will be discussed with I-V, C-V characteristics of single alucone and Al_2O_3/Alucone/Al_2O_3 thin films with time after fabrication, and bending stress. Also, FIB, FT-IR, XPS, AES depth profile results and electrical Ca-test measurement will be discussed in order to investigate more detail film properties.

**AA-SuP-14 Characteristics of Low-k Film at Low Temperature Using SDP System*, Minho Cheon*, *D Lee,* JUSUNG Engineering, Republic of Korea

As channel length scales further into in the nanometer regime, the parasitic capacitances and series resistance are going to seriously impact the transistor performance. Low-k spacer is a good candidate to minimize parasitic capacitance for high-speed applications.

In this study, we present a newly developed SDP system with a wide range of process temperature by both rotating the substrate and dividing the space area.

We have investigated the characteristics of SiCN and SiOCN thin film composition by reactant gas containing nitrogen like N_2, NH_3 & doping gas containing oxygen like N_2O, O_2, etc. and Amine series for Si source at low process temperature ranging from 350℃ to 550℃. We obtained the following results by experiment : SiCN result shows the uniformity less than 1% , step coverage 100% at aspect ratio of 10:1, wet etch rate 0.038Å/sec @100:1 DHF. And Low-k SiOCN result shows the uniformity less than 1% , step coverage 100% at aspect ratio of 10:1, wet etch rate 0.1Å/sec @ 100:1 DHF, Dielectric constant(k) 4.75. In case of Low-k SiOCN obtained condition that the Leakage Current <1.0E-8A/㎠ and substrate on Metal oxidation free, Cl Free.

AA-SuP-15 High Quality ALD of Silicon Nitride Films via Microwave Plasma*, Kihyun Kim*, Samsung Electronics, Republic of Korea*; J Provine, P Schindler, F Prinz,* Stanford University

Modern integrated circuit processing for DRAM, flash, and logic devices require silicon nitride (SiN) spacer layers with exacting requirements for chemical, physical, and electrical performance. High quality SiN thin films can be achieved by low pressure chemical vapor deposition (LPCVD) at elevated deposition temperatures (>800°C). However, modern device design rules require low thermal budget (<400°C) for these and other applications.

In this abstract, we demonstrate with a custom built PEALD system utilizing a high power (~1kW) microwave plasma source. Utilizing this system, we can achieve composition with low oxygen, carbon, and hydrogen content similar to what is achieved in higher temperature LPCVD reactions.

The dependence of the SiN film properties on processes parameters including plasma power and plasma treatment cycle, are investigated. Specifically, the wet etch rates in dilute hydrofluoric acid (H_2O:HF 200:1) with respect to plasma power and treatment cycle times can be varied because of the effects of radicals and ions generated by the plasma source during deposition. Wet etch rates comparable to LPCVD SiN films can be demonstrated at significantly reduced temperature by PEALD. X-ray reflectometry (XRR) and X-ray photoemission spectroscopy (XPS) studies show the higher plasma power and extended plasma treatment cycles can vary the density and the composition of SiN films.

AA-SuP-16 Improved Corrosion Resistance and Mechanical Properties of CrN Hard Coatings with an Atomic Layer Deposited Al_2O_3 Interlayer*, Zhixin Wan*, *S Park, S Kwon,* Pusan National University, Republic of Korea

Chromium nitride (CrN) hard coatings have been applied as a replacement for electroplated hard chromium in various applications due to the high hardness, corrosion, wear and anti-oxidation properties. However, the hard coatings present intrinsic defects (columnar structures, pinholes, pores, cracks and discontinuities) that allow contact between the steel and its environment, which can lead to accelerated deterioration through pitting corrosion when substrates are active alloys like steel.

In this work, CrN/Al_2O_3/CrN multilayered coatings were synthesized by a hybrid process of both high power impulse magnetron sputtering (HIPIMS) and atomic layer deposition (ALD) techniques, aiming to modify the CrN hard coating properties. Detailed studies on the microstructure, surface roughness, mechanical properties and corrosion behaviors, investigated by SEM, XRD, AFM, polarization curves and the hardness indenter, were used to characterize the influence of Al_2O_3 interlayer addition. The results indicated that the dense Al_2O_3 interlayer addition lead to a significant decrease of the average grain size and surface roughness, which greatly improved the mechanical properties and corrosion resistance of the CrN coatings. The thickness increasing of the Al_2O_3 layer and intercalation position altering to be approaching to the coating surface resulted in better mechanical properties and corrosion resistance. The mechanism can be explained by that the dense Al_2O_3 interlayer played an excellent barrier for dislocation multiplication and diffusion of the corrosive substance.

AA-SuP-17 ALD Thin-Films for Micro-Channel Plate based Detectors*, Nitin Deepak*, University of Liverpool, UK*; S Harada, T Conneely,* Photek Ltd., UK*; R Potter,* University of Liverpool, UK*; J Milnes,* Photek Ltd., UK

Micro-channel plate (MCP) based photon detectors are used for numerous applications such as night vision cameras, x-ray detection, neutron detection, plasma fusion diagnostics, defence applications etc. Fast rise time (<100ps), high gain, stable operation in magnetic fields, and low power consumption have made these detectors attractive candidates for these applications.

An MCP is a highly resistive (10 to 100 mega ohms) thin slab of glass through which millions of pores are etched in a hexagonal pattern. Each pore acts as an amplification channel for electrons impinging on its walls. A gain of 10^6 can easily be achieved using MCPs. In this work, we have used atomic layer deposition (ALD) to enhance the gain and lifetime of these detectors. ALD is capable of coating 3D surfaces with very high surface areas and we have used this capability for our product development. MCP pores were coated with an Al_2O_3 layer, using our detector characterization capabilities, we have shown how the growth parameters of Al_2O_3 thin films can have a dramatic effect on the gain and lifetime characteristics of these detectors. We will discuss the detector failure mechanism and how ALD helps to improve lifetime and boost gain.

AA-SuP-18 The Effect of SiOx/SiNx Multilayer Structure using Low Temperature Plasma Enhanced Atomic Layer Deposition for Gas Diffusion Barrier

Ju-Hwan Han, Hanyang University, Republic of Korea*; C Kim, K Lim, S Lee, H Choi,* LG Display, Republic of Korea*; J Park,* Hanyang University, Republic of Korea

Flexible organic light emitting diodes (F-OLEDs) have recently been considered to be the most promising device for next-generation displays.[1] One of main issues for F-OLEDs is to develop the thin film Encapsulation (TFE) technique regarding materials, processes and structures. The technique has been already adopted with plasma enhanced chemical vapor deposition, evapoartion, and ink-jet printing.[2],[3] However, those techniques are struggling with the followin issues : thickness, particle, conformaility, and robust diffusion barrier propety etc.. Atomic layer deposition (ALD) is rapdily emerging as one of suitable deposition methods for thin film deposition since this technique provide excellent conformality, less-particle and very thin diffusion layers.[4] Although there are previously reported with several gas diffusion barrier layers,[5],[6] it was limited to a few materials and structures for TFE applications. In thin study, the SiOx/SiNx multilayer and structure are deposited plasma enhanced ALD even below 100°C, using di-iso propyl aminosilane ($SiH_3N(C_3H_7)_2$, DIPAS) as the Si precursor and N_2 plasma and (Ar + O_2) plasma as the reactant respectively.As a preliminary result, SiOx/SiNx layer sturcture exhibited about 2 times lower WVTR of 3.79 ´ 10^{-3} g/m^{2}day at 25°C/50%R.H. than that (7.05 ´ 10^{-3} and 8.53 ´ 10^{-3} g/m^{2}day) of the single layer (SiOx and/or SiNx), respectively.

AA-SuP-19 Reduced Thermal Conductivity of ALD Synthesized PbTe/PbSe Nanolaminates Grown on Nanopatterned Substrates

Xin Chen, Old Dominion University*; M DeCoster,* University of Virginia*; P Lin, K Zhang,* Old Dominion University*; P Hopkins,* University of Virginia*; H Baumgart,* Old Dominion University

The conversion efficiency of the thermoelectric device is related to the dimensionless figure of merit ZT, which is expressed as $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature. Reducing thermal conductivity is one of the powerful strategies to meet the requirement of improving ZT. This can be realized in nanocomposite TE materials, low dimensional structured materials and phononic crystal nanostructures. The reduced thermal conductivity results from phonon scattering by numerous interfaces and phonon-boundary in these structures.

In this study, we investigated the effect of patterned substrates on the thermal properties of ALD deposited PbTe/PbSe nanolaminates (NL). Square porous patterns and stripe patterns were investigated in the work. The thermal conductivity of a series of the PbTe/PbSe NL films with different periods (the thickness of each layer in NL structure) grown on porous and non-porous patterned substrates were measured using Time-Domain Thermoreflectance (TDTR) method. The results indicate the films grown on porous patterned exhibits lower thermal conductivities by nearly a factor of two lower than the ones grown on non-porous substrates, and the thermal conductivity is strongly dependent on the period of the NL structure. This is attributed to phonon boundary scattering. The higher Seebeck coefficient was observed in the porous samples resulting from its lower thermal conductivity. In addition, we use finite element analysis COMSOL to calculate the effective thermal conductivity of the PbSe film grown on stripe patterned substrate as the function of the width of stripe pattern varied from 0.1 to 1 um. It is revealed that the width of stripe pattern plays an important role in reducing the effective thermal conductivity of the film, and the effective thermal conductivity is further reduced by depositing thinner films due to the thin film thickness related to mean free path of the phonon in the deposited films.

AA-SuP-20 The Effect of Titanium Tetrachloride-based Plasma Enhanced ALD TiN on the Threshold Voltage of Gate Last-Like Processed FD-SOI MOSFET with ALD HfO_2 Gate Dielectric

Y Kim, M Chae, ***Changhwan Choi,*** Hanyang University, Korea

For the reliable CMOSFETs, low and symmetric threshold voltage (V_{th}) is required, which is typically controlled by dopant implant to poly-Si gate and channel doping into the substrate. This V_{th} control was limited by metal gate work-function and substrate doping concentration since the poly-Si was replaced by metal gate. This constraint can raise the difficulty of V_{th} control in the extremely scaled device due to material and process issues (ex. thermal stability, gate etch). Beside the highly or moderately-doped bulk Si, the low doping or intrinsic substrates have been also attractive to the SOI device and TFET for the low power applications. In this case, V_{th} control becomes more challenging because substrate doping cannot be contributed to decide V_{th}. Therefore, the selection of metal gate and its relevant process play an important role to attain the multiple V_{th}.

We demonstrated the possibility of multiple V_{th} using titanium tetrachloride ($TiCl_4$)-based PEALD TiN within gate last-like processed FDSOI MOSFET with ALD HfO_2 system. Reactant gas was used with NH_3. The deposition temperature window for ALD process was observed between 250 and 300 °C. From the MOS capacitor, the work-function values are 5.0 and 4.77 eV for HfO_2 and SiO_2 gate dielectrics, respectively, with negligible EOT and gate leakage current density variation. Increasing TiN thickness leads to higher flatband voltage (V_{FB}) shift up to 350 mV and increased work-function by 0.2 eV. Impacts of deposition temperature, reactant pulse time, and plasma power on the V_{FB}/V_{th} variation are not significant compared to TiN thickness change. From the FDSOI MOSFET, thicker TiN induces 180 mV V_{th} shift without remarkable transistor parameter degradation such as subthreshold swing and I_{on}/I_{off} variation. This result could be attributed to more oxygen content within thicker TiN similar to the reported PVD TiN result. TiO_xN_y (i.e., TiN containing small amount of oxygen) is known to be p-type work-function metal, related to be high work function or high V_{FB}. Another popular ALD TiN precursor, tetrakis-dimethylamido titanium (TDMAT), shows the similar V_{th} modulation trend. However, it contains the carbon residue within ALD TiN or high-k thin films leading to increased J_g or reliability instability. Our finding indicates that $TiCl_4$-based TiN could be an effective path to attain the multiple V_{th} by simple thickness change in low-doped substrate for FDSOI FET and TFETs.

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AA-SuP-21 Atomic Layer Deposition of Transition Metal Dichalcogenide MoS_2 Thin Films

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Transition metal chalcogenide (TMDC) materials, layered 2-dimensional hexagonal structure materials, such as MoS_2, $MoSe_2$, WSe_2 and WS_2 have recently been significantly investigated since a monolayer of these TMDC materials has a direct band gap. The presence of the direct band gap facilitates the TMDC materials in the application of electronic and optoelectronic systems, such as transistors, photodetectors, electroluminescent, and bio-sensing devices. Among these TMDC materials, MoS_2 with a direct bandgap of 1.8 eV of monolayer, exhibits not only good thermal stability and high melting point, but also excellent light absorption, fast photo-response and sizeable band gap properties. Therefore, these unique properties make MoS_2 a promising material for various electronic devices, photodectors, sensors and catalysis applications [1, 2].

Various efforts have been made to synthesize MoS_2 films with a few monolayers on different substrates in recent years, for instance, exfoliation, hydrothermal synthesis, pulsed laser deposition (PLD), physical vapor deposition, chemical vapor deposition (CVD). However, very little is known about atomic layer deposition (ALD) synthesis of MoS_2 films. ALD technique exhibits self-limiting atomic layer reactions in each introduced ALD cycle. It can accurately control film layer thickness stoichiometry, composition, uniformity, and sharp interface. Furthermore, ALD also can be used to deposit conformal film onto very complex structures.

Here we report on a large-area synthesis of MoS_2 films on various substrates by ALD system using Molybdenum hexacarbonyl ($Mo(CO)_6$) and dimethyldisulfide (CH_3SSCH_3, DMDS) as the chemical ALD precursors for Molybdenum and Sulfur, respectively. The as-prepared MoS_2 thin films exhibit amorphous phase. Post annealing of the as-deposited MoS_2 thin film at high temperature in the Sulfur atmosphere facilitated the amorphous films was crystallized. The Raman spectroscopy analysis show the MoS_2 thin films demonstrate the characteristic of E^1_{2g} and A_{1g} Raman modes. Seebeck Coefficient results for MoS_2 thin film indicates n-type semiconductor due to the Seebeck Coefficient being negative. The absorption spectra and transient absorption spectra for the ALD MoS_2 thin films at a pump-probe delay of various time were also presented.

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AA-SuP-22 The Impact on GaN MOS Capacitor Performance of *in-situ* Processing in a Clustered ALD/ICP/RIE Tool*, **Dilini Hemakumara, X Li, S Cho, K Floros,* University of Glasgow, UK*; I Guiney,* University of Cambridge, UK*; D Moran,* University of Glasgow, UK*; C Humphreys,* University of Cambridge, UK*; A O'Mahony, H Knoops,* Oxford Instruments Plasma Technology, UK*; I Thayne,* University of Glasgow, UK**

We report a route to the realization of GaN/Al_2O_3 MOS-capacitors (MOSCAPs), which avoids air exposure of the GaN surface by utilizing in-situ deposition of SiN_x as the final part of substrate growth. Subsequently, processing was performed in a clustered plasma etch and atomic layer deposition (ALD) tool to avoid air exposure of the gate oxide. The optimized process described in this work enabled a ~4x reduction in flatband voltage hysteresis, indicative of a significantly improved GaN-Al_2O_3 interface as a consequence of only exposing the GaN surface to process gases and plasmas in the cluster tool. In addition, using an in-situ ALD deposited TiN gate metal after Al_2O_3 dielectric deposition resulted in both a 37% increase in accumulation capacitance and a 73% increase in maximum rate of change of capacitance with voltage (dC/dV) indicative of an improved metal/dielectric interface as a consequence of not exposing the Al_2O_3 to atmosphere.

The Metal Organic Chemical Vapour Deposition grown wafer of this study included an n-doped GaN layer which was capped with 5nm SiN_x. The SiN_x capped samples were first etched using reactive ion etching (RIE) in an SF_6 plasma (50 W, 50mT, 45 s) in the etch chamber of the cluster tool before transfer under vacuum to the ALD chamber where, following an N_2 plasma treatment (5 mins 150 W), 20nm of Al_2O_3 was deposited using a 200^0C thermal TMA/H_2O process. The effects of an in-situ metal gate was quantified with a process split using an ALD deposited TiN before ex-situ Au-based contact metal deposition. The completed MOSCAP structures with ex-situ grown Pt/Au gates were first evaluated by room temperature 1 MHz capacitance-voltage measurement. This comprised a voltage sweep from -5V to +5V and then back to –5V, enabling the determination of flatband voltage hysteresis. A 60mV hysteresis was attained, which is significantly lower than in [1] where 250mV was reported for MOSCAPs without an in-situ SiN_x capping layer.

Further, comparison between the 20nm in-situ deposited TiN MOSCAP at 350^0C using TDMAT and N_2 and H_2 plasma and ex-situ Pt/Au gates depicted an increase in both the accumulation capacitance from 0.32µF/cm^2 to 0.44µF/cm^2 and the maximum rate of change of capacitance with voltage from 0.149µF/cm^{2}V to 0.259µF/cm^{2}V.

These results highlight the advantages of processing gate stacks for GaN MOSFETs in a cluster tool, and the importance of avoiding air exposure of both the GaN and Al_2O_3 surfaces.

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AA-SuP-23 Plasma-Enhanced ALD of Dielectrics on Aluminum and *in-situ* FUV Spectroscopy*, **Brianna Eller, R Nemanich, P Scowen,* Arizona State University**

It is being recognized that a veritable revolution is about to happen in astronomical diagnostic work for targets ranging from protostellar and protoplanetary systems, to the intergalactic medium that feeds gas supplies for galactic star formation, to the most distant of objects in the early universe. These diagnostics are rooted in access to a forest of emission and absorption lines in the far ultraviolet (FUV) and near ultraviolet (NUV) passbands. Dielectric protected aluminum surfaces with low flatness and minimal oxide are the surfaces of choice for space-based telescopes.In light of these challenges, our work uses plasma-enhanced ALD (PEALD) to implement stable protective overcoats which can achieve high UV reflectivity and unprecedented uniformity to leverage innovative ultraviolet/optical filter construction. In particular, our PEALD system is coupled by UHV transfer to a custom UV reflectivity system that enables *in situ* reflectivity measurements to 150 nm and ultimately below 90 nm wavelengths. More specifically, we will use a range of metal fluoride layers on aluminum mirrors, where all processes are enabled by PEALD. Our designs indicate that by using PEALD, we can further reduce adsorption and scattering in the optical films as a result of the lower concentration of impurities and increased control over the stoichiometry to produce vastly superior quality and performance. In the initial stage of the project, PEALD aluminum oxide films on aluminum have been used as a proof of concept giving good reflectivity to 180 nm as characterized by the in-situ FUV measurements. Future work will utilize a custom PEALD system for aluminum and metal fluorides layers, incorporating plasma steps into the process to enable additional control of the film properties. These capabilities will allow us to push the blue edge in usable UV reflectivity of protected aluminum well below the current 115 nm limit.

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AA-SuP-24 ALD on Textiles for Wearable Electronics*, **Wade Ingram, J Jur,* North Carolina State University**

Textiles are low-cost, lightweight, flexible, and have a high surface area that when processed using ALD, can be conformally coated with a wide range of thin film materials commonly used in microelectronics. Current research of ALD on textile substrates has shown many applications in textile-inspired wearable electronics[1]. Research has demonstrated ZnO and TiO_2 thin film growth on nylon6 in conjunction with UV-photodeposition of Ag nanoparticles (NPs) to create conductive channels on the textile[2]. Ag NPs are deposited from an aqueous solution of $AgNO_3$ onto the surface of the ZnO coated fibers through a redox reaction, bonding the NPs to the surface. This method is transferable to many redox reactions including Fe, Au, Cr or As. Our team’s prior research has demonstrated that this can be done using a UV lamp flood exposure for non-specific deposition or designed patterns using a mask, or a UV laser that is translated across the textile mat. While the results show unique electronic functionalization of the textiles, the metal particulate films are dependent on the microstructure and surface energy of ALD thin film coating[2]. An additional challenge is observed in the formation of cracking in the ALD films at the fiber level.

In this work, the mechanism of ALD thin film cracking on the ZnO and TiO_2 thin films based on the ALD thermal conditions and the subsequent influence of the coating properties on the UV-photodeposition of metallic coatings. Specifically, cylindrical polymer fibers are compared to planar films demonstrate the influence of additional degree of freedom for thermal expansion of the fiber form. The thermal cycling of the ALD process results in expansion and contraction of the fiber, forcing the ALD film to contact in parallel, forming cracks and ridges. Reducing the ZnO and TiO2 deposition temperature results in a change in surface texture of the film, in turn affecting the growth of UV-photodeposited materials.

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AA-SuP-25 Enhancement of ZnO Nanorod Gas Sensors with AZO Nanolaminate Coating by Atomic Layer Deposition*, **Pengtao Lin, X Chen, K Zhang, H Baumgart,* Old Dominion University**

Metal Oxide Semiconductor (MOS) gas sensors have been paid significantly attentions as a proving material for detection of volatile and toxic gases. Among various gas sensors based on suitable semiconductor materials, ZnO has been highly investigated for its electronic and photonic applications due to its low cost, good electrical conductivity, wide band gape of 3.37 eV, ~60 meV large exciton binding energy. Currently gas sensors based on ZnO nanorods have been widely investigated due to their high electrochemical stability, nontoxicity, high surface-to-volume ratios, suitable doping. Especially, Al doped ZnO (AZO) thin film coatings were synthesized on the surface of ZnO nanorods by ALD to enhance the sensing performance of ZnO nanorod gas sensors.

In this study, the ZnO seed layers used for hydrothermal growth and the AZO coating for ZnO nanorod gas sensor were synthesized by Atomic Layer Deposition (ALD). After the ALD synthesis of the ZnO seed layers, the ZnO nanorods were grown by hydrothermal technique in the solution with dissolving hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and hexamethylenetetramine ($(CH_2)_6N_4$) in 60 ml DI water at 80 ^{o}C for 16 hours. The final step is to coat the surface of the synthesized ZnO nanorods with Al doped ZnO thin films by ALD.

A gas sensor testing system was designed with a sealed reaction chamber to investigate the sensing performance of ZnO nanorod gas sensor to Ethanol vapor under various temperatures. The physical change of ZnO gas sensor to Ethanol vapor is resistance. Therefore, the mechanism of this testing system is to indicate the resistance changes of ZnO nanorod gas sensor after introduced Ethanol vapor. A Resistance Temperature Detector (RTD) was introduced to indicate the temperature in the reaction chamber. Also, the sensing responses of ZnO nanorod gas sensor to various volumes of Ethanol vapor were indicated by measuring the resistance changes of ZnO nanorods gas sensor. An interface was designed by LabView to indicate and record the real-time values of the circuit current, voltage on reference resistor, voltage on ZnO gas sensor, resistance of ZnO gas sensor, and the temperature of the testing chamber.

AA-SuP-26 A Comparison Study of Atomic Layer Deposition (ALD) of Ceria (CeO_2) Films using $Ce(^iPrCp)_2$ (^{i}Pr-amd) and $Ce(^iPrCp)_3$ Precursors*, **Maryam Golalikhani**, P Van Buskirk, J Roeder,* Sonata LLC

CVD side reactions during the atomic layer deposition of thin films play an important role in the uniformity of deposited films. In-situ quartz crystal microbalance and time-resolved quadrupole mass spectroscopy were used for real-time investigation of growth characteristics and deposition kinetics during ALD of CeO_2 thin films. The effect of growth parameters on CVD-like reaction are compared for liquid heteroleptic $Ce(^iPrCp)_2$ (^{i}Pr-amd) and solid $Ce(^iPrCp)_3$ as precursors using water as the oxygen source.

AA-SuP-27 Theoretical Study of Si-N Film Atomic Layer Deposition Mechanism with Hydrazine and Diclorosilane Precursors and their Derivatives*, **Alexander Goldberg**, M Halls, H Kwak, T Seidel,* Schrodinger, Inc.

Silicon Nitride (SiN) films possess exceptional thermochemical properties and they have been widely used in microelectronics. Recently several group investigated Atomic Layer Deposition (ALD) of silicon nitride films applying silane (SiH_4) and ammonia (NH_3) as precursors. In this work, we determine preferred silane precursors derivatives for ALD SiN growth using hydrazine (N_2H_4). These precursors react with the underlying substrate by adding Si and then N using N_2H_4 or NH_3. The study is based on the Density Functional Theory (DFT) where surface was approximated by a cluster model. Different cluster models representing Si-H and N-H surface termination were considered. The reaction mechanism, including activation barriers and reaction energies, was studied. Applying high-throughput approach over various derivatives of silane, such as dichlorosilane, tetrachlorosilane and dichlorosilane, as well as a number of commercially available precursors with organic ligands such as $SiCl_2(CH_3)_2$ (by Gelest) and Cl_3SiCH_3 (by Sigma Aldrich) were examined for the first reaction step of adding Si to the SiN surface. Comparative analysis of the obtained energy data between N_2H_4 and NH_3 was made. We found that hydrazine is thermodynamically preferred precursor compared to ammonia. The work also revealed several candidates that have not been widely known or studied in the commercial ALD precursor industry.

AA-SuP-28 Nucleation and Growth Characterization of Metallic Ruthenium Films Grown by PEALD on Surface Treated Si (100) at Low Substrate Temperatures*, **Nicholas Strnad**,* University of Maryland*; G Rayner,* The Kurt J. Lesker Company*; D Potrepka,* U.S. Army Research Laboratory*; B Liu,* The Pennsylvania State University*; J Pattison,* University of Maryland*; M Rivas,* University of Connecticut*; R Polcawich,* U.S. Army Research Laboratory

Ruthenium metal has been given significant attention in the ALD community for its high conductivity, high density, high melting point and compatibility with microelectronic devices. The majority of ruthenium metal ALD studies have been carried out at substrate temperatures between 175°C to 250°C. Recently the Air Liquide precursor ToRuS^{TM} has been used to grow ALD ruthenium at substrate temperatures as low as 100° C with near-bulk values of resistivity and extremely low carbon impurity levels, while PEALD ruthenium films were grown at even lower temperatures. Novel electronic devices with flexible polymer substrates could utilize the low-temperature ToRuS^{TM} ALD process to achieve conformal metallization. Although significant work has been done to investigate the effect of the starting surface on the nucleation of Ru islands for conventional processes with higher substrate temperatures, little work has been done in that regard for the low temperature ToRuS^{TM} process.

We demonstrate a baseline PEALD process on a Kurt J. Lesker Company, Inc. ALD 150-LX platform using ToRuS^{TM} and plasma enhanced H_2 as co-reactants on a variety of readily available ALD-grown dielectric and metallic surfaces deposited on 150mm Si(100) substrates. Examples include TiO_x, HfO_x, AlO_x, TiN and AlO_xN_x. The substrate temperature for the ruthenium growth was varied between 50°C to 100°C. In-situ, dynamic spectroscopic ellipsometer data were collected with a J.A. Woollam Co. M-2000 through inert gas purged optical viewports. Wafer-scale characterization such as thickness measured by x-ray reflectivity, thickness measured by field emission scanning electron microscopy, and sheet resistance uniformity measured by four-point probe are presented. Additionally, surface roughness measurements performed by atomic-force microscopy are tabulated.

AA-SuP-29 Challenge the Productivity of ALD for High Volume Manufacturing of High Efficiency Solar Cells*, **Wei-Min Li**, X Li,* Jiangsu Leadmicro Nano-Equipment Technology Ltd., P.R. China

High efficiency silicon solar cells are increasingly adopted by manufacturers worldwide with call for more advanced process technology and higher productivity. In particular, recent development of PERC and PERT/PERL solar cells are expected to dominant the market growth[1].The passivation layers used are predominantly Al_2O_3 thin film, while ALD is favored over PECVD technology due to its precise thickness control and excellent passivation quality[2]. HVM that meets the required throughput and uptime are still challenges with existing commercial products.

Recent advance in batch thermal ALD reactor design in combination with customized automation have enabled a breakthrough for HVM of PERC/PERL/PERT cells. The ALD system features two reaction chambers with each upholds 1600 wafers per batch. It takes as fast as 10s to complete an ALD cycle for a fully charged batch of Al_2O_3 deposition. Integrated with state-of-art high speed automation, high throughput at above 4000 wafers per hour has been achieved for a 10 nm Al_2O_3 passivation layer. The thin film thickness uniformity is excellent, well below 2% in range. Furthermore, TMA consumption is incredibly low, at below 1 mg/wafer with fully charged batch. A proprietary cassette design can efficiently reduce the so-called wrap around effect to minimum to address the need of mono-facial passivation.

The production results have proven that batch ALD reactor is an excellent choice for high efficiency solar cell manufacturing. With ALD Al_2O_3 passivation a conversion efficiency of near 22% has been achieved. A further improvement can be expected with the advancement of commercial screen printing paste that is tailored for firing step with Al_2O_3 passivation layer. A study of contact resistance of a novel Ag paste used on a stack of $Si/Si^{n+}/SiN_x/Al_2O_3$ after co-firing showed that ALD layers with a thickness up to 5 nm has positive effect on the contact resistance with lowered firing temperature, at mean time, the optimum temperature window appears wider in comparison to the control, indicating a further improvement on cell conversion efficiency is possible[3].

In conclusion, a commercial available, fully automatic batch thermal ALD system has shown superior productivity. While an increase of conversion efficiency can be achieved for high efficiency solar cell manufacturing, the cost-of-ownership is also significantly reduced. With continuous improvement of materials used and process integration, further enhancement for high efficiency solar cells are expected.

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AA-SuP-30 Role of Cu in ALD Grown Cu:ZnS *p*-type Transparent Conductor*, **Shaibal Sarkar**, N Mahuli,* Indian Institute of Technology Bombay, India

Cu:ZnS films are grown using a custom built laminar flow type ALD reactor equipped with *in-situ* characterizations like quartz crystal microbalance (QCM), Fourier transform infra-red spectroscopy (FTIR) and electrical resistivity measurements. Diethylzinc (DEZ) and Cu(II) hexafluoropentanedionate ($Cu(hfac)_2$) along with Hydrogen sulfide (H_2S) are used as metal and chalcogen precursors respectively. A single cycle of CuS is stacked in-between ‘n’ cycles of ZnS where ZnS cycles are varied to achieve variable copper incorporation in ZnS. *In-situ* QCM and FTIR characterizations indicate the probable growth mechanism involved in these multi-stacked films.

Controlled conductivity is achieved by varying Cu concentration in the stack however that results decerease in transparency in the visible regime. For optimised case with highest conductivity and resonably transmission is achieved with CuS:ZnS = 1:80.

In this presentation I would like to elucidate the role of Cu in the crystallographic, electronic and optical properties of this unique material. At lower dopant concentration, no strain in the lattice is observed however increased conductivity is highly evident. Dopant segregation is observed at relatively higher Cu concentrations revealing its relative low solubility in the host lattice.

The role of the dopant in transport mechanism is the biggest question. A combination of temperature dependent electrical measurements supported by EXAFS, XENS and XAS measurements are performed to establish our hypothesis on the role of the Cu in the hole transport properties of the Cu:ZnS films.

**AA-SuP-31 *In-situ*Investigation of Electrical Properties in Cu Incorporated ZnS Thin Films Grown by Atomic Layer Deposition*, Debabrata Saha,* *S Sarkar,* Indian Institute of Technology Bombay, India

Thin films of transparent conducting semiconductors (TCSs) are extensively used as electrodes in numerous technological applications such as solar cells, light emitting diodes, flat panel displays etc. Commercially available TCSs are mostly *n*-type conducting. However, to realize transparent electronics using bi-polar junction devices, growth of *p*-type TCSs are essential. There are only few metal oxides which are reported to be *p*-type TCSs such as binary oxides (NiO, doped ZnO:N/As/P) and ternary delafossites ($CuMO_2$; M = Cr, Al, Ga, In). However, high hole conductivity, decent optical transparency along with stable and reproducible electrical properties cannot be realized in these *p*-type TCSs.

Recently we have demonstrated growth of *p*-type Cu alloyed ZnS thin films at low deposition temperature of 150^0C using a flow-type thermal atomic layer deposition (ALD) reactor. We have achieved thin film resistivity as low as ca. 6×10^{-3} Ω cm with an average optical transmittance > 85% in the visible spectral range. These values are significantly superior compared to the widely investigated *p*-type metal oxide thin films. All the films are grown by alternate vertically stacking n-cycles of ZnS and 1 cycle of Cu_xS.

In this presentation, I elucidate *in-situ* measurements of the electrical properties during the film growth to gain fundamental insights into the dopant incorporation, activation and diffusion processes. The role of the Cu interlayer deposition and its temperature and time dependent diffusion process that evolves out from these measurements will be discussed in detail. The results of such study are highly useful to grow ultra-thin *p*-type TCSs with desired electrical and chemical compositional properties.

AA-SuP-32 All ALD Hybrid Photoelectrochemical Systems Based on Self-Organized TiO_2 Nanotubes Coated with Chalcogenides*, Jan Macák,* University of Pardubice, Czech Republic

Even though, the overall efficiencies of advanced photovoltaic devices (amorphous Si-H, CIGS, CdTe, perovskite cells) have grown up significantly, there is so far no solar cell that would have reliable stability and performance over many years of the cell service, that would be cheap, environmentally reasonable and potentially flexible . One of most competing technologies to silicon solar cells, when considering the efficiency, low-cost production and stability is based on thin films of semiconducting chalcogenides, such as $Cu(In,Ga)Se_2$ (CIGS) and $Cu_2ZnSn(Se,S)_4$ (CZTS). Both became recently materials of the choice as they represent in thin film solar cells chromophores of adjustable band gaps, good radiation stability and high optical absorption coefficient.

For solution processed CIGS and CZTS thin film PVs cells, however, the limiting factors for further enhancement of the conversion efficiency involve the shape, size and grain boundaries of the chromophore films. The film morphology, defects and character of the grain boundaries predetermine the mobility (the loss) of free carriers in the chromophore film resulting in conversion efficiency maximum beyond ~11 % for CZTS materials and multilayer solar cell design.

A promising pathway to improve the carrier mobility of semiconducting chalcogenides to the highest possible level is to use hybrid photocells employing a highly ordered TiO_2 nanotube film /chromophore interface . However, the major issue to extend the functional range of nanotubes is to coat homogenously tube interiors by semiconducting chalcogenides in order to achieve the best possible contact of both components on their interface. This is especially crucial when high aspect ratio semiconducting TiO_2 nanotube arrays are utilized and thus the Atomic Layer Deposition technique becomes beneficial.

The presentation will show initial photo-electrochemical results for anodic TiO_2 nanotubes employed as highly ordered electron-conductive supports for host materials coated using ALD with secondary materials to enhance light absorbing capabilities of such hybrid systems. We will focus on all ALD photo-electrochemical devices based on inorganic chalcogenides .

AA-SuP-33 Electrical, Optical and Mechanical Properties of ALD-Ti doped ZnO Thin Films prepared on Corning® Willow® Glass for the Application of Flexible Transparent Oxide Substrate*, Woo-Jae Lee,* *C Kim, Y Kim, S Kwon,* Pusan National University, Republic of Korea

Flexible devices have received considerable attention for their applications of electronics, displays, solar cells, and etc. And, flexible transparent conducting oxide(TCO) substrate is one of the most important parts for those flexible devices. In most studies, various kinds of polymer materials have been generally adopted as a flexible substrate for TCO thin films. However, those polymer materials has their inherent demerits of low thermal stability, which limits the growth temperature of the post-deposition processes and degrades the electrical and optical properties of TCO thin films. On the other hand, recently developed Corning® Willow® Glass, known as flexible glass substrate, has attracted much attention due to its many advantages such as reliable mass-production friendly roll-to-roll manufacturing process, its high flexibility and high thermal stability.

Herein, we investigated the electrical, optical, and mechanical properties of ALD-Ti doped ZnO transparent conducting oxide on the Corning® Willow® Glass for the application of flexbile transparent oxide substrate. It was very important to optimize the thickness of ALD-Ti doped ZnO to realize adequate electrical and optical properties without degrading its flexibility.

AA-SuP-34 Surface Passivation of Nanoparticle via Rotation Fluidization Coupled Atomic Layer Deposition Reactor*, K Qu, C Duan, K Cao,* Huazhong University of Science and Technology, China*; **Rong Chen,*** Huazhong University of Science and Technology, P.R. China

Atomic layer deposition (ALD) is an attractive approach for atomically controllable and conformal coatings on nanoparticles (NPs) for the fields of catalysts, optical detections, biomedicines, etc. There have been many kinds of ALD reactors for particles. Some of these designs are static reactors which rely on long time precursor diffusion to coat particles. Fluidized bed reactors utilize gas flow to disperse nanoparticles for enhanced gas-solid interactions, though obtaining steady fluidization of nanoparticles and limited precursor residence time are challenges. Rotary reactors disperse particles through rotary agitation and increase precursor usage by a static exposure stage.

In this talk, a rotation fluidization coupled atomic layer deposition reactor will be introduced. In the deposition procedure, the coating process could be expedited due to the enlarged and homogenized void fraction in the particle bed, large gas distribution area and higher particle concentration in the rotating fluidized bed. The rotation not only enhances the gas-solid interactions to stabilize fluidization, but also provides large centrifugal force to break up soft agglomerates together with the fluid drag force and the inter-particle collision. Under high precursor feed rate, the precursor utilization was improved to nearly 100% with thicker rotating bed. As an example, magnetic Fe_3O_4 nanoparticles have been uniformly coated with ultrathin Al_2O_3 passivation layers. With 5 nm coating layer, the nanoparticle could be stable under oxidation resistance with minimum magnetization loss (less than 10%). This is quite attractive in practical magnetic based biomedical applications. Well controllable amorphous Al_2O_3 layers were also deposited on crystalline AlH_3 particles. The Al_2O_3 layers acted as physical barriers to prevent the particles from erosion by water and oxygen in ambient conditions, encapsulating hydrogen capacity nearly 4 times higher than the uncoated ones after hydrothermal aging. The oxide layers also served as thermal insulators to retard friction heat transferring to α-AlH_3 cores, as thin as 7 Å oxide layer on Al nanoparticles could effectively prevent them from reacting with hot water. All these examples show that ALD has a great potential as an effective nanoparticle surface passivation method.

AA-SuP-35 Atomic Layer Deposition of Doped Zinc Oxide as an Alternative to Fluorine Doped Tin Oxide for Transparent Contacts in Perovskite Solar Cells*, Louise Ryan,* Tyndall National Institute, Ireland*; A Walsh, M McCarthy,* Tyndall National Institute, University College Cork, Ireland*; S Monaghan, M Mondreanu,* Tyndall National Institute, Ireland*; S O'Brien, M Pemble, I Povey,* Tyndall National Institute, University College Cork, Ireland

Inorganic halide based perovskite solar cells have attracted attention due to their good absorption properties both in the visible and infrared electromagnetic spectrum and their good conversion efficiencies. However, problems can still be seen when an attempt to scale up is made, observing difficulties with reliability and traces of lead still remaining in the films. As a result, more work is required to solve these issues. As the demand for high conversion efficiencies of solar cells increases, there is an increase in the likelihood of the perovskite cells to be incorporated into a tandem solar cell in which the complex structure cannot be exposed to temperatures in excess of 200^oC. Due to this requirement, each layer of the tandem must be studied, in particular the transparent conducting oxide layer, which, to date uses fluorine-tin oxide (FTO) which requires deposition at temperatures >400^oC to produce good quality films. Zinc oxide (ZnO) is a possible replacement (band gap 3.37eV) which can be deposited by atomic layer deposition (ALD) at low temperatures (<200^oC) while retaining its high transparency. However, undoped ALD ZnO does not exhibit a carrier concentration sufficient for this application. This work investigates how doping ZnO with Al_2O_3, HfO_2 and TiO_2 changes its properties for use as a TCO. Thin films (60-600nm) were deposited by ALD at temperatures ranging from 120-240^{o}C. The properties of the films are discussed according to their suitability as a TCO in single junction perovskite solar cells and silicon-perovskite tandem solar cells.

AA-SuP-36 Oxides Nanomembranes Deposited by Atomic Layer Deposition for Lithium Ion Batteries*, **Gaoshan Huang**, Y Zhao, Y Mei,* Fudan University, China

Intensive exploration have been focused on discovering potential materials and fabrication techniques for superior safe and stable lithium ion batteries because of the increasing importance of battery technology as an environmentally benign power source. We have synthesized oxides nanomembranes via atomic layer deposition (ALD) using sponge template. In the process of ALD on sponge, a uniform nanomembrane was coated on all exposed surfaces of the template, and was then disrupted into numerous pieces of nanomembranes when crushing the porous structure after removal of the sponge by high temperature post-treatment. This ALD-based strategy provides remarkable advantages: (1) precise control of thickness by simply changing deposition cycles; (2) high throughputs and yields; (3) ability of synthesizing various functional materials. Here, TiO_2 and ZnO nanomembranes synthesized by this approach exhibits good performance (high reversible capacity and superior cyclability) as anode materials of lithium ion batteries. For TiO_2 nanomembranes, no degradation was observed after 80 discharge/charge cycles at various current densities and following 500 long cycles at 1 C. The enhanced performance is then ascribed to the flexibility of the nanomembranes which can effectively accommodate the volume changes/strain during charging/discharging. In addition, we noticed that the nanomembranes thickness showed significant influence on both bulk and capacitive capacities.Detailed voltammetric analyses were conducted to reveal the mechanism. Precisely controllable synthesis in this approach can flexibly adjust both bulk and surface Li storage and thus has important application potential.

AA-SuP-37 Enhanced Photoelectrochemical Efficiency of Self-Organized TiO Nanotubes Films due to Secondary Materials*, **Jan Macák**,* University of Pardubice, Czech Republic

Considerable scientific and technological interest has been focused on self-organized TiO_2 nanotube layers over the past 10 years motivated by their unique architecture, high surface area, semiconductive properties and biocompatibility. In addition, 1D TiO_2 nanotube layers are synthesized by a low-cost electrochemical anodization of Ti. All these features enabled utilization of TiO_2 nanotube layers in a wide number of applications such as photo-catalysis, solar cells, hydrogen generation and biomedical uses [1] . However, the main shortcoming of TiO_2 is its limited absorption to the UV light (wavelengths < 390 nm). In order to extend the absorption spectra range into the visible light, TiO_2 has been doped by N [2] or C [3].

Another promising approach to extend the functional range of TiO_2 nanotubes is the coating of the tube interiors with secondary materials. Additional ultrathin surface coating of TiO_2 by secondary materials such as Al_2O_3 [4], ZnO [5] or MgO [6] have been demonstrated to annihilate electron traps at the TiO_2 surface and thus increase the photogenerated concentration of charge carriers. Recently, it has been demonstrated that just a single cycle of Al_2O_3 [7] or ZnO [5] deposited by atomic layer deposition (ALD) efficiently improve charge transport properties of the heterostructure while gradual passivation appears with increasing ZnO thickness due to stronger band-bending [5].

The presentation will focus in detail on the unique ability of ALD to coat high aspect-ratio TiO_2 nanotube arrays by secondary materials. The resulting composite nanotubular structures revealed synergic effects, improving strongly photo-electrochemical properties of nanotube films. Experimental details and some very recent photocatalytic [8] results will be presented and discussed.

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AA-SuP-38 Atomic Layer Deposition of Ru and RuO_2 on Powder*, **Jaehong Yoon**,* Yonsei University, Korea*; Y Lee,* Incheon National University*; H Kim,* Yonsei University, Republic of Korea*; H Lee,* Incheon National University, Republic of Korea

Ruthenium (Ru) is one of noble metals with good thermal and chemical stability, low resistivity (7.1 μΩcm), and large work function. In addition, its oxide, RuO_2, has also attractive properties, such as low resistivity (35 μΩcm) and good chemical stability. So Both of Ru and RuO_2 have received many attentions since those have potentials for many applications in catalysts of electrochemical devices and electrodes of secondary batteries. In order to maximize the performance, nanostructuring of materials from 2D to 3D is important to increase surface to volume ratio. In particular, core shell particles composed of earth-abundant core with an atomically thin shell is advantageous in the aspect of surface volume ratio as well as material cost. In this study, cheap SiO_2 nanoparticles were uniformly coated with Ru and RuO_2 by atomic layer deposition (ALD). For ALD on nanoparticles instead of planar substrate, a novel reactor designed for ALD on powder was employed. The reactor was composed of a rotational drum which has two mesh filtered faces for infiltration of precursor and reactant. The phase and microstructure between Ru and RuO_2 were controlled by varying exposure time of Ru precursor and O_2 counter reactant. The thickness uniformity and growth characteristics of ALD Ru and RuO_2 were systematically investigated by changing various parameters, such as rotational speed and size of SiO_2 nanoparticles.

AA-SuP-39 Plasma-free Atomic Layer Deposition of Nickel and Nickel-based Alloy Thin Films for Nickel Silicide*, **Shunichi Nabeya**, S Jung, S Kim,* Yeungnam University, Republic of Korea

Metal silicides are silicon compounds with metals, and they have low resistivity like metals as well as good compatibility with Si and metals. So,metal silicides, which has been formed by metal deposition on Si followed by post silicidation annealing, have been used for contact materials in Si devices. $TiSi_2$ have been widely used for contacts, however NiSi and $CoSi_2$ are applied to sub-100 nm Si devices since $TiSi_2$ shows narrow line width effect that is increase in $TiSi_2$ resistivity with decreasing linewidth. In order to overcome limitations of current Si devices in downscaling, emerging nanodevices have been intensively studied, and their structures are moved from 2D planar to 3D structure. So, the schemes of contact fabrication used for 2D devices are changed in 3D emerging nanodevices, and conformality of metal thin films is the most important requirement to be achieved. In view of this, ALD is a good alternative to conventional PVD techniques for fabricating the silicide contact. Earlier, ALD Ni films was deposited using rather complex steps, such as the formation of NiO ALD using $Ni(Cp)_2$ and H_2O followed by H_2 plasma reduction step due to the lack of a suitable Ni precursor and reducing agent. It was reported that the Ni film could be grown by thermal ALD using $Ni(dmamb)_2$ and H_2 or NH_3 molecules but its properties were not good as compared to those of plasma enhanced ALD (PEALD) Ni film prepared by using NH_3 plasma and the same Ni precursor. Despite this, the conformality of a plasma-based process onto high AR structures is rather limited due to the possible recombination of reactive radicals and development on a suitable thermal ALD Ni process is needed. In this study, a plasma-free new thermal ALD Ni process was proposed by introducing a novel Ni precursor and molecular H_2 or NH_3 as reactants at the temperatures ranging from 300 to 350 ^{o}C. The properties of as-deposited ALD-Ni films were characterized using various tools such as XRD, RBS, XPS, 4-point probe, TEM. We also evaluated the silicidation behavior of thermal ALD-Ni film after post annealing using TEM analysis. Finally, to improve the thermal stability of ALD-Ni film, the novel metal, which was also prepared by ALD, was incorporated into ALD-Ni films.

AA-SuP-40 Room Temperature Atomic Layer Depostion of $Al_xSi_{1-x}O$ and its Application for Dye Sensitized Solar Cells*, T Imai, K Kanomata, M Miura, B Ahmmad, S Kubota, **Fumihiko Hirose**,* Yamagata University, Japan

Zeolites are alminosilicates containing minerals, used as adsorbents of ions in polluted water. We are investigating the applicability of zeolites for dye sensitized cells as the dye absorber on the TiO_2 electrodes. In this study, we developed $Al_xSi_{1-x}O$ atomic layer deposition by using the room temperature technique, where trimethyl aluminum and tris-dimethyl aminosilane are precursors of the metals and plasma excited humidified argon is used as an oxidizer. To design the gas introduction process, we monitored the gas saturation characteristics of the source gases. In the conference, we release the related experiments results and demonstrate the enhancement of power conversion efficiency in the dye sensitized solar cells.

AA-SuP-41 Tungsten Thin Films Nucleation, Adhesion and Conductivity Improvement using Nanocomposite Barrier Layer Grown by Atomic Layer Deposition*, Anil Mane,* *J Elam,* Argonne National Laboratory

Thin layer of W is extensively used for semiconductor microelectronics devices wiring and contact metallization. The most common precursor used for ALD/CVD processes to grow W layers is WF_6, and reduced with SiH_4, B_2H_6, Si_2H_6, H_2, etc. Prior to W layer growth, a high quality an intermediate thin metal barrier such as WN, TiN, TaN, etc is used avoid tungsten silicide formation as well as damage to underlying especially Si surface due to fluorinated chemistry. This metal barrier helps W to adhere well to substrate surface and also it helps W nucleation. This allows the W layer survive during chemical mechanical polishing (CMP) step. As 3D device dimension getting smaller and smaller, this extra thin metal barrier causes the major issues such as it takes physical space in small trenches/vias add high resistance in total line resistance. This metal barrier deposition also adds-up additional deposition tool, process steps and time.

Here we present work on development of ultra-thin nanocomposite barrier layers by atomic layer deposition method especially for W but not limited to other metal growth. Using this we have improved the adhesion of W on Si, Cu and other wafers. Additionally, nanocomposite barrier layer also offers minimum nucleation delay for W growth, improve the conductivity of the W and reduce overall ALD processing time.

AA-SuP-42 Textile-based Heater Fabricated by Atomic Layer Deposition for Artificial Muscles*, Jong Seo Park,* *I Oh,* Yonsei University, Republic of Korea*; T Han,* Incheon National University, Republic of Korea*; H Kim,* Yonsei University, Republic of Korea*; H Lee,* Incheon National University, Republic of Korea

Electronic textiles (e-textiles) are electrically conductive textiles which are potentially important for future wearable electronic systems. Recently, we reported that atomic layer deposition (ALD) could be a good method to functionalize conventional non-conductive textiles to conductive textiles just by depositing Pt on cotton textile without any damage. In this work, we fundamentally investigated deposition mechanism and surface reactions of ALD Pt on cotton textile by using various analytic techniques, such as X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and density functional theory (DFT) calculation. ALD on cotton substrates seems to be hard since it has rare reactive sites of ALD reaction such as surface hydroxyl group. From XPS and DFT calculation, it was found that Pt precursor molecules directly react with chemical species of the reactive sites of cotton textile, and ALD Pt layer forms with very high durability on cotton textile surface through organic-inorganic hybridization. By using this flexible and durable e-textile fabricated by ALD, we demonstrated e-textile heater for artificial muscle applications. We evaluated basic heating performance of the e-textile heater, and the maximum steady-state temperature was 106 °C at 1.0 V, which was operated just by a single AA battery. The e-textile heater was integrated to artificial muscles system made by polymer wire. We demonstrated an artificial-muscle-assisted glove operated by the e-textile heater with very low power consumption which is potentially used for disabled persons and the others who need additional force to grab heavy stuffs. This fundamental and application-driven practical researches of ALD-Pt-based e-textiles could be extended to other future applications of wearable electronics.

AA-SuP-43 Bio-Templated *Morpho* Butterfly Wings by ALD for Photocatalysis*, Robin Rodriguez,* *S Agarwal, D Das,* University of Michigan*; W Shang,* Shanghai Jiao Tong University, China*; R Goubert, R Skye, E Kazyak,* University of Michigan*; T Deng,* Shanghai Jiao Tong University, China*; N Dasgupta,* University of Michigan

Hierarchical nanostructures found in nature have unique properties that inspire bio-mimetic engineering. These natural nanostructures present design principles of bottom-up nanomanufacturing for materials with tunable properties. For example, structural coloration is a phenomenon observed in natural materials that takes advantage of nanoscale geometries to tune reflection and absorption properties through photonic resonances. This combination of strong photonic resonances and high surface area make these naturally occurring materials an ideal template for photocatalysis.

Morpho butterfly wings are particularly interesting examples of structural coloration, which occurs due to hierarchical nanostructures on the wing surfaces. ALD is uniquely suited for conformal bio-templating, which was utilized in this study to preserve the *Morpho*'s complex 3-D nanoscale structures and tune the optical and catalytic properties by coating them with ZnO, which serves as a functional material. SEM analysis showed conformal coating of the complex 3-D nanostructured wing surface. By controlling the ALD film thickness, the natural structural coloration could be tuned across the visible spectrum by controlling both the periodicity and refractive index of the wing nanostructures. Finite-difference time-domain (FDTD) modeling was performed to simulate the light reflection and absorption properties of the *Morpho* wings with varying ZnO thicknesses. The model was validated against experimental optical absorption and reflection measurements, allowing for parameterization of the spectral response.

To demonstrate that these tunable optical materials can serve as efficient functional catalysts, ALD-coated butterfly wings were tested as UV photocatalysts to oxidatively remove methylene blue dye from water. The precise thickness control of ALD allowed for a study of thickness-dependent photocatalytic activity, which was compared to ALD films on planar substrates. The Morpho bio-templates showed superior photocatalytic dye-degradation activity by a factor of >10 relative to planar thin film samples, which was attributed to enhanced light absorption and increased surface area from the butterfly's hierarchical structures. 15nm of ZnO was determined to be the optimal thickness on the butterfly wings, while thicker films showed a decrease in activity. FDTD simulations demonstrate that this is based on a tradeoff between absorption, reflection, and surface area. This study demonstrates bio-templating with functional materials by ALD is a powerful platform to tune and optimize material architectures, and has the potential of extending bio-inspired engineering to new applications.

AA-SuP-44 Atomic Layer Deposition of $ZrSiO_4$ and $HfSiO_4$ Thin Films using a Newly Designed DNS-Zr and DNS-Hf Bimetallic Precursors for High-Performance Logic Devices*, Da-Young Kim,* *S Kwon,* Pusan National University, Republic of Korea*; S Jeon, H Lim, S Jo, J Park, W Chae, S Yim, J Park,* DNF.Co.Ltd, Republic of Korea*; S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

Future scaling of complementary metal-oxide semiconductor (CMOS) technology requires high *k* dielectrics with metal gate electrodes to obtain higher gate capacitances and low gate leakage current. Of various candidates for gate dielectrics, Zr or Hf based silicates ($ZrSiO_4$ and $HfSiO_4$) prepared by atomic layer deposition (ALD) have received great attention for this application due to its high dielectric constant, low leakage current, and their thermodynamic stability with Si. However, such ALD-$ZrSiO_4$ and $HfSiO_4$ dielectrics have been generally prepared by alternating ALD-ZrO_2 (or HfO_2) and SiO_2 using multiple ALD precursors, which increased the process complexity and occasionally resulted in the fluctuation of electrical performance due to the composition inhomogeneity between Zr (or Hf) and Si within the gate dielectric films.

Herein, therefore, we demonstrated a reliable ALD process of $ZrSiO_4$ and $HfSiO_4$ dielectrics using newly designed bimetallic precursors, DNS-Zr and DNS-Hf. H_2O and O_3 was applied as suitable reactants for those bimetallic precursors. Our bimetallic precursor for $ZrSiO_4$ and $HfSiO_4$ enables a simple and reliable ALD process for depositing stoichiometric $ZrSiO_4$ and $HfSiO_4$ compounds on Si substrate. And, the detailed growth characteristics of both dielectrics are systemically investigated. Also, their electrical performance including current-voltage (I-V) and capacitance-voltage (C-V) was carefully evaluated. The result indicated that our bimetallic precursor based ALD-$ZrSiO_4$ and $HfSiO_4$ processes can be potentially used as future gate dielectrics of high performance of logic devices.

AA-SuP-45 Enhanced Thermal Stability and Catalytic Activity of Metal Oxide Coated Platinum Catalyst via Atomic Layer Deposition*, J Cai,* Huazhong University of Science and Technology*; K Cao, B Shan,* Huazhong University of Science and Technology, China***; Rong Chen,*** Huazhong University of Science and Technology, P.R. China

Platinum nanoparticles (NPs) play an important role in the catalytic applications such as conversion of automotive exhaust, fuel cells, nano sensing and so on. For majority catalytic applications, sintering of Pt NPs is undesirable since the coalescence decreases the number of active sites of the catalyst. Herein we report the utilization of active oxide layers to encapsulate Pt NPs through atomic layer deposition (ALD) method. We will demonstrate a series active oxide coating on Pt nanoparticles prepared via ALD method. The thickness of oxide coating layer was controlled accurately by varying the ALD cycles. The effect of layer thickness towards catalytic properties and thermal stability for CO oxidation is investigated. The coating structure shows high activity for CO oxidation even after high temperature annealing. The thickness of oxide coating layer has a great influence on the catalytic property. For example, a coating layer can cause both increase and decrease of the catalytic property. With proper modulation, the oxide coating could prevent sintering and improve catalytic performance simultaneously. Characterizations including TEM, XPS, and FTIR have been undertaken to explore the origin of the CO oxidation catalytic activity. The enhanced CO oxidation catalytic activity is mainly contributed by the metal-oxide interface and the stability can be attributed to the physical anchoring of the active oxide coating layer.

AA-SuP-46 Selective Atomic Layer Deposition of Bimetallic Core Shell Nanoparticles Towards PROX Reactions Modulated with Pt Shell Thickness*, Y Lang, J Yang, K Cao, J Zhang, B Shan,* Huazhong University of Science and Technology, China*; **Rong Chen**,* Huazhong University of Science and Technology, China, P.R. China

Bimetallic nanoparticles (NPs) have attracted great attention due to their unique properties for catalytic applications. Compared with the physical mixture of monometallic NPs or the alloyed bimetallic NPs, the formation of core shell structure could further enhance the activity, selectivity and stability. Synthesizing core shell nanoparticles (NPs) with well controlled shell thickness and composition is of great importance in optimizing their reactivity. Here we report synthesis of core shell NPs using selective atomic layer deposition (ALD) technique. The size, shell thickness, and composition of the NPs can be precisely controlled by varying ALD cycles. The catalytic performance towards preferential oxidation of CO under excess H_2 (PROX) reaction was studied with different Pt shell thickness. Core shell NPs exhibit both great selectivity and enhanced activity and density functional theory simulations have been carried out to explain such behavior towards PROX reactions. More interesting, the catalytic activity of hybrid nanostructure can be tuned continuously with shell thickness and facet selectivity. The selectivity originates from electron structure modification and lattice mismatch, which is consistent with first-principles calculations of Pt ALD on different ruthenium facets. Such selectivity results in the co-existing of Ru and Pt facets, which shows the superior selectivity and activity.

AA-SuP-47 Deposition of Tungsten Carbide and Tungsten Nitride Films from Halogen-Free Tungsten Precursors*, **Moo-Sung Kim**,* Versum Materials Korea, Republic of Korea*; S Yabut, S Ivanov,* Versum Materials

Further shrinkage of electronic devices brings new challenges for thinner barrier films with lower resistivity and better barrier properties. For a number of years conducting material used in semiconducting industry has been tungsten deposited by CVD process with tungsten hexafluoride. Titanium nitride is used to form a barrier layer between silicon oxide and tungsten. Scaling titanium nitride becomes challenging due to granular structure of the film and potential diffusion of fluorine atoms during deposition of tungsten nucleation layer on titanium nitride substrate. In addition, conformal deposition of titanium nitride from halogen-free precursors is very challenging. One option to further reduce the thickness of combined barrier layer and tungsten nucleation layer is to deposit tungsten nitride or tungsten carbonitride barrier films using halogen-free tungsten precursor. In this study several tungsten precursors, including tungsten hexacarbonyl ($W(CO)_6$), cyclopentadienyltungsten tricarbonyl hydride ($CpW(CO)_3H$) and diisopropylcyclopentadienyltungsten dihydride ($(^iPrCp)_2WH_2$), were used to deposit tungsten-containing films by thermal CVD, thermal ALD and PEALD. Only CVD process can be demonstrated for tungsten hexacarbonyl, while W_2N nitride was deposited from two cyclopentadienyl precursors by ammonia PEALD and tungsten carbide films were deposited by hydrogen PEALD. Film properties and deposition rates on various substrates will be presented.

AA-SuP-48 Improvement of Corrosion and Mechanical Properties of NiTi Implants by using Atomic Layer Deposited TiO_2 Protective Coating*, **Chi-Chung Kei**, Y Yu,* National Applied Research Laboratories, Republic of China*; D Vokoun, J Racek, L Kadeřávek,* Institute of Physics of the ASC Prague

Prevention of Ni ion release in human body is crucial to commercialization of biomedical NiTi implant. Therefore, atomic layer deposition (ALD) is applied to deposit TiO_2 protection coating on NiTi samples by using $TiCl_4$ and H_2O precursors. *M*echanical tester equipped in a scanning electron microscope allows us to observe generation of tensile-load-induced microcracks on NiTi samples. As shown in Fig. 1, atomic layer deposited TiO_2 protective coating can withstand 8% tensile strain. Whereas the TiO_2 layers grown thermally by oxidizing NiTi at temperature around 450°C contained densely distributed microcracks during loading. We found excellent corrosion properties of TiO_2 coated NiTi samples by using ALD.

AA-SuP-49 UV Reflectance Measurement Results of ALD-ALE Modified Al Mirrors for Future Astronomical Missions.*, **Christopher Moore**,* University of Colorado - Boulder*; J Hennessy,* Jet Propulsion Laboratory, California Institute of Technology*; C Carter,* University of Colorado - Boulder*; A Jewell, S Nickzad,* Jet Propulsion Laboratory, California Institute of Technology*; K France,* University of Colorado - Boulder

Recent advances in ALD technology have provided new opportunities to advance mirror coatings. Specifically, an ALD and ALE hybrid process can be used to improve UV mirror coatings performance for future astronomical satellite missions. Al mirrors are used for their high intrinsic reflectivity from 85 – 2,000 nm but suffer from oxidation, which degrades reflective performance below 250 nm. ALE can be used to remove a substantial amount of this native oxide (Al_2O_3) layer and subsequent ALD metal fluoride coatings to protect this Al mirror from re-oxidation. Layers of AlF_3 less than 20 nm are usually sufficient to mitigate environmental degradation of Al mirrors, but very thin layers (< 3 nm) are necessary to best recover the intrinsic Al reflectance down to 90 nm. We present results on the optical performance of Al mirrors processed by an ALE oxide removal and subsequent ALD capping process, with an emphasis on UV reflectance.

AA-SuP-50 Modification of Borohydride Materials for Hydrogen Storage by ALD*, **Katherine Hurst**, S Christensen, P Parilla, T Gennett,* National Renewable Energy Laboratory

Atomic layer deposition (ALD) provides important routes for tailoring material properties in order to tune their performance as hydrogen storage materials for fuel-cell vehicles. Currently available hydrogen fuel-cell vehicles systems rely on hydrogen stored in compressed tanks at 700 bar. While this hydrogen storage system is partially fostering early-market deployment, the compressed gas system presents several practical challenges and expenses related to infrastructure and delivery that could limit widespread adoption. Metal borohydrides are an important material that can reach DOE system capacity targets for hydrogen storage. However, other targets such as those related to kinetics, desorption temperature, pressure and cyclability are not met. In particular, reaction pathways for uptake and release of hydrogen by metal borohydrides lead to capacity degradation; efforts to remedy this in borohydride materials are still under investigation. It is well known that a nanostructured hydride phase and catalyst additives both greatly enhance the kinetics, lower operating temperatures, and increase cyclability. Recent work at the National Renewable Energy Laboratory has applied ALD to capture some of these improvements. We show that over-coating plays a key role in maintaining the kinetics and cyclability needed for onboard storage. This presentation will discuss advancements in over-coating metal borohydride materials for hydrogen storage applications.

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AA-SuP-51 Color Modification of Metal Surfaces by Transparent ALD Film Stacks*, **Ritwik Bhatia**, A Bertuch,* Ultratech

ALD has been used in optical applications like band pass filter [1], broad spectrum anti-reflective coating [2], Bragg reflector [3] etc. ALD is of interest in optical applications due to precise thickness control, ease of scale up and ability to coat curved surfaces uniformly.

In this work we discuss a different optical application for ALD – modifying the color to metals like aluminum and silver. A target color is defined in terms of its reflection spectrum or color coordinates. The optical stack is modeled using Fresnell equations and the film thicknesses required to meet the target are optimized using a differential evolution algorithm. Figure-1 show the targeted green and blue colors achieved by coating aluminum with the appropriate stack of ALD Al_2O_3 and TiO_2 films. More generally, the range of colors achievable depends strongly on the underlying substrate. Figure-2 shows the chromaticity diagram in coordinates defined by CIE 1976. On this diagram we have superimposed one polygon per substrate material – the interior of the polygon defines the range of possible colors. This shows that colors palette achievable on titanium is much larger than that achievable for aluminum, silver or gold.

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AA-SuP-52 Fabrication of New Type Electrode Based TiO_2-coated Metal Foam using ALD Process for Decomposition of Methane Gas for Fuel Cell Application, ***Sung Pil Woo,*** Yonsei University, Republic of Korea*; K Lee, Y Lee, I Kim, J Ko, S Shin, Y Yoon,* Gachon University, Republic of Korea

Natural gas contain methane (CH_4), carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2), and other components. Among the many components of natural gas, methane is the simplest organic compound consisting of one carbon atom and four hydrogen atoms around carbon atom. Methane is a natural gas that can be generated biological routes and production during transport of oil and natural gas. However, methane is powerful greenhouse gas. Recently, many researchers are conducting studies for methane emission reduction and methane removal and reduction. Fuel cell is attractive electric generation technology without release pollution. Among the many fuel cell system, proton exchange membrane fuel cell (PEMFC) which used hydrogen as fuel is the most suitable fuel cell for portable and mobile application due to low operating temperature, short initial operating time, low weight, and small volume. Our group fabricated system of low temperature fuel cell used methane gas as fuel. In this system, oxide based catalyst was used to decompose methane for hydrogen production. We developed TiO_2 coating layer on the stainless steel foam (SUS foam) that is electron supporter instead of carbon based material such as CNT, graphene, fullerene, and etc. A TiO_2 coating layer was formed using ALD process. After then, TiO_2 coated SUS foam immersed solution dispersed Pt catalyst. Finally, we fabricated Pt@TiO_2@SUS foam electrode and measured XRD, SEM, TEM, and electrochemical characterization compared to TiO_2@SUS foam electrode. Hence, we can propose Pt@TiO_2@SUS foam to be a promising new type electrode for fuel cell used methane gas as fuel.

AA-SuP-53 Plasma-assisted ALD of Ru Nanoparticles on Electrospun Polymeric Nanofibers for Catalysis*, K Ranjith, A Haider,* Bilkent University, Turkey*; **Necmi Biyikli,*** Utah State University*; T Uyar,* Bilkent University, Turkey

This study reports the surface functionalization of electrospun polymeric nanofibers with Ruthenium nanoparticles (Ru-NP) by plasma-assisted atomic layer deposition (PA-ALD). The uniform one-dimensional morphology of polymeric nanofibrous templates were preserved during the plasma-assisted growth process with the help of a conformal metal-oxide passivation layer coated with thermal ALD.

Atomic layer deposition of Ru was performed on polymeric nanofibers using Bis(cyclopentadienyl)ruthenium(II) and NH_3 plasma in a customized PA-ALD reactor with a stainless steel hollow-cathode plasma source. One unit growth cycle consisted of two pulses of Bis(cyclopentadienyl)ruthenium(II) (pulse length=1 s), Ar purge (10 s), NH_3 plasma exposure (20 s), and Ar purge (10 s). Bis(cyclopentadienyl)ruthenium(II) was heated to 80°C before the growth and kept at this temperature during the entire growth experiment which was performed at a substrate temperature of 230°C.

The particle size determination, detailed morphological, structural, and chemical characterization of the Ru-NP/nanofiber nanocomposite was performed by high-resolution SEM and TEM analysis, XRD, and high-resolution XPS measurements. The Ru-NP is known for its efficient catalytic property. Hence, the catalytic performance of Ru-NP/nanofiber nanocomposite was investigated by the hydrogenation of styrene, cyclohexane, and quinolone compounds. Moreover, the re-usability of the Ru-NP/nanofiber nanocomposite material was also investigated for the long-term performance of the catalytic reactions.

In brief, Ru-NP by ALD is more applicable and portable through surface decoration onto the electropsun polymeric nanofibers. In addition, the high surface area of nanofibers provides significantly enhanced active sides for the nanoparticles, so they will be able to show higher and more efficient catalytic activity. Hence, with the PA-ALD of Ru-NP on electrospun nanofibers, it will be possible to improve catalysis systems having high performance, re-usability, flexibility, and portable properties.

AA-SuP-54 The Adhesion of Thermal ALD to Metal Surfaces at Low Temperatures*, J Kelliher,* ***William Sweet,*** *N Crain, C Roske,* Northrop Grumman

Atomic Layer Deposition (ALD) is a thin film technique that offers high conformality and sub-nanometer thickness control on structures of different surface chemistry. Its application to microelectronics, flexible electronics, packaging, and MEMS often requires low deposition temperature due to thermal budget constraints.

In this work, thermal ALD is used to deposit ZrO_2 on silicon, as well as various oxides and metals, in order to study film adhesion. Films were deposited at 120-250° C, and analyzed using optical and x-ray techniques to determine thickness and roughness. In addition, the water contact angle of the films was measured using the sessile drop method. Film adhesion was determined using the ASTM D3359-02 standard tape test method on various oxide and metal surfaces. Adhesion issues were observed when ZrO_2 was deposited at lower temperatures on certain metal surfaces.

AA-SuP-55 ALD-Frequency Multiplied Fresnel Zone Plates for Hard X-rays Focusing*,* ***Nicolaie Moldovan,*** *H Zeng,* Advanced Diamond Technologies*; R Divan, L Ocola, V De Andrade,* Argonne National Laboratory

Fresnel zone plates are convenient diffractive focusing devices for X-rays, due to their ease of use and high imaging resolution capabilities. As applications evolve towards higher photon energies, the requirement of patterning of micrometers-thick absorber materials collides with the capability of patterning zones with ~20 nm widths, as necessary for high resolution imaging. Aspect ratios of tens to hundreds are necessary, and impossible to achieve only by lithography and etching or electroforming - the traditional methods of fabrication of such devices.

A straightforward approach is to pattern low-Z scaffold materials with larger-width circles, then do a frequency multiplication by deposition highly conformal layers of high-Z materials on these scaffolds. Due to the high conformity of the deposition and control capabilities of thickness in the nanometer range, ALD is an ideal candidate process for this application. Here we report on formation of zone plates on ultra-nanocrystalline diamond (UNCD) scaffolds, with tungsten ALD coatings. The diamond scaffolds have 60 nm wide zones achieved by electron beam lithography and reactive ion etching, and the tungsten film, deposited by ADL, has 20 nm thickness. The thickness of the absorber material, in the direction of the optical axis is 1.6 mm. Details of the fabrication are presented in Fig.1. Fig.2 shows a typical scanning electron microscopy image of a UNCD scaffold, with 60 nm minimal-width circular zones. A “composite zone plate” configuration is adopted, in which an outer zone plate with triple widths zones is added, such that the third order focus of the outer zone plate coincides with the first order focus of the inner zone plate, contributing to higher efficiency. This is meant to compensate in part the loss in efficiency due to the frequency multiplication, which deviates from the ideal Fresnel zone rule of equal zones area. Fig. 3 shows a finite, ALD-coated scaffold with 20 nm tungsten. The zone plates were tested at 9.1 keV photon energy in imaging mode, on beam line 32-ID-C of the Advanced Photon Source of Argonne National Laboratory.

The diamond scaffolds were fabricated at the Center of Nanoscale Materials, of Argonne National Laboratory, under proposals 38658 and 45427. Use of the Center for Nanoscale Materials and Advanced Photon Source, Office of Science user facilities, was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

AA-SuP-56 Synthesis of Highly Dispersed and Highly Stable Supported Au-Pt Bimetallic Catalysts by a Two-step Method*,* ***Xiaofeng Wang****, X Liang,* Missouri University of Science and Technology

Highly dispersed and highly stable supported bimetallic catalysts were prepared by a two-step process. Highly dispersed platinum (Pt) nanoparticles (NPs) were first deposited on porous γ-alumina (γ-Al_2O_3) particles by atomic layer deposition (ALD) in a fluidized bed reactor at 300 ºC. Gold (Au) NPs were synthesized using gold(III) chloride ($HAuCl_4$) and tetrakis(hydroxymethyl)-phosphonium chloride (THPC) as precursors, and then stabilized on ALD Pt/γ-Al_2O_3 particles. TEM analysis showed that the particle sizes of Pt, Au and Au-Pt was around ~1.3 nm, ~2.2 nm, and ~3.0 nm, respectively. STEM/EDS observation verified that most of the metal NPs on Al_2O_3 were Au-Pt bimetallic NPs. The composition of the bimetallic NPs was further verified by pair distribution functions (PDF) and X-ray absorption spectroscopy (XAS) analysis. All catalysts were subjected to catalytic testing to determine their relative activities for glucose oxidation to gluconic acid in aqueous solution. The Au-Pt bimetallic catalysts were highly active, due to the synergetic effect of two metal elements, and highly stable, due to the facts that Pt NPs were deposited and strongly anchored on the substrate surface by chemical bonds. The interaction between Pt and Au is strong. This method of Au-Pt synthesis overcomes the leaching problem and improves the stability of Au-Pt catalysts greatly.

AA-SuP-57 Atomic Layer Deposited Cobalt Oxide Thin Films as Photoanodes for Photoelectrochemical Water Splitting*, **Soonyoung Jung, B Jang,* Yeungnam University, Republic of Korea*; S Oh, Y Lee, J Oh,* KAIST, Republic of Korea*; S Kim,* Yeungnam University, Republic of Korea

Cobalt oxides have attracted a great interest in view of their potential applications including electrochromic devices, sensors, ReRAM, catalysts and intercalation compounds for energy storage due to their useful electronic and magnetic properties. Cobalt oxide is known to exist in two different stable phase, one is Co_3O_4 that is mixed valence compound $Co^{II}Co^{III}_2O_4$ with the normal spinel structure. The other thermodynamically stable oxide is the high temperature phase CoO which crystallizes in a rocksalt structure at temperature above 900°C, however kinetically stable at room temperature. Co_3O_4 is more beneficial as an intercalation host material because spinel structure has a larger unit cell (0.808 nm) than the rock-salt structure (0.427 nm) and contains more interstitial sites. Co_3O_4 is the corresponding electrochromic efficiency is relatively high ($\approx 25\ cm^2, C^{-1}$). And also, it can offer large surface area, high conductivity, electrochemically stability. Various kinds of thin film deposition techniques, including such as sputtering, CVD, PLD and ALD have been used for obtaining single-phase Co_3O_4 thin film. But the most of previous studies showed that thin films with dual-phased of CoO and Co_3O_4 were deposited. In the case of ALD, a single-phased Co_3O_4 thin film was obtained only when the very reactive oxidant O_3 or O_2 plasma were used and in case of O_2 molecules, very high temperature was required. It means that it have been difficult to obtain single phase Co_3O_4. In this study, at first, the controlled growth of various cobalt oxides thin films was investigated by ALD using a novel Co metallorganic precursor and O_2 molecules as a reactant at a deposition temperatures ranging from 125 to 300 ^oC. XRD and Raman analysis indicated that deposition temperature range from 125 and 250 ^oC, CoO and Co_3O_4 dual-phased thin film was deposited. And, a single-phased Co_3O_4 was formed from temperature at 265 ^oC. The RBS analysis indicated that at 275^oC, almost stoichiometric Co_3O_4 thin film was deposited. From UV-Visible analysis, a single-phased Co_3O_4 film optical band gap was determined as 1.98 eV. The ALD cobalt oxides thin films prepared in this study were evaluated as a heterojunction p-CoO_x/n-Si photoanode for photoelectrochemical (PEC) water splitting.

AA-SuP-58 ALD of Nanolaminate Doped Electron Transport Layers for Perovskite Solar Cells*, **Melissa McCarthy**, A Walsh, L Ryan,* Tyndall National Institute, University College Cork, Ireland*; A Walter, B Kamino,* Centre Suisse d'Electronique et de Microtechnique*; J Werner,* Ecole Polytechnique Fédérale de Lausanne*; S Moon, S Nicolay,* Centre Suisse d'Electronique et de Microtechnique*; C Ballif,* Ecole Polytechnique Fédérale de Lausanne*; F Laffir,* University of Limerick*; S O'Brien, M Pemble, I Povey,* Tyndall National Institute, University College Cork, Ireland

Organometallic halide perovskite (PK) devices have attracted considerable interest in recent years due to their low cost, high efficiency, and potential uses in tandem devices. The ongoing investigation into these solar devices have allowed power conversion efficiencies (PCEs) to increase dramatically to over 20% over a brief period of time.[1-4] To date, the majority of reported efficiencies for these devices have been obtained on a notably lower scale than 1 cm^2. Scalability and stability over time have remained the principal challenges of this upcoming technology.

Despite TiO_2 being used by most as the electron transport layer (ETL), it has been shown to reduce the long-term stability of the cell by restricting charge transport. This has been associated with oxygen induced defects contained within the TiO_2, as well as a conduction band misalignment with the perovskite layer. This type of ETL also produces pronounced hysteresis in the current-voltage curve.[5]

In this work, ETLs comprised of nominally undoped TiO_2 and nanolaminate doped TiO_2 have been deposited using thermal and plasma atomic layer deposition (ALD) on fluorine doped tin oxide (FTO) coated glass. These were then fabricated into both planar and mesoporous perovskite devices. All metal oxides were deposited using ALD below 200 °C to align with the requirements of silicon-perovskite heterojunction tandem cells.[6] The composition of the ETLs and the influence of the ALD growth parameters are highlighted and discussed along with the resulting cell performances.

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AA-SuP-59 ALD TiO2 Coating on Nanostructured Silicon with Enhanced Photoelectrochemical Efficiency and Stability*, **Xudong Wang**, Y Yu,* University of Wisconsin-Madison

Intense charge recombination and weak electrochemical stability are main limitations that drag the advancement of black silicon (b-Si) in photoelectrochemical (PEC) solar-to-fuel production. Here we report that an ultrathin amorphous TiO_2 film by atomic layer deposition (ALD) can simultaneously promote the charge separation efficiency and improve the operational lifetime of b-Si PEC photoanode. The TiO_2 film was deposited by low-temperature ALD conformally covering the entire nanostructured surface of b-Si. Combined with an optimized $Co(OH)_2$ thin film as the oxygen evolution catalyst, this b-Si/TiO_2/$Co(OH)_2$ heterostructured photoanode was able to produce a very high saturated photocurrent density of 32.3 mA/cm^2 at a low external potential of 1.48 V vs. RHE, noticeably exceeding planar Si and unprotected b-Si photoelectrodes. After systematically investigating their electrochemically active surface area, light absorption and charge separation characteristics, TiO_2-induced photocurrent gain was attributed to the enhanced charge separation efficiency as a result of the effective passivation of defective sites on b-Si surface. Moreover, the 8 -nm ALD TiO_2 layer can impressively extend the function endurance of b-Si from less than half an hour to four hours. This research established a promising strategy for using ALD to develop efficient and stable b-Si electrochemical systems.

AA-SuP-60 Fabrication of Lithium Titanate inside TiO_2-Coated SUS Foam as a Binder-free Anode Material for All-Solid-State Battery*, **Sung Pil Woo**,* Yonsei University, Republic of Korea*; K Lee, Y Lee, I Kim, J Ko, S Shin,* Gachon University, Republic of Korea*; J Kim,* Hallym University, Republic of Korea*; J Shim,* Korea University, Republic of Korea*; W Lee,* Yonsei University, Republic of Korea*; Y Yoon,* Gachon University, Republic of Korea

Lithium titanate ($Li_4Ti_5O_{12}$, LTO) as a potential anode material in lithium-ion battery and all-solid-state battery has attractive advantages: (1) cycle stability which is zero-volume change during charge and discharge cycle, (2) high operating voltage plateau at 1.55 V versus Li/Li^+, (3) intercalate three lithium ions per molecule, (4) stable electrochemical operation and long cycling life, (5) high reliability. However, LTO has major disadvantage such as low theoretical specific capacity (175 mAh g^{-1}) and electrical conductivity (ca. 10^{-13} S cm^{-1}), and poor diffusivity of lithium ion (ca. 10^{-9}-10^{-13} $cm^2\ s^{-1}$). Several strategies have been used to enhance performance of LTO. These include metallic and non-metallic conductive surface coating and modification, nano-sizing of LTO, and cation doping for improving electrical conductivity. In this study, we synthesized anode material of LTO using metal foam for increasing electronic conductivity. However, interfacial resistance occurs at the interface between metal foam and anode active material. We investigated TiO_2 thin film on the stainless steel (SUS) foam surface to reduce interfacial resistance between LTO anode material and SUS foam and develop binder-free anode material. The SUS foam of 3D macro porous material acts as conductive current collectors which serve as a fast electron transfer without conducting additives and polymeric binders. We formed a thin film using ALD process, which is thin film deposition technique using chemical vapor of gaseous species of chemical precursors. TiO_2 was prepared using titanium isopropoxide and H_2O at 120 ^oC. After then, the LTO powder which synthesized hydrothermal method was mixed and filled inside SUS foam. The synthesized TiO_2-coated SUS foam with LTO material pressed by hot-press. The synthesized anode material have been measured by XRD, SEM, TEM, and EDS for obtained structural and elementary analysis. The cross-section of pressed binder-free anode material was identified by FIB etching and resistance value was determined using impedance analyzer. The electrochemical performance of binder-free anode material with SUS foam evaluated in the voltage range of 1.0-3.0 V. The binder-free anode material show a high specific initial capacity of 158.68 mAh g^{-1} and capacity retention of as high as 70.2% after 100 charge and discharge cycles at a scan rate of 0.2 mV s^{-1}. The electrical conductivity of binder-free LTO anode material is higher than that of a normal LTO anode material. Therefore, the binder-free anode materials are expected to be applicable to future-oriented binder-free lithium-ion battery and all-solid-state battery.

AA-SuP-61 ALD-Y_2O_3/GaAs(001) Having Extremley High Thermal Stability at 900 °C and Very Low Interfacial Trap Densities - Comparative Studies with ALD-Al_2O_3 and HfO_2 Gate Dielectrics*, Yen-Hsun Lin,* *H Wan, L Young, C Cheng, K Lin,* National Taiwan University, Republic of China*; Y Cheng,* National Chia-Yi University, Republic of China*; W Chen,* National Synchrotron Radiation Research Center, Republic of China*; C Cheng,* National Chia-Yi University, Republic of China*; T Pi,* National Synchrotron Radiation Research Center, Republic of China*; J Kwo,* National Tsing Hua University, Republic of China*; M Hong,* National Taiwan University, Republic of China

The perfected SiO_2/Si interface was the key enabling the successful high-performance complementary metal-oxide-semiconductor (CMOS) technology for the last 50 years. Two critical parameters for that interface are the excellent thermal stability at very high temperatures over 1000°C and the extremely low interfacial trap densities (D_{it}). Push for high-speed devices with low power consumption requires high electron mobility III-V compound semiconductors in replacing Si channel in the inversion-channel MOS field-effect-transistor (MOSFET). Again, attainment of low D_{it} is equally adamant for the high-performance III-V MOSFETs. Atomic-layer-deposited (ALD) Al_2O_3 on GaAs has been feverishly studied on the interfacial electrical and electronic/chemical characteristics, compared with the hetero-structures of other high K dielectrics on III-Vs. However, the ALD-Al_2O_3/GaAs cannot endure annealing with temperatures higher than 700°C and the D_{it} is high of 10^{13} $eV^{-1}cm^{-2}$ with a high peak value at the mid-gap.[1] Similarly, the commonly employed ALD-HfO_2 has been used to passivate $In_{0.2}Ga_{0.8}As$(001);[2] the D_{it} values are lower than those of ALD-Al_2O_3/GaAs(001). The recently discovered ALD-Y_2O_3/GaAs(001) has shown extremely thermal stability with rapid thermal annealing (RTA) to 900°C and dwelling there for 60 sec, as shown in a high-resolution cross-sectional scanning transmission electron microscopy (STEM). Very low D_{it} values were obtained in the ALD-Y_2O_3/GaAs(001).[3,4] In this work, we compare the thermal stability and the oxides/GaAs(001) interfacial characteristics. We will also correlate the interfacial electronic characteristics with the electric performances.

[†] YHL and HWW have made equal contributions to this work.

* MH and JK are the corresponding authors.

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AA-SuP-62 PEALD of Nickel Thin Film using bis(1,4-di-iso-propyl-1,4-diazabutadiene) Nickel*, Jae-Min Park,* *S Kim,* Sejong University, Republic of Korea*; J Hwang, J Kim,* Sejong University*; J Lee, W Han, W Koh,* UP Chemical Co., Ltd., Republic of Korea*; W Lee,* Sejong University, Republic of Korea

NiSi is used for source and drain contact metal of CMOS devices. NiSi offers low resistivity (15~20 μΩ·cm) at narrow linewidth and low Si consumption as compared with other metal silicides. The conventional PVD technique may suffer from poor step coverage in complex structures of the next-generation devices. ALD is considered as the ideal technique for the conformal deposition of Ni film, therefore Ni precursor with good reactivity, thermal stability, and high vapor pressure is needed. The most of the commercially available Ni precursors are solid at room temperature and showed low growth rates or high impurity levels due to limited reactivity or stability [1]. In the present study, we report the PEALD of nickel thin film using bis(1,4-di-iso-propyl1-1,4-diazabutadiene)nickel ($Ni(dpdab)_2$) and NH_3 or H_2 plasma. $Ni(dpdab)_2$ is liquid at room temperature, and the vapor pressure is 0.23 Torr at 80°C. The saturation dose of the Ni precursor and the ALD process window were investigated, and the RF power and the time of NH_3 plasma were optimized to obtain high-purity Ni film with low resistivity. NH_3 plasma produced the Ni film with low carbon concentration, however, nitrogen impurities (~10%) was incorporated into the deposited film. Nitrogen concentration of the PEALD film can be reduced to less than 1% by thermal annealing in an H_2 ambient at 400°C.

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AA-SuP-63 Lifetime and Gain Improvement in MCP-based Detectors with ALD Thin-films for High-energy Particle Detection Applications*, Nitin Deepak,* University of Liverpool, UK*; S Harada, T Conneely,* Photek Ltd., UK*; R Potter,* University of Liverpool, UK*; J Milnes,* Photek Ltd., UK

Atomic Layer Deposition (ALD) is a very powerful technique used for the deposition of thin films for numerous applications ranging from optics to electronics where atomically smooth films are required. In this work, the conformal nature of ALD thin films has been exploited to improve the gain and lifetime of a micro-channel plate (MCP) based detectors. MCPs usually have a high aspect ratio (80:1, 60:1). These sealed tube detectors use multi-alkali photocathodes for the detection of UV, visible, or infrared light and the MCP acts as an electron amplifier. The constant bombardment of electrons on the MCP pores create +ve ions which degrade and eventually kill the photocathode. With the help of a very thin film of Al_2O_3 deposited by ALD, we are able to suppress the generation of +ve ions from the pores. Tuning the film growth parameters enables us to achieve massive improvements in both the gain and lifetime (from 0.1C-cm-2 to 5C-cm-2) of the detector (figure 1). Long lifetimes are important since these detectors are used in particle accelerators with high signal levels.

AA-SuP-64 Durability of Silver Mirrors Protected with Combinations of Evaporated and ALD Barrier Overlayers*, David Fryauf,* *J Diaz Leon,* University of California Santa Cruz*; A Phillips,* University of California Observatories*; N Kobayashi,* University of California Santa Cruz

This work investigates different barrier materials deposited on silver thin film mirrors and compares reflectivity with mirror durability after environmental stressing. Physical vapor deposition of various fluorides, oxides, and nitrides in combination with conformal layers of oxides and nitrides deposited by atomic layer deposition (ALD) are used to develop several novel multilayer coating recipes. Samples undergo aggressive high temperature (80°C) plus high humidity (80%) (HTHH) testing for ten days. Reflectivity of mirror samples is measured before and after HTHH testing, and image processing techniques are used to analyze the specular surface of the samples after HTHH testing. Mirror durability results are discussed with attention given to the silver diffusion-limiting properties of the material immediately adjacent to silver, as well as the density and chemical properties of the top barrier layer. Because higher durability is often observed in samples with less transparent barrier layers, we propose a figure of merit based on post-HTHH testing reflectivity change and spectrally reflective mirror surface area remaining after HTHH testing in order to judge overall barrier performance.

AA-SuP-65 Atomic Layer Deposition onto Carbon Fiber Fabrics*, C Militzer, P Dill,* ***Werner Goedel,*** Chemnitz University of Technology, Germany

Carbon fiber fabrics, consisting of interwoven bundles, each bundle comprising 3000 single fibers, were coated with Al_2O_3 using the atomic layer deposition (ALD) process, exposing the fabrics to alternating pulses of trimethyl aluminium and water vapors. The thickness and uniformity of the coatings were investigated using scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The obtained coatings were conformal, 84 ALD cycles gave rise to approximately 20 nm thick coatings and 168 ALD cycles to approximately 40 nm thick coatings. It was found, that a uniform coating can be obtained at a purge time of 40 s. Reducing purge times below 20 s gives rise to increased particle growth and thus the coating becomes inhomogeneous. Initially, the samples that were coated had a size of 2 × 10 cm (thickness 0.3 mm). The area of the fabric was subsequently increased up to 8 cm × 20 cm and a uniform coating of the same quality was obtained. By oxidizing the coated fabrics, fabrics composed of interwoven alumina microtubes were obtained. Infiltration of the microtubes with solutions of two distinguishable fluorescent dyes showed that interchange of the dyes between warp and weft microtubes occurs, but is absent at approximately 20% of the crossovers. Taking all our results into account, we conclude that the majority of the fibers were separated from each other by the coating prior to the oxidation. This work demonstrates that ALD is a suitable method to produce thin, conformal coatings on the surface of carbon fiber fabrics.

AA-SuP-66 Increasing Li-ion Battery Performance by Spatial ALD Coating of Separator Membranes with Al_2O_3*, E Balder, L Haverkate,* TNO/Holst Center, Netherlands*; Y Creyghton,* TNO, Netherlands*; P Poodt,* TNO/Holst Center, Netherlands*;* ***Fred Roozeboom,*** TNO/Holst Center, The Netherlands, Netherlands*; S Unnikrishnan,* TNO/Holst Center, Netherlands

Future Li-ion battery technology requires superior materials and processing to achieve improved performance (higher power and energy densities), as well as safer operation. One of the prime challenging failure modes in a battery is the thermal shrinkage of the separator membrane due to thermal run-away, which increases the probability of shorts between electrodes, causing limited lifetime and additional safety hazards.

Thin Al_2O_3 coatings are known to mechanically stabilize separator membranes. For example, they can be used to decrease the thermal shrinkage of the separator membranes. Moreover, the wettability of the non-polar separator membrane with polar electrolytes can be improved, yielding better (liquid) electrolyte retention throughout the polymer separator and thus improved ionic conductivity of the total Li-ion cell. To ensure the applicability of these membranes, it is important that the pores remain open and the electrical resistance remains high.

Especially in the case of high-porosity membranes, ALD is the current coating method of choice. Here, spatial atmospheric pressure ALD holds the best promise for a process enabling sufficient deposition rates at low deposition temperatures (50 °C) [1,2].

To this end, we used a rotary s-ALD reactor to deposit Al_2O_3 layers on a representative Celgard® 2325 membrane, with a porosity of 39 % and average pore diameter of 28 nm. The reactor is capable of thermal and plasma deposition as described elsewhere [1]. Typically, we deposited coatings made of 5 to 40 cycles with exposure times of approximately 320 ms.

Figure 1 shows a representative SEM cross-section of an alumina coated membrane, and the corresponding EDX elemental line scan for Al. They show a fully uniform Al-content across the entire porous membrane. This points to a full penetration of the TMA precursor and oxygen reactant into the porous structure.

We will also show the preliminary results on the membrane's wettability and electrical performance. Finally we will also present the first attempts on roll-to-roll ALD processing of these separator membranes, paving the way for large area polymer membrane coating by spatial ALD.

Figure 1. Cross-section SEM image of a Celgard® 2325 membrane coated with nominally 4 nm Al_2O_3 (40 cycles), with corresponding EDX line scan, showing a uniform coverage of aluminum across the porous structure.

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AA-SuP-67 Total-Dose Radiation Response of Atomic Layer Deposition Al_2O_3 Films, *C Nixon, B Triggs,* Semicoa*; N Sullivan,* ***Huazhi Li****,* Arradiance

In space applications, radiation response and reliability of alternative gate dielectrics in the integrated circuits (ICs) are critical [1]. Spacecraft rely on advanced microelectronic devices to perform actions in outer space such as power conversion, communication and computing,. These devices are unavoidably exposed to space radiation, which may cause storage failure, device degradation, and even break down. To meet the need of reduced leakage currents and feature scaling in advanced devices, atomic layer deposited (ALD) high dielectric constant (high-k) gate dielectric (e.g. Al_2O_3, HfO_2, & etc) films have been investigated as a replacement for the thermal SiO_2 gate dielectric in microelectronics [2]. The objective of this work is to determine whether ALD gate oxides can be used to improve device performance under space radiation conditions by studying the total-dose radiation response of the devices.

Alumina (Al_2O_3) was chosen for this study because Group III oxides are the most stable and reliable dielectrics and have been studied extensively. The favorable properties that make it desirable are the large band gap and band offset, thermodynamic and kinetic stability, low bulk defect density, and high radiation resistance. These properties satisfy most of the guidelines for an ideal gate oxide. It is also the most studied ALD materials.

In the presentation, we will report the total dose radiation tests that were performed on ALD Al_2O_3 coated substrates such as Si and SiC and discuss the effects of different surface preparation and post deposition treatments. For Si substrate we see virtually no flatband shift post 50 Krad radiation showing the excellent stability of ALD Al_2O_3/Si stack (the following graph: blue indicates before radiation while red indicates post radiation).

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AA-SuP-68 Tuning the Switching Properties of ZnO Thin Film Memristors by Al Doping via ALD*,* ***Cecilia Giovinazzo****, S Porro, C Ricciardi,* Polytechnic of Turin, Italy

Metal/Insulator/Metal (MIM) memristors were recently proposed to tackle the increasing request of scalability, low power consumption and fast response of new generation electronic devices. Their wide range of applications from analog computation to new generation memories and neuromorphic circuits requires memristors to possess highly adaptive capability and performance control. In this scenario, the opportunity to tune the electrical response by doping the metal oxide during the ALD process is particularly interesting.

In this work Al:ZnO (AZO) thin film devices are fabricated by ALD in a Beneq TFS200 tool using Diethylzinc (DEZ) and Trimethylaluminum (TMA) as metal precursors and water as oxidant. The ALD doping process consists of single cycles of TMA/H_2O periodically inserted in a given number of DEZ/ H_2O cycles, resulting in an alloy structure, where ZnO film locally contains Al_2O_3 partial layers. The presence of Al^{3+} ions intrinsically changes the structural and electrical properties of the thin film, allowing tuning the device's memristive response. At substrate temperature of 200°C, which is inside the temperature windows of both materials, the two species exhibit very different properties: ZnO films are poly-crystalline and conducting, while Al_2O_3 films are amorphous and insulating. Therefore the properties of the thin film can be tuned over the range of values defined for the two pure oxides. The variation of growth per cycle rate, chemical composition and crystallinity were investigated by electron microscopy, micro-Raman spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy, revealing a gradual decrease of crystallinity with doping of AZO films. Four probes Hall measurements in Van Der Pauw configuration show that pure ZnO films are naturally n-type doped with low resistivity ($9x10^{-3}$ Ωcm), which decreases with small Al concentration in the film until a minimum value (~5% Al). In AZO samples, the carrier concentration rapidly increases to reach a saturation value of $2x10^{21}$ cm^{-3}, while mobility decreases adding Al partial layers that act as local barriers.

To test the electrical response, Pt/Al:ZnO/Cu structures were realized on a Si wafer and tested in voltage sweep mode using a 4200 Keithley ReRAM module. Lightly doped samples (1-5% Al) show a decrease in OFF resistance state and switching voltages. In addition, a change in switching mechanism influenced by the variation of resistivity and mobile carrier concentration is presented.

Tuning the switching parameters by a combination of different oxides via ALD impacts on the MIM structures engineering, adding a degree of freedom in memristor realization and fine control.

AA-SuP-69 Atomic Layer Deposition of Bulk Layered Heterojunctions for Efficient Electrocatalyst*,* ***Changdeuck Bae****, T Ho, H Shin,* Sungkyunkwan University

We describe the spontaneous formation of a composite chalcogenide materials that consist of two-dimensional (2-D) materials dispersed in bulk and their unusual charge transport properties for application in hydrogen evolution reactions (HERs). When MoS_2 as a representative 2-D material is atomic layer deposition-deposited on transition metals such as Cu in a controlled manner, the sulfidation reactions also occur with the metal. This process results in remarkably unique structures, i.e., bulk layered heterojunctions (BLHJs) of Cu-Mo-S that contain MoS_2 flakes inside, which are uniformly dispersed in the Cu_2S matrix. The resulting structures were expected to induce asymmetric charge transfer via layered frameworks and tested as electrocatalysts for HERs. Upon suitable thermal treatments, the BLHJ surfaces exhibited the efficient HER performance of approximately 10 mA/cm^2 at a potential of as low as -0.1 V versus a reversible hydrogen electrode (RHE). The Tafel slope was approximately 30 to 40 mV/dec. The present strategy was further generalized by demonstrating the formation of BLHJs on other transition metals such as Ni. The resulting BLHJs of Ni-Mo-S also showed the remarkable HER performance and the stable operation over 10 days without using Pt counter electrodes by eliminating any possible issues on the Pt contamination.

AA-SuP-70 Atomic Layer Deposited Ultra-thin Ta-Ni-N Films for Cu Diffusion Barriers*,* ***Yong-Ping Wang****, Z Ding, W Liu, S Ding,* Fudan University, China

Recently, tantalum nitride (TaN) has been widely used in integrated circuits as a diffusion barrier for Cu interconnects due to its relatively good diffusion barrier effect and thermal stability. However, the TaN barriers deposited by atomic-layer-deposition (ALD) usually suffer a high resistance due to incorporation of C and O impurities from the precursors. In order to improve the conductivity of ALD TaN, novel Ni-doped TaN films were deposited by plasma-assisted ALD at 250 °C. Pentakis(dimethylamino)tantalum (PDMAT) and nickelocene ($NiCp_2$) were used as Ta and Ni sources and NH_3 plasma as a reducing agent, respectively. The relative contents of TaN and Ni in the Ta-Ni-N films were controlled by the reaction cycle ratio of PDMAT-NH_3 (m) to $NiCp_2$-NH_3 (n).

Firstly, we investigated the influence of the relative contents on the characteristics of the deposited films, including chemical composition, surface morphology, resistivity, film density and thermal stability. The deposited films contain Ta, Ni, N, C and O elements, of which the relative percentage of O is less than 9%. As the reaction cycle ratio (m:n) decreases from 2:1 to 2:6, the RMS increases from 0.150 to 0.527 nm, and the resistivity decreases from 0.18 to 0.011Ω×cm. After annealing at 400 ^{o}C for 30 min in N_2/H_2, the films exhibit unchanged resistivity and amorphous matrix, indicating good thermal stability. Furthermore, the good step coverage of the Ni-doped Ta N film is also demonstrated in an array of Si nano-pillars with an aspect ratio of about 6.

Secondly, the stacks of Cu(50nm)/barrier(5nm)/Si were prepared and annealed at different temperatures in order to study the capabilities of different composition Ta-Ni-N barriers against Cu diffusion. When the annealing temperature was increased to 500 ^{o}C, the barriers with a deposition cycle ratio of < or = 2:5 failed. In order to maximize Cu volume and reduce interconnect resistance, decreasing the thickness of diffusion barrier is an effective option. Therefore, ultra-thin barriers were further evaluated by leakage current measurement of metal-oxide-Si (MOS) capacitors. Herein, the Cu(50nm)/ barrier (4nm or 3nm) /SiO_2 (20nm) /Si structures were fabricated using a lift-off process. The results indicate that both the films have a smooth surface with a RMS value between 0.157nm and 0.413nm, and the 4nm barriers with a deposition ratio of > or = 2:4 still retain a good diffusion barrier property after annealing at 450 ^{o}C for 30 min. In conclusion, the present study indicates that addition of appropriate Ni to TaN can improve the conductivity while maintaining a good barrier property against Cu diffusion.

AA-SuP-71 Improved Electrical Properties of $ZrO_2/ZrSiO_4/ZrO_2$ (ZSZ) based MIM Capacitors using DNS-Zr Bimetallic Precursor*, **Sang Yong Jeon,*** DNF.co.Ltd, Republic of Korea*; H Lim,* DNF Co. Ltd, Republic of Korea*; S Jo,* DNF.co.Ltd, Republic of Korea*; J Park,* DNF Co. Ltd, Republic of Korea*; W Chae, S Yim,* DNF.co.Ltd, Republic of Korea*; J Park,* DNF Co. Ltd, Republic of Korea*; S Lee,* DNF.Co.Ltd, Republic of Korea*; M Kim,* DNF Co. Ltd, Republic of Korea*; D Kim, S Kwon,* Pusan National University, Republic of Korea

As the size of the dynamic random access memory (DRAM) is continuously scaled down, the new high-k dielectric materials, such as TiO_2 and $SrTiO_3$ have received great attention. However, these high-k materials inevitably require noble metal electrodes such as Ru and Ir because of their relatively narrow band gap. Although noble metal electrodes for DRAM application have been studied for over a decade, there still remains a lot of process limitation that need to be overcome for successful application of TiO_2 and $SrTiO_3$. Atomic layer deposited ZrO_2 films with ultra-thin Al_2O_3 leakage blocking layer, so-called ZAZ structure, has been successfully adopted as an efficient high-k capacitor dielectric of current DRAM. However, it is doubt that the current ZAZ capacitor structure will be continued for next generation DRAM production because the continuous improvement of dielectric properties of ZAZ capacitor structure seems not to be easy.

Herein, therefore, we proposed a simple but mass-production friendly ALD-$ZrO_2/ZrSiO_4/ZrO_2$ (ZSZ) approach to overcome current ALD-ZAZ capacitors. By simply substituting Al_2O_3 with $ZrSiO_4$, a further improvement of dielectric properties of capacitor structure was successfully demonstrated. ALD-$ZrSiO_4$ using DNS-Zr bimetallic precursor exhibited a comparable leakage current property with Al_2O_3. And, its dielectric constant was higher than that of ALD-Al_2O_3. A use of DNS-Zr bimetallic precursor provided a simple ALD process, a homogeneous deposition on high-aspect ratio patterns, and stable electrical performance. Based on our observation, it was believed that our ZSZ structure by simply substituting Al_2O_3 with $ZrSiO_4$ can be potentially used for future DRAM technology.

AA-SuP-72 ALD Metal Oxides for Passivation of Si/SiO_2 Interface in BSI CMOS Image Sensors*, **Evan Oudot**, M Gros-Jean, K Courouble,* STMicroelectronics, France*; C Vallée,* Univ. Grenoble Alpes, CNRS, France*; F Bertin,* LETI, France

Back-Side Illuminated CMOS Image Sensors (BSI CIS) requires an anti reflective coating layer (ARC) at the backside interface. Moreover this ARC have to play the role of passivation layer in order to reduce the dark current level due to thermal generation of electrons at the backside Si/SiO_2 interface. Indeed, defects at the Si/SiO_2 interface imply energy levels into the silicon band gap, commonly called interface traps (D_{it}), and then assist the generation of electrons. In this study we focus on the passivation layer properties, i.e the reduction in electron's generation rate at the interface, U_s. To do this, there are two possibilities. First, reduce the density of interface traps which is the root cause of electrons' generation. This first solution is called *chemical passivation*. Secondly, by introducing negative charge in the ARC. Indeed, this permits to accumulate holes at the Si/SiO_2 interface which allows to pull the Fermi level toward the valence band and thus to empty the interface states. This second solution is called *field effect passivation*. Therefore, the new ARC proposed in this work is a stack composed of three layers. First a layer of metal oxide (HfO_2 or Al_2O_3) deposited by ALD on a silicon oxide (SiO_2) interlayer for their passivation properties, and then a layer of Ta_2O_5 using for his anti reflective property.

The aim of our work is to understand origin of defects and charges in ARC to control their quantity and so reduce the dark current. For this we review here the results concerning charges (Q_{tot}) and density of interface traps (D_{it}) obtained using two passivation materials, HfO_2 and Al_2O_3. These results are obtained from COCOS (Corona Oxide Characterization Of Semiconductor) measurements on full sheet wafers. In particular we focus on the impact of ALD process and anneal.

AA-SuP-73 Graphene-based Flexible Electrode Preparation with Aid of ALD Layer and its Electrochemical Applications*, **Yekyung Kim**, D Lee, J Seo, S Lee, K Hong, S Chang, S Cho, H Kim,* Korea Electronics Technology Institute, Republic of Korea

The demand of transparent electrode, in these days, are gradually increasing with the technological development in the field of smart films-with the function of electrochromic, thermochromic, heating and others-, OLED lighting, display and so on. Graphene is considered as a candidate for the next generation of transparent electrode. However, its electrical property is not reached as much as the rigid transparent conducting oxide (TCO) so far. Therefore, in this study, a type of rigid TCO of indium tin oxide (ITO) was deposited on the flexible graphene/PET substrate to ensure the electrical conductivity and flexibility as a transparent flexible electrode. However, during the ITO deposition process of physical vapor deposition (PVD), graphene was exposed to the oxygen plasma which cause serious defects. To prevent the additional defect production during electrode preparation, an ALD layer was introduced beneath the ITO layer. As an electrochemical application of the prepared transparent electrode, an electrochromic cell was fabricated with the electrochromic layer of tungsten oxide and its pair-electrochromic layer of nickel-tungsten oxide, in this study. The electrochromic device is recently getting attention due to the high requirement of energy saving technology and multi-functioning device. Also, advancement of paired technology such as light-responding mirrors, smart window, light shutter, etc. helps for the increase of needs. Tungsten oxide or nickel-tungsten oxide was deposited on the prepared ITO/ALD/graphene/PET film by PVD. The two different electrodes with electrochromic layer were then laminated together using gel-like electrolyte. The electrochromic cell prepared with ALD layer introduction successfully worked and showed reasonable coloration performance. The electrochemical and optical properties of the ALD introduced electrode showed a feasibility as a transparent flexible graphene electrode.

AA-SuP-74 Teaching Perovskites to Swim: ALD Oxide Overcoating for Liquid Water- and Heat-Resistant Photovoltaics*, I Kim, **Alex Martinson**,* Argonne National Laboratory

Despite rapid advances in conversion efficiency (>22%), the environmental stability of perovskite solar cells remains a substantial barrier to commercialization. Here, we show a striking improvement in the stability of inverted perovskite solar cells against liquid water and high operating temperature (100 °C) by integrating an ultrathin amorphous oxide electron extraction layer via atomic layer deposition (ALD). These unencapsulated inverted devices exhibit a stable operation over at least 10 h when subjected to high thermal stress (100 °C) in ambient environments, as well as upon direct contact with a droplet of water without further encapsulation.

AA-SuP-75 Highly Stable High Mobility Oxide Thin-film Transistor with N_2O Plasma Treatment and Gate Insulator by Means of Atomic Layer Deposition*, **Jong Beom Ko**, K Park, Y Nam, S Lee, S Park,* Korea Advanced Institute of Science and Technology, Republic of Korea

The oxide thin-film transistors (TFTs) are actively researched for the driving device of the display, due to their good electrical characteristics and low cost process. The self-aligned (SA) TFT is a good candidate due to their small parasitic capacitance, which have benefit of low RC delay. However, the quality of gate insulator (GI) and their deposition environment must be carefully considered, especially in high mobility condition. The thermal ALD and plasma-enhanced (PE) ALD are the good candidates for the deposition methods of high quality GI. However, the thermal ALD causes hydrogen incorporation to the active and degrade on/off characteristics significantly in high mobility TFTs. While, the PEALD induce plasma damage to the front-channel surface and bias stability can be worse. Therefore, we tried to obtain high mobility TFT with good stability by N_2O plasma treatment followed by thermal ALD GI deposition.

We fabricate the TFTs with top-gate staggered structure with different kinds of GI deposition process. The Al_2O_3 was deposited as the GI by using thermal ALD and PEALD, separately. Another group of TFT was treated by N_2O plasma to the active, and deposit GI by means of thermal ALD. As expected, it tends to be conductive when GI is processed by thermal ALD process, due to hydrogen incorporation. While, the TFT with GI by means of PEALD shows good on/off characteristics and turn-on voltage, however, it has hysteresis issue. In contrast, the plasma treated TFT with ALD GI shows on/off characteristics without hysteresis. It shows 30.6 cm^2/Vs and 0.096 mV/dec of mobility and subthreshold swing, respectively. It also exhibits good stability characteristic, compare with PEALD GI in PBTS condition. The V_{th} was shifted about 0.60V in TFT with PEALD GI, however, it shifted only 0.01V in plasma treated TFT with ALD GI, after 7200s of PBTS stress. The plasma damage during the PEALD process may generate more trap site at the front channel interface. Actually, the trap site also can be generate during the plasma treatment, however, it may passivated by hydrogen from H_2O reactant during thermal ALD GI process. We found the feasibility of applying thermal ALD process for the GI deposition to the top-gate structured high mobility oxide TFTs by controlling carrier density with plasma treatment.

AA-SuP-76 Zinc Oxide Infiltration of Two-Photon Polymerized Structures*, Jacek Lechowicz,* University of Illinois at Chicago*; L Ocola, R Divan,* Argonne National Laboratory*; I Paprotny,* University of Illinois at Chicago

The properties of zinc oxide (ZnO) have various applications in gas sensing, semiconductors, and optics. Recently, it has been shown that poly(methyl methacrylate) (PMMA) can be infused by ZnO through the process of sequential infiltration synthesis (SiS), allowing for lithographically patterned ZnO/PMMA structures(1).

In this work, we investigate SiS of two-photon polymerized (2PP) polymers with ZnO. X-ray spectroscopy indicates an infiltration depth of approximately 1 mm in IP-L 780 photoresist thin films. Three dimensional (3D) structures infiltrated with ZnO were readily amenable to electron microscopy without the need of conductive coating. Preliminary studies of 2PP 3D structures (25 x 25 x 50 mm) indicate a higher infiltration depth, with distribution of ZnO observed throughout the entire structure, opening the possibility for the application of this method in sensors and photonics.

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AA-SuP-77 Investigating Li-ions Transport Through ALD Al_2O_3 Coatings on NMC Cathode in a Li-ion Battery*, M Laskar,* ***David Jackson****, S Xu, Y Guan,* University of Wisconsin-Madison*; M Dreibelbis,* Dow Chemicals*; R Hamers,* University of Wisconsin-Madison*; M Mahanthappa,* University of Minnesota*; D Morgan, T Kuech,* University of Wisconsin-Madison

A thin amorphous coating of Al_2O_3 obtained via atomic layer deposition (ALD) has demonstrated the ability to improve cycle-life for several cathode materials in rechargeable Li-ion batteries [1]. However, due to the insulating nature of Al_2O_3, the coatings on cathode particles impede the transport of Li-ion and electrons during the battery cycling. Therefore, a large overpotential on the cathode surface can develop leading to significant capacity loss at higher C-rates and for thicker coatings. In this work, we describe a method to estimate the overpotential of amorphous ALD Al_2O_3 coatings on $Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O_2$ (NMC) cathode and can be extended to any other coating materials. At 1C-rate (2.062mA), the estimated Al_2O_3 overpotential is about 0.82 mV/nm yielding an estimation of effective resistivity 6.3 MΩm and Li-ion diffusivity of $1.7x10^{-14}$ cm^2/s.

We found that the Al_2O_3 overpotential varies linearly with coating thickness and also with driving current, implying an "Ohmic" behavior. Based on the theoretical model [2], these observations lead to conclude that coatings acts like an electrolyte, consisting of positively charged Li ions and negatively charged electrons. In such a mechanism, Li-ions take part in the ionic transport across coating and the counter-balancing negative charges (electrons) remain trapped in localized electronic states within the coating. Those electrons are originally donated by protons incorporated in the coating resulting from the ALD process and then ion-exchanged with Li^+ during battery operation. Since the resistivity is inversely proportional to Li^+ concentration, the concentration of the protons in the original coatings determines the resistivity and overpotential value. We support this hypothesis by demonstrating a higher overpotential for Al_2O_3 coatings of a lower proton concentration. The presence of proton concentration in ALD Al_2O_3 coatings were confirmed by Rutherford backscattering.

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Nanostructure Synthesis and Fabrication
Room Plaza Exhibit - Session NS-SuP

Nanostructures Synthesis and Fabrication Poster Session

NS-SuP-1 Refractive Index and Bandgap Variation in Al_2O_3-ZnO Ultrathin Multilayers Prepared by Atomic Layer Deposition*, Javier López Medina,* CONACYT - Centro de Nanociencias y Nanotecnologia - UNAM, Mexico*; E Solorio, H Borbón, F Castillon, R Machorro,* Centro de Nanociencias y Nanotecnologia - Universidad Nacional Autónoma de Mexico, Mexico*; N Nedev,* Universidad Autónoma de Baja California, Mexico*; M Farias, H Tiznado,* Centro de Nanociencias y Nanotecnologia - Universidad Nacional Autónoma de Mexico, Mexico

This research focuses on the study of the refractive index and bandgap behavior in ultrathin multilayer films of Al_2O_3-ZnO bilayers grown via atomic layer deposition (ALD) technique on Si(100) substrates. The multilayer configuration stack consists in alternate layers of constant thickness Al_2O_3 (2 nm) and varying thickness ZnO films in order to obtain a total thickness of ~100 nm. A set of 10 samples based on bilayers with various 2:X thickness ratios were prepared, where X refers to the ZnO layer thickness. X is proportional to the number of cycles (N) of the ZnO precursor, varying from 1 to 100. The sample morphology was studied via Atomic Force Microscopy and the results show that the surface roughness of the multilayers varies from 0.2 to 1.2 nm, as the ZnO layer thickness increases. In all cases, the roughness values remain below 2% of the total thickness of the multilayer. The refractive index n(λ) and optical bandgap, E_g, of each multilayer sample were studied via spectroscopic ellipsometry (SE). A General Oscillator optical model was utilized to fit the experimental data in order to obtain the total thickness, refractive index and absorption coefficient. Cross-sectional mode scanning electron microscope images verified the multilayer total thickness and corroborated the accuracy of the optical model. The refractive index varies significantly from values close to the Al_2O_3 refractive index when the bilayer thickness is small, up to values corresponding closely to ZnO for thicker bilayers. The refractive index, as a function of bilayer thickness, varies between 1.63 and 2.3, for $\lambda \approx 370$ nm (UV region), showing high sensitivity. In addition, the optical bandgap energy, E_g, determined using the Tauc model, decreases when the bilayer thickness increases, with a maximum variation of ΔE_g ~1.6 eV. These results reveal that the refractive index and optical bandgap of Al_2O_3-ZnO material can be modulated systematically as a function of the bilayer thickness. Such behavior is of great importance for optoelectronics applications, in particular for the development of devices with response in the UV spectral range.

Acknowledgments

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NS-SuP-2 Controlled and Selective Etches for Gate All-Around Device Fabrication*, Subhadeep Kal,* *J Smith, N Mohanty, Y Su, C Pereira, A Mosden, P Biolsi, T Hurd,* Tokyo Electron

In scaling beyond the 5nm technology node there is an impetus for gate all-around (GAA) device architecture. A basic requirement for GAA is the formation of silicon-germanium (SiGe) and silicon (Si) nanowires (NW). Fabricating either Si or SiGe NW (also known as NW release) requires an extremely selective, isotropic and precise SiGe (shown in Fig.1, step 1) and Si etch, respectively. After the Si NW release (or SiGe etch), the SiN gate spacer is formed around the Si NW, making a continuous and sealed gate spacer (Fig.1, step 2). In the case of a partial NW release (Fig.1), the SiGe etch must be controlled with an accuracy of >5A since this recess will effectively define the gate spacer thickness in the area above and below the Si NW after spacer etch (SE)/liner etch (step 3, Fig.1). Here we highlight why a precise etch control is essential: (1) if the SiGe recess is too small, the reformed gate spacer thickness will be under specification and will result in capacitance problems between gate and adjacent source/drain bar metals. (2) If the SiGe recess is too much, the reformed gate spacer will penetrate into the replacement gate and will decrease the amount of gate metal wrapping around the nanowire and will impact gate functionality. Once only the silicon wire is protruding through the seamless gate spacer (Fig.1, step 3), SiGe:B can be grown from the ends of the silicon wires protruding through the gate spacer (Fig.1, step 4). In addition to the above requirements, etch selectivity towards to the gate and low K material around the gate (not shown in Fig 1) is also preferable. Therefore, a process flow enabled with extremely high selective etches, where the selectivity is a function of film properties and/or etch chemistry is a quintessential advantage. In this article, we demonstrate the significance of such selective etches for Si NW formation step (Fig.1, step 1) and corresponding SiGe NW fabrication.

Fig.1 (step 1), shows the process performance of a selective gas phase SiGe etch for Si NW (SiGe etch) formation. Research is ongoing to explore further how these techniques can be optimized together to obtain a straight SiGe and Si etch front. Similar etch techniques has also proved to be essential for full NW release, where the requirements are selective, isotropic and complete etch of Si or SiGe stacks. In addition we will also show an alternate selective etch technique to fabricate corresponding SiGe NW (Si etch) formation.

NS-SuP-3 Wafer-Scale Synthesis of High-Quality and Few-Layer WS_2 Films on Si/SiO_2 Substrates*, **Yung-Ching Chu,*** National Chiao Tung University, Republic of China*; C Jong,* NARLabs, Republic of China*; Y Ho,* National Chiao Tung University, Republic of China*; P Lu,* UCLA*; C Zhong,* National Chiao Tung University, Republic of China*; H Hsu,* ITRI, Republic of China*; Y Tu,* National Chiao Tung University, Republic of China*; J Woo,* UCLA*; E Chang,* National Chiao Tung University, Republic of China

Due to their attractive properties for next-generation electronic and optoelectronic devices, two-dimensional (2D) layered transition metal dichalcogenides (TMDs) materials such as MoS_2, WSe_2 and WS_2 have attracted a great deal of attention recently. Among these 2D TMDs materials, few-layer tungsten disulfide (WS_2) is particularly attractive for electronic applications due to its potential high hole mobility. The theoretically predicted room temperature mobility of WS_2 is 1,103 $cm^2 \cdot V^{-1} \cdot s^{-1}$, much higher than that for MoS_2 (304 $cm^2 \cdot V^{-1} \cdot s^{-1}$) and WSe_2 (705 $cm^2 \cdot V^{-1} \cdot s^{-1}$)[1]. In addition, few-layer WS_2 with a direct band-gap about 2.0 eV is suitable for electronic and optoelectronic devices. While remarkable methods for other TMDs large area preparation have been reported, large area synthesis of WS_2 remains a challenge.

In this study, a novel scalable method of realizing wafer-scale well controlled WS_2 films is proposed and demonstrated. The synthesis of WS_2 films start by depositing tungsten trioxide (WO_3) films on 4-inch heavily doped silicon substrate with 80-nm SiO_2 cap layer by e-gun evaporation. These films were then converted into few-layer WS_2 via sulfurization with hydrogen sulfide (H_2S) at elevated temperatures. Figure 1(a) shows that a uniform WS_2 film is achieved, fully covering the 4-inch substrate wafer. The WS_2 film thickness can be controlled by adjusting the e-gun evaporated tungsten oxide film thickness, which was confirmed by cross-sectional transmission electron microscopy (TEM). Figure 1(b) shows the cross-section TEM image for 1 nm WO_3 film converted to a continue WS_2 film. The inset is a high resolution TEM showing 2~3 layers of WS_2. Both Raman and photoluminescence (PL) spectra of the samples were acquired using a Raman microscope system with a laser excitation wavelength of 532 nm. Raman spectrum (Figure 1(c)) indicates that the as-synthesized WS_2 thin films have two characteristic peaks of the in-plane vibrational mode, E^1_{2g}, at about 353 cm^{-1} and the out-of-plane vibrational mode, A_{1g}, at about 418 cm^{-1}. PL spectrum of as-synthesized WS_2 (Figure 1(d)) shows the major PL peak (A) at approximately 1.98 eV associated with the direct band-gap transition at K point. The weak PL peak (I) associated with the indirect band-gap transition.

In conclusion, a promising method for the synthesis of wafer-scale high quality WS_2 on insulating substrates that could enable batch fabrication of 2D electronic and optoelectronic devices were proposed. TEM, Raman and PL were performed on these samples to demonstrate their excellent material qualities.

Reference

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NS-SuP-4 Towards Producing Bulk Monolithic Core/Shell Nanocomposites*, **Boris Feigelson,** J Wollmershauser, K Manandhar,* U.S. Naval Research Laboratory

With designed bulk nanostructured solids, one could potentially combine properties that are mutually exclusive in a single bulk material, and, as a result, dramatically improve the desired performance. However, a major research challenge and roadblock is how to produce 3D nanostructured materials consistently with the required phases arranged in designated spatial order that are at the same time fully dense without porosity and detrimental phases. Known state-of-the-art techniques for producing bulk nanostructures cannot simultaneously meet all these requirements. As a result, the inherent properties of such bulk monolithic nanostructured materials are greatly unknown and unexplored.

We developed an Enhanced High Pressure Sintering (EHPS) process to consolidate oxide, metal, and semiconductor nanoparticles into 3-dimensional monolithic nanostructured materials. EHPS incorporates stringent environmental control and utilizes high pressures to break agglomerates while simultaneously exploiting the increased pristine surface potential of nanoparticles for surface-energy-driven densification without microstructural changes. Using this approach, monolithic nanocrystalline transparent ceramics with grain size bellow 30 nm are demonstrated. Such ceramics exhibit a 30% increase in hardness over a corresponding order of magnitude reduction in grain size and suggest that Hall-Petch type (strengthening via grain size reduction) relations exist in ceramics at least down to 25nm [1].

Core/shell nanoparticles offer fundamentally new means for nanostructured solids design and tailoring basic properties of these artificial materials. To provide flexibility in core/shell nanoparticles design, a particle atomic layer deposition (pALD) reactor was incorporated in the EHPS facility. The new setup allows to controlling environment during all stages of the nanoparticles processing, atomic layer deposition and sintering. Spinel/alumina core/shell nanoparticles were the first material system tested for producing the first core/shell ceramic nanocomposite. Alumina shell was grown on spinel nanoparticles, and then core/shell nanoparticles sintered under pressure without exposing to atmospheric air. The developed nanocomposite ceramics demonstrated better hardness and fracture toughness than pure nanocrystalline spinel.

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NS-SuP-5 Nanolaminate Copper Barriers of Ru/TaN_x Thin Films by Inductively Coupled Plasma Enhanced Atomic Layer Deposition*, **Bo-Heng Liu,** W Cho, C Kei,* National Applied Research Laboratories, Republic of China

Ru/TaN nanolaminate barriers and Cu interconnect were sequential directly grown on dual damascene nano-porous dielectrics by inductively coupled plasma enhanced atomic layer deposition (PEALD). Ru/TaN thin films were successfully deposited by home-built PEALD using $[Ru(EtCp)_2]$ and $Ta(NC_2H_6)_5$ as precursor with high energy reductive Ar/H_2 and Ar/O_2 plasma. The substrate temperature of Ru/TaN thin films were 300 and 250 °C with 500 cycles to PEALD process. The N_2 purge time and plasma power were held on 5 s and 400 W. Ru/TaN thin films were analyzed by X-ray photoelectron spectroscopy (XPS: Perkin Elmer PHI 670) and HRTEM (JEOL JEM-2100F). The resistivity was measured by using Hall effect measurement system (Accent/HL 5500PC). Fig. 1 shows the XPS of Ru 3d spectra deposited by PEALD. The energy states of $3d_{5/2}$ (at 280.2 eV) and $3d_{3/2}$ (at 284.3 eV) indicated metallic Ru. However, the lower intensity peaks at 281.2 eV and 285.9 eV are from RuO_2. Growth rate of Ru the films was increased significant from 0.01 to 0.1 nm/cycle by using dc biased PEALD. The resistivity of Ru thin films prepared by PEALD was 40 $\mu\Omega$ cm. The growth rate of TaN thin films was 0.05 nm/cycle as s the PDMAT pulse time is more than 2 s. Cross-section HRTEM image in Fig. 2 shows that the Ru/TaN nanolaminate barriers were formed. In summary, Ru/TaN nanolaminate barriers were prepared by using $Ru(EtCp]_2]$ and $Ta(NC_2H_6)_5$ precursor with the aid of the high energy reductive Ar/O_2 and Ar/H_2 plasma in ITRC PEALD system.

NS-SuP-6 On the Possibility of the Development of Vicinal Superlattices in Quantum Wires on Semiconductor Low - Index Surfaces*, **Victor Petrov,*** Russian Academy of Science, Russian Federation

As is well known, vicinal superlattices (VSLs) are realized in 2D electron systems on semiconductor high-index Miller surfaces. The existence of SL effects in VSLs is due to the appearance in these systems of a new cristallographic translation period in the plane of quantum wells A >> a_0 (a_0 is the lattice constant). A new translation period A produces minigaps (MGs) in the energetic spectrum of the particles in these systems and, as a result, different SL effects. At the present time, all these VSLs are developed only in 2D systems. At the same time, it is known that superlattice effects should be maximal in quantum wires (QWR) when the SL period A appears along the axis of the QWR.

In this work we suggest a new method of development of VSL in QWR on semiconductor low-index surfaces. For this purpose we suggest to orient the axis of the QWR at the necessary angles to the basic translation vectors on a low-index surface. In this case in the QWR the new basic translation period along the axis of the QWR A > > a_0. Thus, the period A along the surface in the one-dimensional VSL is selected by the orientation of the QWR on the low-index surface. If the QWR is realized in the MOS system with the use of a narrow gate then the orientation of the wire will be determined simply by the appropriate orientation of the gate. The analytic expressions of the new periods A were obtained as a function of the angles which determine orientation of the QWR for the different low-index surfaces GaAs and Si. The positions of MGs in the one-dimensional k-space were determined. It is should be noted that in the region of the particle wave function localization in the QWR there are many crystallographic planes which form a SL energetic spectrum of the particle. Illustrative estimates of the magnitude of the MGs for the QWR of the rectangular cross-section made in the weak coupling approximation demonstrate their dependence on the geometric parameters of the cross-section, on the period A as well as on the crystal potential.

NS-SuP-7 Rational Design of Hyperbranched Nanowire Systems for Tunable Superomniphobic Surfaces Enabled by Atomic Layer Deposition, *Ashley Bielinski, M Boban,* University of Michigan, USA*; Y He,* University of Pittsburgh*; E Kazyak, D Lee,* University of Michigan, USA*; C Wang,* Pacific Northwestern National Laboratory*; A Tuteja, N Dasgupta,* University of Michigan, USA

The hierarchical assembly of semiconductor nanostructures to form heterogeneous material systems has the potential to advance a range of technologies including electronics, optics, sensors, mechanical resonators, and energy conversion. Semiconductor nanowire (NW) arrays have already been successfully applied in these fields, but challenges such as lack of deterministic control of feature size, shape, and position limits the development of more complex geometries. One example, hyperbranched NWs, have been synthesized for a variety of applications, but the ability to tune the morphology along a spectrum at each level of hierarchy requires further development. Here we demonstrate surface and interface modification via atomic layer deposition (ALD) to control the fabrication and bottom-up solution growth of ordered hyperbranched NW systems.

Existing techniques for the assembly of complex nanostructures generally rely on either nanoscale patterning, or solution based processes. The patterning techniques while slow and costly on planar substrates, often become impossible on high aspect ratio surface geometries. The solution-based approaches offer scalability and lower cost, but the results are often disordered and difficult to tune. ALD is an enabling technique for the control of low-cost, scalable hydrothermal NW synthesis. This process relies on atomic-scale precision of conformal films deposited on nanowire arrays, for which ALD is an ideal process.

We start by demonstrating the control of ZnO NW array properties such as density and orientation by tuning the crystallographic orientation, roughness, and surface stress of ALD films used to seed the NW nucleation.[1] We then show how ALD can be used to overcome the challenges that arise when transitioning from simple NW arrays to complex branched structures. Sub-monolayer deposition of inert blocking layers were used to reduce NW density independent of orientation in order to make room for subsequent branched NW growth. ALD interlayers were then used to prevent epitaxial ALD growth of subsequent seedlayers on the single crystalline NWs. These techniques were all combined to fabricate hyperbranched NW arrays. The array properties were controlled with ALD at each level of hierarchy to produce superomniphobic (repellent to high and low surface tension liquids) with tunable contact angles for different liquids.[2]

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(2) Bielinski, A. R.; Boban, M.; He, Y.; Kazyak, E.; Lee, D. H.; Wang, C.; Tuteja, A.; Dasgupta, N. P. *ACS Nano***2017**, *11* (1), 478–489.

NS-SuP-8 Designing Low Density Foams by ALD Templating, *Monika Biener,* Lawrence Livermore National Laboratory

Low density foams with precisely controlled architectures, compositions and densities have many promising applications in the fields of energy storage, catalysis, biomaterials, and high energy density physics. Here, atomic layer deposition offers a unique opportunity for rapid on-demand development of functional nanoporous bulk materials by applying the principle of templating to material systems for which robust synthesis strategies have already been developed. I will summarize recent progress made in synthesis and characterization of ALD-derived ultralow density target materials that are important for inertial confinement fusion (ICF) experiments. As porous substrates we use Polystyrene beads deposited by electrophoretic deposition, additively manufactured 3D micro lattices and nanoporous gold. Nanometer-thick metal oxide ALD coatings (ZnO, Ta_2O_5, Al_2O_3) provide the desired functionality and often dramatically improve the mechanical properties of the porous substrate. Even only nanometer thick coatings can be mechanically so robust that the substrate can be removed without collapse of the structure. The resulting materials can have air-like densities which, for example, enable the realization of brighter X-ray sources and promise to improve the performance of ICF targets.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

NS-SuP-9 Fully CMOS-Compatible Synthesis and Photodetector-Integration of Ultrathin, Parallel-Aligned ZnO Nanowire Arrays by Infiltration Synthesis, *Chang-Yong Nam, A Stein,* Brookhaven National Laboratory

Semiconductor nanowires with reduced diameters enable high-performance chemical sensors and photodetectors owing to their large surface-to-volume ratios and enhanced surface band bending. Synthesis of nanowires and their device integration by CMOS (complementary metal-oxide-semiconductor)-process-compatible methodologies can be extremely powerful for various technological applications of nanowires. Here we report fully CMOS-compatible synthesis and ultraviolet (UV)-photodetector-integration of ultrathin (~30 nm diameter), parallel-aligned, polycrystalline ZnO nanowire arrays by infiltration synthesis, a type of inorganic-organic hybridization technique derived from atomic layer deposition. The ultrathin ZnO nanowire array was generated by infiltrating diethylzinc (DEZ) and water vapors into lithographically patterned polymer nanowire template made of a negative-tone resist SU-8. The integrated ZnO nanowire array photodetectors featured ultralow dark currents <20 fA unchanging with the number of nanowires, photocurrent on-off ratios over 10^6 leading to >120 dB linear dynamic range, and super-linear photocurrents causing unusually increasing photodetector performance parameters for a higher incident light power. Considering the temperature-dependent field-effect transistor characteristics of the ZnO nanowire arrays, we explained the observed super-linear photoconductivity by the new type of photo-thermionic emission mechanism involving the reaction of chemisorbed oxygen and photo-generated holes at grain boundaries. The developed rationale provides guidelines for utilizing polycrystalline semiconductor nanostructures for photodetectors and other sensors. The demonstrated synthesis and fabrication methods based on the infiltration synthesis have potentials for CMOS-integration of nanowire sensor devices and circuitries.

NS-SuP-10 Monodispersed, Highly Interactive Facet Oriented Pd Nanograins Grown by ALD onto Electrospun Polymeric Nanofibers, *Kugalur Ranjith, A Celebioglu,* Bilkent University, Turkey*; H Eren,* Delft University of Technology, Netherlands*; N Biyikli,* Utah State University*; T Uyar,* Bilkent University, Turkey

We present a membrane form of templates for the growth of Pd nanograins through the atomic layer deposition (ALD) on the electrospun polymeric nanofibers such as Nylon 6.6, PAN and Polysulfone. Under the selective atmosphere, the stable flexible polymeric nanofibers were utilized as a template and the Pd nano grains were made to interact with the polymer surface and decorated on it. Utilizing the template avoided the aggregation of the nanograins during growth and initiated mono dispersive nature of the Pd nanostructures immobilized with the size of 2 nm. Template form of Pd decorated nanofiber network exhibited an effectualness towards the reduction of 4-nitrophenol into 4-aminophenol through hydrogenation process. Even under low loading capacity of Pd nanoparticle, effective catalytic performance was exhibited which was ascribable to the exposure of single crystalline highly interactive (111) plainswith high surface area on the nanofiber surface. With the aid of Pd nanograins decorated polymeric fibers, the catalytic reduction can be finished within 35 mins, even when the content of Pd ions was as low as 2 wt%. Pd nanograins exhibited thermal stability and structural integrity even after 3 consecutive reactions. Improvisation of the catalytic performance on Pd loading in different polymeric fibers was evidently a resultant of the higher surface area of the nanofibers with higher surface interaction. The method opens up possibilities for synthesizing decorative metal nanostructures on functional polymeric fibers based membranes for multifunctional applications.

ALD Applications
Room Plaza E - Session AA+NS-MoM

Energy: Catalysis and Fuel Cells I (8:00-10:00 am)/Nanoparticles and Nanostructures (10:45 am-12:00 pm)

Moderators: Riikka Puurunen, Aalto University, Finland, Necmi Biyikli, Utah State University, Joseph Spencer II, ALD NanoSolutions, Inc.

8:00am **AA+NS-MoM-1 Performance of Promoted Rh Catalysts for C_{2+} Oxygenate Production***, **Arun Asundi**, N Yang, C MacIsaac, S Bent,* Stanford University

Environmental and economic concerns regarding the rapid consumption of non-renewable energy resources have motivated the development of sustainable methods for fuel and chemical production. The catalytic conversion of biomass-derived syngas (CO + H_2) to ethanol and other higher oxygenates is a promising path towards sustainable energy production. However, a commercial catalyst for this process has not yet been developed due to the many kinetically favorable side reactions that shift selectivity away from the desired products. Experimental and computational studies have shown that rhodium-based catalysts have moderate intrinsic selectivity towards higher oxygenates and that the performance can be improved through the use of metal oxide promoters. However, the performance of Rh-based catalysts can vary greatly depending on a variety of factors, including preparation method and choice of promoter. Fundamental understanding of how these factors affect catalyst performance will allow for more intelligent catalyst design.

Catalysts are commonly prepared using co-impregnation since it is a fast, easy, and scalable method for the deposition of catalyst materials. However, study of the effects of catalyst structure on performance requires a method of catalyst synthesis with atomic-level control not provided by co-impregnation. Atomic layer deposition (ALD) has emerged as a technique for the design of catalysts on the atomic scale, thus allowing for the study of the effects of catalyst structure on performance. In this work, promoted Rh nanoparticles were tested in the conversion of syngas to higher oxygenates. Rh nanoparticles were prepared on porous silica particles using incipient wetness impregnation. By depositing MoO_x on the particles with ALD before and after Rh impregnation, the effects of MoO_x were studied as support and over layers. Promoted Rh catalysts prepared by ALD were compared to those made by conventional wet impregnation.

Rh nanoparticles promoted with MoO_x show a large increase in activity and higher oxygenate selectivity relative to a pure Rh catalyst. As a support layer, ALD MoO_x shows increasing selectivity with higher MoO_x loadings, while an over layer results in equally high selectivity regardless of MoO_x loading. The oxidation states and reducibility of the Rh and MoO_x species prepared by ALD and wet impregnation were studied with temperature-programmed reduction and x-ray photoelectron spectroscopy experiments. Catalysts containing MoO_x show a decrease in CO chemisorption, relative to the pure Rh catalyst. Together, these results demonstrate that MoO_x significantly alters the physical and chemical properties of the Rh catalysts.

8:15am **AA+NS-MoM-2 Facile Synthesis of Three-Dimensional Pt-TiO2 Nano-networks: A Highly Active Catalyst for the Hydrolytic Dehydrogenation of Ammonia–Borane***, **Hamit Eren**,* Delft University of Technology, Netherlands*; N Biyikli,* Utah State University*; M Guler,* Northwestern University

Three-dimensional (3D) porous metal and metal oxide nanostructures have recently attracted considerable interest because assembly of bulk inorganic materials into 3D nanomaterials possesses extraordinary properties such as low density, high porosity, and high surface area. In this work, we exploited supramolecular self-assembled peptide nanostructures as 3D nanonetwork and sacrificial organic template for the fabrication of 3D Pt@TiO_2 nano-networks. A 3D peptide nanofiber aerogel was conformally coated with TiO_2 via atomic layer deposition (ALD) featuring sub-monolayer thickness precision. The 3D peptide-TiO_2 nano-network was further decorated with highly monodisperse Pt nanoparticles by using ozone-assisted ALD. 3D TiO_2 nanonetwork decorated with Pt nanoparticles shows superior catalytic activity in hydrolysis of ammonia borane generating 3 equivalents of H_2.

Pt particle size and loadings were tuned by altering the number of Pt ALD cycles. The Pt25@TiO_2 with ca. 2.4 nm particle size showed superior catalytic activity in H_2 generation from AB with a TOF value of 311/min at room temperature. Moreover, Pt leaching was fairly low from 3D Pt@TiO_2 nano-networks. Combination of supramolecular peptide nanofiber 3D templates with ALD technique allows facile, straightforward, and highly reproducible preparation of metal, metal oxide, and semiconductor 3D nanomaterials as next-generation nanocatalysts with light weight, highsurface-area and porosity.

8:30am **AA+NS-MoM-3 Cobalt/Alumina Interactions in ALD Synthesized Catalysts for Fischer-Tropsch Synthesis***, **Jacob Clary**, S Van Norman, H Funke, J Falconer, C Musgrave, A Weimer,* University of Colorado - Boulder

Cobalt metal was deposited onto an alumina (Al_2O_3) support using atomic layer deposition (ALD) to create dispersed catalysts for Fischer-Tropsch Synthesis (FTS). These catalysts are highly active for the FTS reaction, exhibiting triple the cobalt mass activity of standard incipient wetness catalysts at similar reaction conditions. HRTEM imaging shows that cobalt has simultaneously deposited during ALD in both crystalline plane and nanoparticle regimes, regardless of the number of ALD cycles. However, it was found that the number of ALD cycles alters the activity of these catalysts, with 4 and 8 cycle catalysts being much more active than the 1 cycle catalyst. The known structure sensitivity of FTS indicates that the crystalline cobalt regions are the active regions for FTS. The ALD process allows deposition of metallic cobalt onto Al_2O_3 with protective organic capping ligands, preventing cobalt oxidation and reconstruction in air prior to reaction. Additional ALD experiments on different phases of Al_2O_3 followed by FTS testing proves the influence of support structure on the cobalt deposition regime and consequently FTS activity. Finally, density functional theory (DFT) calculations were done to understand the metal/support properties responsible for planar vs. nanoparticle growth during ALD and explain the high activity shown by these catalysts.

8:45am **AA+NS-MoM-4 ALD of Platinum on Metal Organic Framework Nodes: Toward Single Site Synthesis and Sinter-Resistant Catalysts***, I Kim,* Argonne National Laboratory, USA*; **Alex Martinson**,* Argonne National Laboratory

The connectivity of NU-1000, a metal-organic framework (MOF), gives rise to Zr6 nodes with hydroxyl-containing functional groups pointing into the large 1D mesoporous hexagonal channels of the framework. These free and exposed –OH groups are ideal grafting sites for atomic layer deposition (ALD). Through ALD in MOFs (AIM), we demonstrate the ability to form monodisperse Pt clusters with atomic precision without significantly changing the overall structure of the framework. An experimentally and computationally informed mechanism for the low temperature surface reaction of MeCpPtMe3 will be presented. The resulting platinum clusters on Zr6 nodes also provide a unique opportunity to test the ability of MOF node "islands" to inhibit Pt atom migration under catalytic conditions. Computational, synchrotron, and in situ and operando analytical methods including FTIR and extended X-ray absorption fine structure (EXAFS) are brought to bear on this uniquely active ethylene hydrogenation catalyst.

9:00am **AA+NS-MoM-5 Particle Atomic Layer Deposition for Stabilization of Pt/C Fuel Cell Catalysts***, **William McNeary**, A Lubers, M Maguire,* University of Colorado - Boulder*; S van Rooij,* Ecole Polytechnique Fédérale de Lausanne, Switzerland*; S Bull, A Weimer,* University of Colorado - Boulder

As a highly efficient, portable, non-greenhouse gas emitting source of electrical power, the proton exchange membrane (PEM) fuel cell holds great potential as a replacement for the internal combustion engine. One of the most significant development challenges in the commercialization of the PEM fuel cell is the long-term durability of the catalyst material. Cathode potential cycling—resulting from the variable voltage loads imposed during vehicular operation—is known to promote agglomeration and growth of the Pt nanoparticle catalyst, which in turn degrades the power output of the fuel cell. In this work, atomic layer deposition (ALD) was used to deposit protective TiO_2 films onto commercial Pt/C catalyst in order to increase its electrochemical durability. Deposition half-reactions during fluidized bed particle ALD were observed via in-situ mass spectrometry, and chemisorption analysis was used to quantify changes in Pt surface area following TiO_2 deposition. Rotating disk electrode analysis indicated that although electrochemical surface area (ECSA) was slightly depressed by the addition of TiO_2 ALD layers, catalyst activity of the coated samples was improved, likely due to beneficial interactions between the metal oxide and Pt. Activity retention during electrochemical durability testing was greatly improved, with TiO_2-coated catalysts retaining upwards of 70% of their initial activity. Examination of catalysts before and after testing also showed that TiO_2 ALD layers were effective at preventing Pt agglomeration under fuel cell operating conditions.

9:15am **AA+NS-MoM-6 ALD CeO_2 to Improve Catalytic Activity and Thermal Stability of Low Temperature SOFC Electrodes***, J Yu, S Oh,* Seoul National University of Science and Technology, Republic of Korea*; W Noh,* Air Liquide Laboratories Korea*; **Jihwan An**,* Seoul National University of Science and Technology, Republic of Korea

Solid oxide fuel cell(SOFC) is an energy conversion device which can convert chemical energy into electrical energy. SOFC is known to have several advantages over other types of energy devices: high efficiency, environmental cleanliness, and so on. SOFCs usually operate at high temperature(800-1000C), which, however, poses practical issues such as thermal degradation and material selection. Low-temperature SOFC(LT-SOFC, operating temperature <500C) is therefore attracting lots of attention from researchers.

Cathodic activation loss is the dominant loss in the operation of LT-SOFCs due to sluggish oxygen reduction reaction(ORR). Also the thermal degradation of metallic cathodes decreases the performance of LT-SOFCs, causing the practical issues in long-term operation. In this paper, we demonstrate that CeO_2 thin films deposited by atomic layer deposition(ALD) can significantly improve the reaction kinetics as well as the thermal stability of the Pt cathode in LT-SOFC. ALD CeO_2 layer can be employed as an interlayer between electrode and electrolyte, or an overlayer on top of electrode. In both ways, ALD CeO_2 helped to improve the oxygen reduction kinetics by up to a factor of 3, and the performance stability at long-term operation(>10hrs, 450C) by approximately one order of magnitude. ALD CeO_2 layer may be also applied to other energy conversion devices for simultaneous enhancement of performance and long-term stability.

9:30am **AA+NS-MoM-7 Atomic Layer Deposition of Metal Oxide Thin Films and Metal Nanoparticles for Improving the Electrode Performance in Photoelectrochemical Applications***, **Valerio Di Palma**, M Verheijen,* Eindhoven University of Technology, Netherlands*; R Sinha, G Zafeiropoulos, A Bieberle, M Tsampas,* DIFFER, Dutch Institute for Fundamental Energy Research*; W Kessels, M Creatore,* Eindhoven University of Technology, Netherlands

Photoelectrochemical water splitting is considered a viable route to store solar energy into hydrogen. However, it presents several technical issues that hinder its development, such as low conversion efficiency and high overpotential, which is required to promote products' evolution. In this contribution we investigate selected ALD layers and their effect on the electrode performance, specifically in terms of current density and electrode stability in aqueous environment. Particularly, we address three case studies:

1) Hematite is known to be a suitable photoanode for photoelectrochemical water splitting. Charge recombination is, however, a limiting factor toward high current densities. ALD ZnO and TiO_2 were adopted as interlayer to prevent charge recombination at the interface between glass/fluorine doped tin oxide (FTO) and hematite. Cyclic voltammetry (CV) was used to compare the samples with and without ALD interlayer. It was shown that a 2 nm thick ZnO interlayer resulted in 25% increase in photocurrent density at 1.5 V_{RHE} along with a 200 mV cathodic shift in the onset potential, with respect to plain hematite thin film. Interestingly, a 1 nm thick TiO_2 interlayer deposited by plasma-assisted ALD showed better electrode performance (67% higher photocurrent at 1.5 V_{RHE}), compared to the thermally grown TiO_2.

2) 3D microstructured $Ti/WO_3/BiVO_4$ photoelectrodes necessitate protective layers to limit the photo-corrosion of $BiVO_4$ under high pH conditions. 2 nm thick thermal ALD TiO_2 was shown to lead to an increase by 25% of the photocurrent density peak in linear sweep voltammetry measurements, when compared to the pristine device.

3) ALD Pt nanoparticles (NPs) serve as electrocatalyst on 3D Ti and TiO_2 substrates. CV measurements show that an increase in the number of ALD cycles from 50 to 100 lead to an increase in electrochemical surface area by a factor of 8. Therefore, ALD prepared Pt NPs result to be highly dispersed and electrochemically active and can be employed in the production of hydrogen or oxygen evolution reaction on cost effective (photo)electrodes.

In conclusion, we showed that ALD is a powerful tool to design and fabricate interlayers, protective layers and metal NPs, with different morphologies (2D and 3D) to improve the photoelectrode performance in photoelectrochemical water splitting.

9:45am **AA+NS-MoM-8 Carbon-templated Nb:TiO_2 Nanostructures as Oxygen Evolution Catalyst Supports for PEM Electrolyzers***, **Alexander Hufnagel**, D Böhm, S Häringer, D Fattakhova-Rohlfing, T Bein,* University of Munich (LMU), Germany

The generation of hydrogen via electrochemical water splitting in proton exchange membrane (PEM) electrolyzers is an appealing means of storing energy from fluctuating renewable generators (e.g. solar and wind). To improve efficiency and to decrease production cost, nanostructured conductive supports for the noble metal oxide oxygen evolution catalyst at the anode are required. Conductive oxides are inherently stable towards oxidation at the high anodic potentials. We used thermal ALD to conformally coat nanostructured carbon (soot) templates with mixed TiO_2/Nb_2O_5 films using alkoxides and water as precursors. The carbon stabilizes the nanostructure during annealing, yielding crystalline materials from which the carbon can be removed without structural collapse. This effectively results in the replication of the carbon nanostructure by the conductive oxide. The conductivity of the oxide material reaches up to 400 S cm^{-1}. This carrier material can be used flexibly as either a pre-formed film for transfer during membrane-electrode assembly (MEA) manufacture or as a powder for ink coating. The carrier was loaded with an OER catalyst developed in our group, consisting of ultrasmall $RuIrO_x$ nanoparticles and the OER performance and stability under operation were investigated.

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10:45am **AA+NS-MoM-12 Atomic Layer Deposition Route to Tailor Nanoalloys of Noble and Non-Noble Metals***, **Ranjith Karuparambil Ramachandran**, J Dendooven, M Filez, V Galvita, H Poelman, E Solano, M Minjauw, K Devloo-Casier,* Ghent University, Belgium*; E Fonda,* Synchrotron SOLEIL, SAMBA Beamline, France*; D Hermida-Merino,* Netherlands Organisation for Scientific Research, DUBBLE@ESRF, France*; W Bras,* Netherlands Organisation for Scientific Research, DUBBLE@ESRF*; G Marin, C Detavernier,* Ghent University, Belgium

Bimetallic nanoparticles (BMNPs) play a pivotal role in optical, magnetic and electronic applications, and are true workhorses during the catalytic transformation of chemicals. In particular, supported Pt nanoparticles alloyed with In, Ga or Sn are highly selective catalysts for the dehydrogenation of propane to propylene. It is well established that the size and composition of the nanoparticles strongly impact the catalytic properties and performance. Yet, conventional synthesis strategies lack proper control over the nanoparticle morphology and composition. ALD has proven its potential for the size and composition controlled synthesis of supported BMNPs, but has to date only been applied for the synthesis of binary noble metal nanoparticles like Pt-Pd, Pt-Ru and Pd-Ru BMNPs. Extension of this approach to BMNPs containing non-noble metals has so far been hampered by unfavorable ALD chemistries to deposit non-noble metals in their elemental state. As a consequence, a strong need has arisen to develop alternative ALD-strategies which can deal with non-noble metals also.

We report a new ALD based procedure for the tailored synthesis of BMNPs containing a non-noble metal next to a noble metal (*ACS Nano*, 2016, **10**, 8770–8777), here exemplified for nanoalloys containing In as non-noble and Pt as noble metal. **Figure 1a** schematically describes the steps involved in the fabrication process of the Pt-In BMNPs. Thin layers of In_2O_3 and Pt are sequentially deposited by ALD, yielding a Pt/In_2O_3 bilayer structure. These bilayers are then subjected to a temperature programmed reduction (TPR) in hydrogen to induce the formation of Pt-In nanoalloys. The BMNP formation during TPR was followed by *in situ* XRD measurements (**Figure 1b**) and was further confirmed by *ex situ* XAS (**Figure 1c)** and SEM measurements. The composition of the formed bimetallic alloys can be tuned by controlling the ratio of the deposited thickness of Pt to the thickness of In_2O_3. **Figure 2a** presents the relation between the as-deposited Pt/(Pt+In) atomic ratio and the alloy phase(s) obtained after TPR. In addition, our method enables tuning of the particle size with high precision in a range from 1 to 30 nm by changing the total thickness of the ALD-grown Pt/In_2O_3 bilayer (**Figure 2b**). Tuning of the particle size while keeping the composition the same can thus be achieved by scaling the layer thicknesses of the Pt and In_2O_3 layers while keeping the Pt/(Pt+In) atomic ratio constant.

Finally, successful BMNP synthesis was achieved on mesoporous silica, resulting in high surface area nanocatalysts which showed promising high activity for propane dehydrogenation (**Figure 3**).

11:00am **AA+NS-MoM-13 Aggregative Growth of Noble-Metal Nanoparticles in Atomic Layer Deposition: Effect of Temperature, Partial Pressure, Exposure Time, Coreactant, and Substrate***, **Fabio Grillo**, H Van Bui, J Moulijn, M Kreutzer, J van Ommen,* Delft University of Technology, Netherlands

Already an established technique for the growth of conformal thin films, atomic layer deposition (ALD) is now emerging as an attractive route for the controlled growth of NPs. Compared to conventional synthesis routes, ALD boasts a number of advantages: atomic-level control over the amount of material being deposited, conformality, scalability to high-surface-area substrates, and its being solvent-free. Yet, bringing the unparalleled precision of ALD of thin films to ALD of NPs is not straightforward. The precision of ALD relies, in fact, on cyclic repetitions of self-saturating surface reactions that lead to the deposition of less than a monolayer per cycle. Hence, if the growth proceeds in a layer-by-layer fashion, as is the case with ALD of thin films, varying the number of cycles translates into tuning the film thickness with atomic-level precision. However, if the as-deposited atoms form into NPs upon deposition, a growth per cycle of less than a monolayer does not necessarily enable atomic-level control over the NP size. This is because the NP morphology (e.g., size, shape and number density) is dictated by atomistic processes other than “ALD reactions” such as surface diffusion and aggregation of atoms and NPs, and atom attachment to and from NPs. Understanding the role of such kinetic processes during the ALD of NPs is therefore crucial to the development of ALD routes for the synthesis of NPs with a well-defined morphology and thus functionality.

Here, we present an atomistic understanding of thermal ALD of Pt and Pd NPs on nanostructured oxides (TiO_2, CeO_2, ZnO, Al_2O_3, SiO_2, V_2O_5) and graphene nanoplatelets. In particular, we study the effect of temperature, number of cycles, coreactant (i.e., O_2 or H_2), and coreactant partial pressure and exposure time on the evolution of the NP size distribution and metal loading. Atomistic modelling of our experiments shows that the NPs grow mostly due to Smoluchowski aggregation, that is, NP diffusion and coalescence, rather than through single atom processes such as precursor chemisorption, single atom diffusion and attachment, and Ostwald ripening. While the metal loading can be precisely controlled over a wide range of temperatures, atomic-level precision over the NP size is retained only at low deposition temperatures (T≤100 °C) when growth by atom attachment/deposition becomes relevant. Furthermore, we show that the coreactant partial pressure and exposure time are far more important parameters for the NP size than the number of cycles. Crucially, high coreactant partial pressures significantly reduce the temperature window at a given exposure time.

11:15am **AA+NS-MoM-14 *In situ* Grazing Incidence Small Angle X-ray Scattering Study of the ALD Growth and Thermal Stability of Pt Nanoparticles***, **Jolien Dendooven**, E Solano, R Ramachandran, M Minjauw,* Ghent University, Belgium*; A Coati,* Synchrotron SOLEIL, France*; D Hermida-Merino,* ESRF, France*; C Detavernier,* Ghent University, Belgium

Supported noble metal nanoparticles (NPs) are widely used in heterogeneous catalysis because of their high resistance against chemical poisoning. ALD can be used to synthesize noble metal NPs on different high surface area supports, and offers sub-monolayer control over the metal loading (atoms per cm^2 of support) [Lu et al., Surf. Sci. Rep. 71, 410, 2016]. However, an improved understanding of how the deposition parameters influence the formation and growth of noble metal NPs is required to fully exploit the tuning potential of ALD. In addition, it is important that the synthesized NPs remain stable at the elevated temperatures typically required to carry out the catalytic reactions. Particle coarsening, leading to a loss of active surface area, is the main cause for a diminishing activity and/or selectivity of NP catalysts.

We developed a synchrotron-compatible high-vacuum setup that enables *in situ* monitoring during ALD growth as well as during thermal treatments [Dendooven et al., Rev. Sci. Instrum. 87, 113905, 2016]. Using this setup, we investigated how the choice of reactant affects the island growth during ALD of Pt with the $MeCpPtMe_3$ precursor at 300 °C. The Pt loading on planar SiO_2 supports was determined by means of X-ray fluorescence (XRF). Grazing incidence small-angle X-ray scattering (GISAXS) provided information on the evolution in Pt cluster shape, size and spacing. Surprisingly, a fundamentally different growth mechanism was found for Pt ALD using N_2 plasma as reactant [Longrie et al., ECS J. Solid State Sci. Technol. 6, Q123, 2012] compared to the more conventional O_2 gas-based ALD process (Figure 1). While surface diffusion of atoms and/or clusters plays an important role during the latter process, a static growth mode is observed for the N_2 plasma-based process. This insight provided the ground for the development of a tuning strategy that is based on combining the O_2-based and N_2 plasma-based ALD processes and offers independent control over NP size and coverage.

Secondly, *in situ* GISAXS was used to investigate the morphological evolution of these supported Pt NPs during annealing under different O_2 partial pressures, providing a nearly continuous set of data on the evolution of average particle size during the annealing (Figure 2). A systematic study revealed that the as-deposited morphology and O_2 concentration largely influence the onset temperature for Pt coarsening: bigger and more widely spaced NPs as well as larger O_2 concentrations entail a higher onset temperature for coarsening. This knowledge is vital towards an improved understanding of the mechanisms that govern Pt NP coarsening.

11:30am **AA+NS-MoM-15 High-Precision Growth of Metal Oxide Nanoparticles on Carbon Composites for Energy Related Applications***, F Yang, **Mato Knez**,* CIC nanoGUNE, Spain

Transition metal oxides show great potential for numerous energy-related applications, including batteries or supercapacitors, due to their excellent catalytic activity or electrochemical properties. Zero-dimensional nanomaterials made of metal oxides, often used as active components in composites for electrode materials, promise great improvement of the performance upon integration into devices. ALD is a thin film deposition technology and therefore commonly used for growing 2D films on various substrates. However, it also offers the possibility to controllably fabricate nanoparticles if the substrate is appropriately chosen and its surface chemistry can be controlled. For example, given the chemical inertness of reduced graphene oxide (rGO) or carbon nanotubes (CNTs), metal oxides (like RuO_2 or Co_3O_4) will grow specifically on defect sites, which can be native or intentionally created. The density of the defect sites and in consequence the nanoparticles after ALD growth can be controlled by initial treatment of the substrate, while the size of the nanoparticles can be controlled with high accuracy by altering the number of applied processing cycles. After the nanoparticle growth, the fabricated rGO/RuO_2 system exhibits improved capacitive performance with great promise for a use in supercapacitors, while the Co_3O_4/CNT system shows excellent oxygen reduction reaction (ORR) activity with exceptional stability/durability upon further stabilization with a thin carbon shell. This presentation will give insight into the fabrication of the composites as well as the characterization of the electrochemical and catalytic performance of the materials.

11:45am **AA+NS-MoM-16 Tuning the Isoelectric Point of Conical Nanochannel Surfaces by Atomic Layer Deposition of Al_2O_3, TiO_2, and SiO_2 to Tailor Selective Ion Transport***, **Nils Ulrich**, A Spende,* GSI Helmholtz Center, Germany*; N Sobel,* TU Darmstadt, Germany*; M Toimil-Molares, C Trautmann,* GSI Helmholtz Center, Germany

Solid state nanopores and in particular ion-track etched channels exhibit unique ion transport properties and functionalities including ion selectivity, ion current rectification, and responsive behavior to external stimuli such as pH-value, temperature or concentration of a specific ion. [1, 2]

The ion conductivity of a nanochannel is described by nanofluidic models exhibiting the surface charge as a determining parameter. [3]

Here, we apply atomic layer deposition of Al_2O_3, TiO_2 and SiO_2 to conformally modify the surface of polymer track-etched membranes, fabricated by swift heavy ion irradiation and chemical etching. [4] The different isoelectric points of these oxides (Al_2O_3 ~pH 9, TiO_2 ~pH 5, SiO_2 ~pH 2 [5]) allow us to tailor the surface charge of the nanochannels. The resulting inorganic and well-defined nanochannels constitute excellent model systems to study ion-transport characteristics.

We will present current-voltage measurements on single conical Al_2O_3, TiO_2 and SiO_2 ALD-coated nanopores exhibiting tip diameters of approx. 100 nm. The dependency of current rectification as a function of surface material and electrolyte pH will be discussed. In all cases, ALD coating improved the stability of the channels exhibiting more reproducible ion conductivity than their uncoated counterparts, and enhanced long term stability.

The ion conductivity data are complemented by a detailed characterization of the channel morphology. For this, a supporting electrode is electrodeposited on the base side of the conical nanopore, the polycarbonate membrane is dissolved in an organic solvent, and the single freestanding cone is imaged by scanning electron microscopy. Complementary measurements on multi-channel membranes reveal a homogeneous deposition of the oxides inside all nanochannels as well as smooth inner and outer surfaces. EDX results prove the absence of contamination in the ALD layers. Moreover, the mechanical stability of the free-standing conical nanotubes reflects the expected behavior.

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[2] Siwy Z.; Gu Y.; Spohr H.A.; Baur D.; Wolf-Reber A.; Spohr R.; Apel P.; Korchev Y.E. *Europhys. Lett. EPL* **2002**, *60* (3), 349-355

[3] Schoch R.; Han J.; Renaud P. *Rev. Mod. Phys.* **2008**, *80* (3), 839-883

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ALD Applications
Room Plaza ABC - Session AA-MoM

Solar Materials I (8:00-10:00 am)/Solar Materials II (10:45 am-12:00 pm)

Moderators: Christian Dussarrat, Air Liquide, Mariadriana Creatore, Eindhoven University of Technology, The Netherlands, Jeffrey Elam, Argonne National Laboratory, Neil Dasgupta, University of Michigan

8:00am **AA-MoM-1 Atomic Layer Deposition Processing for Perovskite Solar Cells: Research Status, Opportunities and Challenges***, **Mariadriana Creatore,*** Eindhoven University of Technology, Netherlands **INVITED**

Organo-metal halide perovskite solar cells have exhibited a sky-rocketing conversion efficiency above 20% in just a few years. In this contribution I will address the opportunities which ALD offers to perovskite solar cells [1] by highlighting its merits of delivering high quality thin metal oxides [2], engineering the charge transport layer/perovskite interfaces [2] and being compatible with low-temperature processing (directly on the perovskite absorber) [3].

Specifically, I will address the following case studies:

- Plasma-assisted ALD TiO_2 (cycles consisting of $Ti(Cp^{Me})(NMe_2)_3$ and O_2 plasma exposure steps) is adopted in $MeNH_3PbI_3$ perovskite solar cells [2], with the purpose of suppressing charge recombination processes at the ITO/perovskite absorber/hole transport layer interface. The superior performance of 10 nm thick ALD TiO_2 layers (up to 16% cell efficiency under $1000/m^2$ illumination and 24% under indoor illumination) with respect to conventionally adopted spray pyrolysis TiO_2 correlates with the lower reverse dark current measured for ALD TiO_2, i.e. its superior blocking character toward charge recombination.

- Plasma-assisted ALD SnO_2 (cycles consisting of $Sn(NMe_2)_4$ and O_2 plasma exposure steps) is adopted as electron transport layer in a n-i-p $Cs_x(MA_yFA_{1-y})_{1-x}Pb(I_z,Br_{1-z})_3$ solar cell. The cell efficiency reaches the value of 15.9±0.5%, while the same solar cell configuration with an electron-beam deposited TiO_2 electron transport layer reaches an efficiency of just 10 ±0.5%.

- Ultra-thin (10-15 ALD cycles) Al_2O_3 is conformally deposited at 100°C by thermal ALD on a $MAPbI_{3-x}Cl_x$ perovskite layer in a n-i-p configuration [3]. The cell exhibits superior device performance with a stabilized PCE of 18%, a significant reduction in hysteresis loss and enhanced long-term stability (beyond 60 days) as a function of the storage time in ambient air, with humidity conditions of 40-70% at room temperature.

This contribution will end by discussing the challenges yet to be met by ALD processing directly on the perovskite absorber [1], in a process window requiring either higher substrate temperature or the application of plasma (as in the case of replacement of organic charge transport layers with ALD metal oxides MoO_x and NiO). In all these cases, a careful interface engineering needs to include several aspects potentially affecting the stability of the active components of the perovskite solar cell.

[1] V. Zardetto et al., Sustainable Energy and Fuels, DOI: 10.1039/c6se00076b (2017)

[2] F. Di Giacomo et al., Nano Energy 30, 460 (2016)

[3] D. Koushik et al., Energy and Environmental Science, 10, 91 (2016)

8:30am **AA-MoM-3 Atomic Layer Deposition of NbC-Al2O3 Nanocomposite Films for Efficient Solar Selective Coatings***, **Jason Avila,*** Argonne National Laboratory*; A Peters,* Northwestern University*; A Mane, J Libera, A Yanguas-Gil,* Argonne National Laboratory*; O Farha, J Hupp,* Northwestern University*; J Elam,* Argonne National Laboratory, USA

Solar selective films hold great promise for improving the efficiency of concentrated solar power (CSP) facilities. In this study, we used atomic layer deposition (ALD) to prepare solar selective films composed of metal-dielectric nanocomposites with tunable optical and electronic properties. We used niobium carbide (NbC) as the metallic component and Al_2O_3 as the dielectric component of the nanocomposite films, and these components were blended at the atomic scale by alternating between the NbC and Al_2O_3 ALD processes. In-situ quadrupole mass spectrometry and quartz crystal microbalance (QCM) measurements were performed to examine the growth of the NbC-AlO composite films as well as to establish the NbC ALD growth mechanism. These measurements revealed that the NbC inhibited the Al_2O_3 ALD, while the Al_2O_3 enhanced the NbC ALD. Next, NbC-AlO nanocomposite films wereprepared over the full range of 0-100% NbC in Al_2O_3 and the physical, optical and electrical properties were measured. We discovered that the band gap and electrical resistivity could be precisely tuned by controlling the composition, and that higher NbC contents yielded a lower band gap and a smaller resistivity. Based on the absorption spectra of the NbC-AlO composite films, we established that 10-20% NbC yield the highest selective absorption efficiencies due their high visible light absorption and low infrared absorption. However, the selective absorption properties of the NbC-AlO composite films were lost upon annealing to 400°C in air as a result of oxidation of the NbC. Our study demonstrates the efficacy for ALD preparing metal-dielectric nanocomposite films with tunable properties to achieve a high selective absorber efficiency. By applying this technique to more thermally robust metallic materials we hope to produce solar selective coatings suitable for deployment in CSP facilities.

8:45am **AA-MoM-4 Refractory Solar Selective Nanocomposite Coatings for Concentrated Solar Power Receivers***, **Jeffrey Elam,** A Mane, J Avila, A Yanguas-Gil, J Libera,* Argonne National Laboratory*; J Hupp, J Liu,* Northwestern University*; U Sampathkumaran, K Yu,* InnoSense LLC*; R Buck, F Sutter,* German Aerospace Center - DLR

We are developing a new strategy for fabricating high-performance selective absorber coatings for concentrated solar power receivers. These coatings are engineered at multiple length scales (Figure 1). In the 0.1-1 µm regime, the coatings have a photonic crystal structure composed of a periodic mesoporous array. This structure alters the photonic density of states to improve spectral selectivity while also mitigating thermal stress for improved lifetime. At the 1-10 nm scale, the coatings are composed of optically absorbing nanoparticles in a transparent matrix where the size, spacing, and composition of the nanoparticles are tailored to tune the optical properties for high visible absorption and low IR emittance - similar to a cermet, but with greater thermal stability. The mesoporous photonic structure is fabricated by self-assembly from a nanoparticle suspension to form a porous matrix. The nanophase composite is created by infiltrating this scaffold using atomic layer deposition (ALD) films composed of metallic and dielectric components. We are evaluating a range of processing methods for the mesoporos scaffold and targeting sturctures guided by finite difference time domain (FDTD) modeling. In addition, we have undertaken a design of experiments (DOE) study of ALD nanocomposite films to establish the effects of composition, metal:dielectric ratio, and thickness on the optical efficiency. These studies have yielded simple design rules to predict the optical properties of the solar selective coatings, allowing us to focus on optimizing the high temperature stability and manufacturability of the materials. We have identified coatings that maintain a high selective solar absorption efficiency of η_{sel} > 0.91 after isothermal treatment and temperature cycling at 650°C with no delamination. This presentation will focus on the growth and optical properties of the ALD nanocomposites.

9:00am **AA-MoM-5 *P*-type Bismuth Sulfide (Bi_2S_3) Grown by Atomic Layer Deposition***, **Neha Mahuli,** D Saha, S Sarkar,* Indian Institute of Technology Bombay, India

Bismuth sulfide (BiS_3) thin films are investigated with a custom built laminar flow atomic layer deposition system. Sequential exposures of bismuth(III)bis(2,2,6,6-tetramethylheptane-3,5-dionate) [$Bi(thd)_3$] and hydrogen sulfide (H_2S) are optimized at 200°C via various *in-situ* and *ex-situ* characterizations. Detailed growth mechanism study with the help of *in-situ* quartz crystal microbalance (QCM) and *ex-situ* X-ray reflectivity (XRR) measurements indicated the film growth governs reasonably longer nucleation periods before entering into linear ALD regime. The saturated growth rate of 0.34-0.37Å per ALD cycle is observed throughout ALD temperature window of 200-250°C.

During this presentation apart from growth mechanism, I will majorly discuss the structural, optical and electrical properties of the as-grown material. Interestingly this material is observed to exhibit presence of direct (1.45 eV) as well as indirect (1.2 eV) band gaps. A relatively high absorption coefficient (> 10^6 cm^{-1}) throughout the visible range makes it a potential photovoltaic absorber.

Contradictory to the conventionally observed, as-grown thin films are found to be highly *p*-type conducting with carrier concentration of ca. 6.8 x 10^{18} cm^{-3} at room temperature. Seebeck measurements and ultraviolet spectroscopy (UPS) also support the *p*-type nature of as-grown films as opposed to *n*-type nature normally found in literature. In the last part of my presentation, I will discuss in detail the MIT transition as studied from temperature dependent electrical resistivity measurement in detail to understand the transport mechanism.

9:15am **AA-MoM-6 Role of Fixed Charge in the Modification of Schottky Barrier Height of Metal Insulator Semiconductor Tunnel Structures***,*

Roderick Marstell*, N Strandwitz,* Lehigh University

Electronic properties of oxide/semiconductor interfaces are important in most semiconductor applications. The effectiveness of an oxide in a given application is dependent on the quality of the electronic properties of the interface, such as fixed charge (N_f), density of interface traps (D_{it}), and Schottky barrier height (ϕ_{bh}). In this study, we investigate the ability of the N_f at the oxide/Si interface to modify ϕ_{bh} of a metal-insulator-semiconductor (MIS) diode. Tunable N_f is available through atomic layer deposited (ALD) Al_2O_3, in which the N_f can be tuned from +1E12 to -5e12 q/cm^2 via post-deposition annealing.[1,2] This tunable N_f has been shown to exist in oxides as thin as 1.5 nm using non-contact techniques (corona charging and second harmonic generation).[3,4] To our knowledge, the ϕ_{bh} of a MIS diode has not been experimentally related to the magnitude of oxide/semiconductor N_f.

According to device physics simulations and analytical calculations[5], the difference in N_f in the as-deposited/annealed states should modify the ϕ_{bh} of a silicon MIS diode by as much as 100 meV. We have confirmed the presence of a negative N_f by analyzing the capacitance-voltage behavior of identical MIS stacks with insulating Al_2O_3 layers (~10 nm). Fixed charge values changed from +1E12 to -3E12 q/cm^2 depending on processing.

We measured the ϕ_{bh} of MIS diodes as a function of oxide thickness from current-voltage-temperature (*IVT*) and Mott-Schottky ($1/C^2$-V) data for oxides in the 1-2 nm range and for intimate metal/Si contact. A large change in ϕ_{bh} between the intimate contact and MIS case was found. The *IVT* data shows a decrease in ϕ_{bh} with increasing oxide thickness for both as-deposited and annealed samples, while $1/C^2$-V data does not display a ϕ_{bh} versus N_f trend. Both *IVT* and $1/C^2$-V trends are inconsistent with the electrostatic models.

Our data does not give evidence that the tunable N_f in Al_2O_3-Si MIS diodes controls ϕ_{bh}. This may indicate that the N_f affects ϕ_{bh} negligibly or not at all. Metal deposition may introduce electronic traps at the metal/oxide interface that alter the oxide/Si interface N_f. Finally, the first few cycles of ALD growth may introduce oxide thickness and/or N_f lateral non-uniformities, thus obfuscating the N_f/ϕ_{bh} relationship. While this work shows an influence of the ALD tunnel oxide layer, evidence of N_f controlling ϕ_{bh} was not found.

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2. G. Dingemans et al, Electrochem. And Solid-State Let. **14,**1H1(2011)

3. G. Dingemans et al, J. Appl. Phys. **110,**093715-1(2011)

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5. R. T. Tung, Appl. Phys. Rev. **1,**1011304(2014)

9:30am **AA-MoM-7 Determination of Energy Barrier Heights between Amorphous Metals and ALD Dielectrics using Internal Photoemission Spectroscopy***,*

Melanie Jenkins*, T Klarr, D Austin, J McGlone,* Oregon State University*; L Wei, N Nguyen,* National Institute of Standards and Technology*; J Wager, J Conley,* Oregon State University

High quality ALD insulators are an enabling technology for thin film metal-insulator-metal (MIM) tunnel diodes.[1] High speed MIM diodes show promise for rectenna based energy harvesting of IR radiation, for IR sensing, and as building blocks for beyond CMOS hot-electron (MIMIM) transistors. Operation of these devices is based ideally on Fowler-Nordheim tunneling, which is exponentially dependent on both the thickness of the insulator and the height of the energy barriers between the metal electrodes and the insulator. Accordingly, smooth bottom electrodes and precise knowledge of metal/insulator barrier heights are critical for predicting, understanding, and optimizing MIM diode device operation. Although insulator thickness can be precisely controlled through ALD, actual barrier heights depend strongly on deposition method as well the exact interface, and typically differ significantly from the simple Schottky-Mott rule. In this work, we use internal photoemission (IPE) spectroscopy to measure and compare the barrier heights between two ultra-smooth amorphous metals (ZrCuAlNi and TaWSi) and several ALD insulators in MIM diode structures. Reports of IPE on MIM structures are relatively uncommon.

MIM diodes consist of either a ZCAN or TaWSi bottom electrode deposited onto 100 nm of SiO_2 on Si. (ZCAN has been shown to function well in MIM diodes,[2] but suffers from thermal instability. TaWSi is a new amorphous metal that has a larger work function than ZCAN and improved thermal stability.) 10-20 nm of Al_2O_3, HfO_2, and ZrO_2 were then deposited via ALD using TMA/H_2O at 300°C, and TEMA-Hf or TEMA-Zr / H_2O at 250°C, respectively. SiO_2 was deposited via PEALD using BDEA-Si/O_2 at 200 °C. Semitransparent (10 nm thick) Al or Au top electrodes were evaporated through a shadow mask.

IPE measurements were performed at both NIST and OSU. Voltage was applied to the bottom electrode and current was measured while photon energy (E_{ph}) was swept from 2 to 5 eV. The measured current was corrected to remove dark current and converted to yield. Voltage dependent spectral thresholds were extracted from plots of the square root of yield vs. E_{ph}. Zero-field barrier heights were obtained from Schottky plots of the spectral thresholds vs. square root of the dielectric field (Fig 1). The TaWSi electrodes show consistently higher barrier heights than the ZCAN electrodes (Fig. 2), indicating promise for application as a thermally stable bottom electrode in MIM tunnel diodes.

Support from NSF Center for Sustainable Materials Chemistry, CHE-1606982.

[1] N. Alimardani et al., J. Appl. Phys. 116, 024508 (2014).

[2] N. Alimardani et al., J. Vac. Sci. Technol., A 30(1), 01A113 (2012).

9:45am **AA-MoM-8 ALD Window and Buffer Layers in Thin Film Solar Cells***,*

A Palmstrom, K Bush, M McGehee, A Hultqvist, T Sone, ***Stacey F. Bent****,* Stanford University

Modern solar cells contain stacks of different semiconducting, insulating and conducting materials with optoelectronic properties that need to be tightly controlled. Atomic layer deposition (ALD) is poised to play a role in generating various component materials for solar cells with a high level of control over composition, structure, and thickness. ALD has already been used to deposit passivation layers, buffer layers, barrier layers, and even in the case of plasmonic solar cells, absorber layers. We will present results on the application of ALD to the buffer layer of Cu(In,Ga)Se_2 (CIGS) cells and to the window layer in hybrid lead halide perovskite solar cells. CIGS thin-film technology provides efficiencies close to those of conventional Si based cells. However, the cells typically contain CdS buffer layers, and alternative, less-toxic buffer layers have not performed as well due to charge recombination at the buffer layer/CIGS interface. We introduce a device design that utilizes a point contact buffer layer, for which fabrication is carried out by a combination of ALD and nanosphere lithography. We demonstrate proof of concept using Al_2O_3 as the passivating material, ZnO as the conductive material, and a silica nanosphere size of ~300 nm in diameter. The resulting point contact CIGS solar cells yield a higher conversion efficiency (6.58 ± 0.58%) than either of the binary buffer layers Al_2O_3 (0%) and ZnO (5.15 ± 0.57%). The improvement over ZnO is attributed to an increased open circuit voltage, which is an indication of a reduced surface recombination. Hybrid lead halide perovskites are promising candidates for low cost, thin film light absorbers; they have a tunable band gap and have demonstrated efficiencies as high as 22.1%. The perovskites are also of interest for wide-bandgap absorbers in tandem photovoltaics. We investigate the use of a bilayer consisting of a semiconductor, tin oxide, and a transparent conducting oxide, zinc tin oxide, deposited on top of perovskite absorbers by ALD as a dual-purpose layer to achieve electron selectivity and sputter protection with high optical transmission. This bilayer is applied to two tandem systems: perovskite-perovskite and perovskite-silicon devices. We demonstrate perovskite-perovskite efficiencies of 17.0% with a monolithic two-terminal tandem and 20.3% with a mechanically-stacked four-terminal cell. We achieve an NREL-certified 23.6% efficiency in a perovskite-silicon monolithic tandem architecture. Furthermore, we show that the perovskite encapsulation, enabled by ALD, results in impressive cell stability by testing for 1000 hrs with less than 10% degradation in performance.

10:45am **AA-MoM-12 Atomic Layer Deposition of Bismuth Vanadate Photoanodes***, **Ashley Bielinski**, J Brancho, B Bartlett, N Dasgupta,* University of Michigan, USA

Artificial Photosynthesis is a promising route for capturing solar energy and storing it in the form chemical bonds to generate useful fuels. For example, solar-driven water splitting to produce H_2 and O_2 is widely viewed as an enabling technology for solar-to-fuel conversion. Many Photoelectrochemical (PEC) cells are limited by low anodic currents, due to tradeoffs between light absorption, carrier separation, and interfacial stability in aqueous electrolytes. A good photoanode must be an n-type semiconductor that absorbs in the visible spectrum and has a valence band that is more positive than the oxygen evolution potential. Bismuth vanadate (BVO) has been demonstrated as one of the most promising visible light absorbing photoanode materials. With a bandgap of 2.4V and favorable band positions, BVO has the potential to achieve high anodic photocurrents. However, BVO suffers from limited electron-hole separation, charge transport, and water oxidation kinetics.

Nanostructured BVO, and particularly core-shell nanowires address these challenges by decoupling the required absorption carrier diffusion lengths.[1] Core-shell heterojunctions can also aid in charge separation and transport. Atomic layer deposition (ALD) is an ideal technique for the conformal coating of complex nanostructures. The development of ALD BVO enables core-shell nanostructured BVO photoanodes with much greater conformal coverage and thickness control than previously demonstrated solution deposition methods.

Herein, we demonstrate ALD of BVO using $Bi(OCMe_2iPr)_3$ as the bismuth source, vanadium(V) oxytriisopropoxide as the vanadium source, and water as the oxidant. This combination of precursors enables full control of the Bi:V ratio, in contrast to the use of bismuth precursors such as $Bi(thd)_3$ and triphenylbismuth, which also suffer from very low growth rates (<0.1 Å/cycle). We demonstrate the deposition of stoichiometric $BiVO_4$ and the annealing of ALD BVO to achieve the photoactive monoclinic phase. X-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and ultraviolet–visible (UV-Vis) spectroscopy are used to study the composition, crystallographic, and optical properties of the ALD BVO. The photoactivity of the ALD BVO for the oxidation reaction was demonstrated on both planar and core-shell nanowire arrays under simulated AM 1.5G illumination, demonstrating the power of ALD to improve light absorption and charge extraction in 3-D nanostructured architectures.

(1) Liu, C.; Dasgupta, N. P.; Yang, P. *Chem. Mater.***2014**, *26* (1), 415–422.

11:00am **AA-MoM-13 High-Efficiency Perovskite Solar Cells with Humidity-Stability beyond 60 Days Achieved via Atomic Layer Deposition***, **Dibyashree Koushik**, Y Kuang,* Eindhoven University of Technology, Netherlands*; V Zardetto,* TNO-Solliance, High Tech Campus, Netherlands*; W Verhees, S Veenstra,* ECN-Solliance, High Tech Campus, Netherlands*; M Verheijen, W Kessels, M Creatore, R Schropp,* Eindhoven University of Technology, Netherlands

Solar cells based on organic-inorganic hybrid perovskites have recently achieved an astounding power conversion efficiency (PCE) of 22.1% placing themselves at the fore-front of many of the current global photovoltaic (PV) technologies. However, in order to scale-up the perovskite PV technology, the issue regarding its device lifetime needs to be addressed, which is one of the major hurdles towards its successful commercialisation. The most conventional and widely used perovskite, the methylammonium lead iodide ($CH_3NH_3PbI_3$) is highly sensitive to oxygen and moisture due to the presence of the weak Pb-I ionic bonds and the volatile CH_3NH_3I component in its lattice structure. Several attempts have been made to address this instability issue, mostly concentrating on the substitution of the organic cations in the perovskite lattice, and on alternatives for the organic charge extraction layers, without laying much emphasis on stabilising the existing, conventional high efficiency $CH_3NH_3PbI_3$/Spiro-OMeTAD based perovskite solar cells (PSCs).

To address the latter issue, we present an atomic layer deposition (ALD) assisted interface engineering approach, which consists of incorporating an ALD Al_2O_3 layer, deposited directly on top of the $CH_3NH_3PbI_{3-\delta}Cl_\delta$ perovskite film.[1-3] This Al_2O_3 layer substantially protects the underlying sensitive perovskite against humidity,[1] and also provides protection from other cell components during their respective depositions on top of the perovskite,[3] thus preventing premature device failure. In addition, it does not preclude the formation of a low-resistance contact to the perovskite layer. The fabricated PSCs exhibit superior device performance with a PCE of 18% (with respect to 15% of the pristine), a significant reduction in the hysteresis loss, and an unprecedented long-term stability (beyond 60 days) as a function of the unencapsulated storage time in ambient air, under humidity conditions ranging from 40% to 70% at room temperature. PCE measurements after 70 days of aging study show that the devices incorporating 10 cycles of ALD Al_2O_3 retain about 60-70% of the initial PCE, while the reference devices drop to about 12% of the initial PCE.[1]

[1] D. Koushik, W. J. H. Verhees, Y. Kuang, S. Veenstra, D. Zhang, M. A. Verheijen, M. Creatore, R. E. I. Schropp, *Energy & Environmental Science* **2017**, *10*, 91.

[2] V. Zardetto, B. L. Williams, A. Perrotta, F. Di Giacomo, M. A. Verheijen, R. Andriessen, W. M. M. Kessels, M. Creatore, *Sustainable Energy & Fuels* **DOI:**10.1039/C6SE00076B

[3] D. Koushik, W. J. H. Verhees, D. Zhang, Y. Kuang, S. Veenstra, M. Creatore, R. E. I. Schropp, *Advanced Materials Interfaces* (**Accepted**).

11:15am **AA-MoM-14 Efficient Surface Passivation of Black Silicon Using Spatial ALD***, I Heikkinen,* Beneq Oy, Finland*; P Repo, V Vähänissi, T Pasanen,* Aalto University, Finland*; V Malinen, **Emma Salmi**,* Beneq Oy, Finland*; H Savin,* Aalto University, Finland

Nanostructured Si surfaces (b-Si) are promising materials in photovoltaic applications, but their large area requires efficient passivation. Remarkable passivation of b-Si has been demonstrated with Al_2O_3 deposited by temporal ALD, and this result has been applied in record-breaking solar cells [1]. Spatial ALD (SALD) aims to increase the deposition rate of conformal coatings and broaden the reach of ALD. SALD is potentially well applicable in the coating of porous structures, as precursors are injected towards the substrate with high concentration, which presumably facilitates the infiltration of reactants to the bottom of the structure [2]. Few studies on coating HAR structures with SALD have been published, but there is growing interest in SALD in *e.g.* the coating of porous battery electrodes [3]. In this study we show that excellent passivation of b-Si can be achieved with SALD.

Both planar and b-Si samples were passivated using a Beneq sheet-to-sheet SALD reactor SCS 1000 with a maximum coating area of 400 mm x 500 mm. 20 nm thick Al_2O_3 layers were deposited on the substrates using TMA and H_2O as precursors at 150°C with line speeds ranging from 1.5 to 9 m/min. Growth per cycle ranged from 1.27 to 1.49 Å/c depending on the line speed, and deposition rates up to 2.9 nm/min were reached. As shown in Figure 1a, efficient passivation of planar substrates was demonstrated with all line speeds, as charge carrier lifetimes τ in the order of 1 ms were reached. Substrates were post-annealed at 370 to 450°C in N_2 and H_2/N_2 atmospheres to study the effect of the annealing conditions to τ. As seen in Figure 1b, the best lifetime for both planar and b-Si samples is obtained by annealing at 370°C in a H_2/N_2 atmosphere.

Similar planar and b-Si wafers were passivated using temporal ALD (Beneq TFS 500) and TMA and H_2O as precursors at 200°C. Previously optimized annealing at 425°C in N_2 atmosphere was chosen for these samples. The highest lifetimes of SALD-coated planar and b-Si wafers were compared with the best results obtained with temporal ALD. Τ as a function of minority carrier density of SALD and temporal ALD passivated wafers are presented in Figure 2. Experiments showed that SALD can provide similar or even better surface passivation in b-Si than temporal ALD. This is a promising indication that conformal coating of HAR structures such as b-Si is feasible and possibly even more efficient with SALD than with temporal ALD. Efficient passivation of b-Si substrates was achieved with an industrially relevant line speed of 1.5 m/min. As high production rates can be reached, passivating b-Si with SALD has great potential in industrial-scale applications.

11:30am **AA-MoM-15 Enhancing Water Oxidation Activity of α-hematite Through Atomic Layer Deposition***, C Du, J Wang,* Huazhong University of Science and Technology, China*; R Chen,* Huazhong University of Science and Technology, China, P.R. China*; Y Wen, **Bin Shan**,* Huazhong University of Science and Technology, China

Photoelectrochemical water splitting holds great potential for solar energy conversion and storage with zero greenhouse gas emission. Among existing semiconductor absorber candidates, hematite (α-Fe_2O_3) stands out with unique combination of ideal band gap (2.0-2.1 eV), non-toxicity, earth abundance and intrinsic N-type behavior. However, its faces sever challenges of low photovotlage and conversion efficiency which greatly limit its practical application at current stage.

Because of its unique self-limiting reaction chemistry, Atomic Layer Deposition (ALD) technique exhibits prominent advantage in fabrication of heterojunctions with controllable film thickness. It plays an important role in enhancing the PEC water splitting performance, especially in the case with high aspect ratio light absorber architectures. In our study, ALD is adopted to enhance the quantum efficiency of nanostructured hematite film through two different strategies, p-n heterojunction and surface modification with co-catalyst. In the first work, p-$LaFeO_3$/n-Fe_2O_3 heterojunction is achieved by depositing La_2O_3 on β-FeOOH nanorod, followed by post thermal treatment at 800 ℃. Due to the well matched band levels of $LaFeO_3$ and α-Fe_2O_3, the onset potential for photocurrent negatively shifted by ~50 mV in the heterojunction photoanode. In the second study, nanostructured hematite film was coated with an ultrathin CoO_x overlayer through Atomic Layer Deposition. The best performing hybrid hematite with 2-3 nm ALD CoO_x overlayer yields a remarkable turn on potential of 0.6 V_{RHE} for water oxidation reaction, with a significant 250 mV enhancement compared bare hematite electrode. Meanwhile, external quantum efficiency (IPCE) obtained on hematite increases 66% at 1.23V_{RHE}. The unique surface amorphous CoO_x /$Co(OH)_2$ prepared by low temperature ALD exhibits good optical transparency and hydrophilic property, which is beneficial to the formation of ideal hematite/electrolyte interface.

11:45am **AA-MoM-16 ALD Stabilization Layers for Quantum Dot Solar Energy Conversion**, ***Theodore Kraus**, B Parkinson,* University of Wyoming

Quantum dot sensitized solar cells (QDSCs) are an emerging area of solar energy conversion research with potential to compete with current Si and thin film solar technologies. Quantum dots (QDs) are intriguing candidates for solar power conversion systems as they have large extinction coefficients and a size dependent tunable band gap allowing for utilization of much of the solar spectrum. Furthermore, upon photoexcitation QDs have shown the ability to inject photoexcited carriers from higher excited states and produce quantum yields for electron flow of greater than 1 via multiple exciton generation (MEG).[1] Despite their useful properties many quantum dot systems are unstable to oxidation under atmospheric conditions and in aqueous electrolytes. These stability issues currently present a challenge for the synthesis and characterization of certain QD systems such as InSb and PbSe QDs that are of particular interest due to their near IR band gaps and potential to exhibit MEG.

In this research metal oxide layers grown using atomic layer deposition (ALD) are investigated as stabilization layers for model QDSC interfaces. Specifically, quantum dot sensitized single crystal metal oxide substrates are prepared and subsequently coated with ALD stabilization layers. Metal oxides are chosen for these stabilization layers as they are typically inert, and have large band gaps that do not block light from reaching the QDs. In addition to these desirable properties, there are numerous of metal oxides that can be deposited using commercially available ALD precursors.[2] In addition to the wide variety of oxide materials that can be prepared using ALD, it is an ideal technique to produce ultrathin, highly conformal stabilization layers in a vacuum environment at lower temperatures compared to chemical vapor deposition. In this work we prepare model QDSC interfaces on well-characterized metal oxide single crystal substrates with thin ALD metal oxide protection layers and test their stability in air and in electrolytes under photoexcitation.

References

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ALD Fundamentals
Room Plaza F - Session AF+AA-MoM

ALD Fundamentals: Plasma ALD (8:00-10:00 am)/Emerging Applications (10:45 am-12:00 pm)

Moderators: Charles Dezelah, EMD Performance Materials, Yves Chabal, University of Texas, Dallas, Virginia Wheeler, U.S. Naval Research Laboratory, Angel Yanguas-Gil, Argonne National Lab

8:00am **AF+AA-MoM-1 ALD - From Ideal to Real**, ***Ola Nilsen,*** University of Oslo, Norway **INVITED**

Atomic layer deposition (ALD) is mostly known as a technique that produces perfect films with atomic resolution on large substrates with complex geometries, even under fluctuating production conditions. This is also true for several processes, but not all...

ALD is a chemical process that relies on available active sites on a substrate, and has proven capable to grow on surfaces one initially would assume to be inert, such as Teflon and gold. The initial stages of such growth deviates from the ideology of a layered growth. How does this affect the evolution in growth?

ALD can produce materials with textures varying from completely amorphous to well crystalline, and their growth dynamics can lead to film evolution that seemingly disobeys the linear growth process most related to ALD. The crystal growth dynamics known from PVD processes does not apply in the ALD regime. What are the factors that determine the evolution in texture?

ALD relies on self-terminating surface reactions to secure robust growth. What happens to the robustness if the bulk of the material is capable of absorbing some of the precursor and act as a reservoir?

ALD is most suited for deposition of binary compounds, and has proven well capable of production of ternary and quaternary compounds. However, control of stoichiometry is not as straight forward as simple combination of several binary processes. What controls the deposited stoichiometry?

These questions, and possibly many more, will be raised during the current contribution.

8:30am **AF+AA-MoM-3 Atomistic View of the ALD of Zinc Oxide**, ***Timo Weckman,*** Aalto University, Finland*; M Shirazi,* Eindhoven University of Technology, Netherlands*; S Elliott,* Tyndall National Institute, University College Cork, Ireland*; K Laasonen,* Aalto University, Finland

The atomic layer deposition of zinc oxide has been under intense research in the past few years. Zinc oxide is a wide band-gap semiconductor with interesting properties that make it suitable for several applications. The most common precursors used in the zinc oxide ALD are diethyl zinc (DEZ) and water.

The surface growth process in terms of surface mechanisms is not entirely clear and many questions remain. While FTIR measurements [1] clearly show that during the DEZ pulse the surface is rapidly saturated with ethyl-groups, a slow deposition of the film is observed after the surface is saturated. This deposition is assumed [1] to occur because of a slow pyrolysis of DEZ on surface.

It has also been shown [2] that during the water pulse the surface ethyl-ligands are not completely removed. Even after prolonged exposures of water, 16% of ethyl-ligands remain on the surface. This is not taken into account in the conventional view of the process.

We have recently published [3] a comprehensive density functional theory study on the different mechanisms on a hydroxylated zinc oxide (100) surface using a slab model. The adsorption and surface reactions of DEZ were explored on an ideal as well as on a stepped ZnO surfaces. We propose that instead of thermal DEZ decomposition, the DEZ undergoes a second ligand-exchange reaction with a surface hydroxyl group that is considerably slower than the initial ligand-exchange reaction. This self-limiting reaction accounts for the FTIR observation of slow ongoing growth even after saturation with ethyl groups.

These studies have been extended to include also reaction mechanisms during the water pulse. We have investigated the adsorption and ligand-exchange reactions of water on the ethyl-saturated surface structured proposed in our previous paper.

These results serve as a basis for an extended kinetic investigation of the ZnO process over multiple ALD cycles using kinetic Monte Carlo (kMC), as previously used in [4]. The Monte Carlo implementation enables a real-time analysis of the atomic scale growth process based purely on mechanistic data from *ab initio* calculations. This combination of atomistic and kinetic modelling enables us to address issues regarding the complete growth process, such as the incomplete ligand elimination during the water pulse and a direct comparison with experiments.

[1] Ferguson J.D., Weimer A.W., George S.M., Journal of Vacuum Science and Technology A (2005) 23.

[2] Mackus A.J.M et al., Journal of Chemical Physics, 2017, 146

[3] Weckman T., Laasonen K., Journal of Physical Chemistry C, 2016, 120, 21460-21471

[4] Shirazi M., Elliott S., Journal of Computational Chemistry, 2014, 25(6), 878-889

8:45am **AF+AA-MoM-4 Selective Deposition of Single Site Vanadium Oxide at Specific Functional Groups of Carbon Supports for Catalytic Applications*, Pascal Düngen,*** *N Pfänder,* Max Planck Institute for Chemical Energy Conversion*; X Huang,* Fritz Haber Institute of the Max Planck Society*; K Böhm,* Max Planck Institute for Chemical Energy Conversion*; S Buller,* Max Planck Institute for Chemical Energy Conversion, Germany*; R Schlögl,* Max Planck Institute for Chemical Energy Conversion

Vanadium oxide single sites on functionalized multi-walled carbon nanotubes (MWCNTs) composite materials are promising catalysts for the oxidative dehydrogenation reaction (ODH) of ethylbenzene to styrene. MWCNTs itself exhibit a significant catalytic activity combined with encouraging stability properties if they contain functional groups on their surface.

Vanadium oxide (VO_x) that is deposited by the reaction of the vanadium (V) oxytriisopropoxide precursor with the functional groups by atomic layer deposition (ALD) increases the catalytic activity as well as the thermal stability of the MWCNTs. The increasing catalytic activity is related to the appearance of single site VO_x, since clustered V_2O_5 exhibits no promoting effect. The enhanced thermal stability is caused by the saturation of the functional groups with covalently bonded VO_x. Furthermore, the immobility of singe site VO_x disable the agglomeration and results therefore also in an increased catalytic stability.

The catalyst requirements needs advanced synthesis techniques like selective ALD. To ensure a sole ALD process fundamental knowledge about the reactivity between the precursor and functional groups is necessary. Furthermore it is essential to investigate the present functional groups of the support material. Modified carbon exhibits different oxygen containing functional groups (lactone, anhydride, ketone, ether, carboxylic, phenol) offering different activity. Characterization of the support materials was performed by spectroscopy (Raman, XPS) combined with thermal decomposition and thus enables the thorough analysis of different functional groups. Moreover the ALD active functional groups were identified experimentally by this approach and could be confirmed by theoretical calculations. Furthermore, ALD saturation curves could be correlated to the consumption of specific active functional groups.

In dependence of the applied pre-treatment methods of the carbon support materials different ratios and densities of distinct active functional groups could be synthesized on the surface. The controlled ALD process could realize a selective deposition and therefore generation of single site VO_x species.

9:00am **AF+AA-MoM-5 Surface Modification of V-VI Semiconductors using Exchange Reactions within Atomic Layer Deposition Half-cycle.*, Christoph Wiegand,*** Leibniz Institute for Solid State and Materials Research Dresden (IFW Dresden), Germany*; R Zierold, R Faust,* Universität Hamburg, Germany*; D Pohl, A Thomas, B Rellinghaus, K Nielsch,* Leibniz Institute for Solid State and Materials Research Dresden (IFW Dresden), Germany

The development of new synthesis techniques has led to nanostructured materials with high purity and crystallinity enabling the discovery of highly conductive topological surface states in 3D topological insulators (TI). Recently, it has been shown, that with adding a thin layer of a certain material onto the surface of a TI, the electrical properties of the topological insulating materials can be drastically modified. Due to its self-limiting nature and conformal coating complex even on high aspect ratio nanostructures, ALD is the method of choice especially for complex structures such as nanowires and nanotubes.

The combination of ALD growth with a quartz crystal microbalance (QCM) enables the *in situ* observation of the precursor interaction with the surface. Since ALD is based on gaseous-solid chemical reaction of surface species with the metalorganic precursor, the deposition might differ significantly depending on the used precursors leading to alternated properties of the interface.

Herein, we show QCM results for interplay of Te- and Se-precursors ($Te(Et_3Si)_2$ and $Se(Et_3Si)_2$) with Sb_2Se_3 and Sb_2Te_3 surfaces focusing on the exchange interactions at the material interfaces. As depicted in Figure 1, we deposit a thin film on the surface of our QCM-crystal and study the evolution of frequency/film thickness when the QCM is exposed to the mentioned precursors. The used precursors $Se(Et_3Si)_2$ and $Te(Et_3Si)_2$ differ in their interaction behavior depending on the used V-VI semiconductor substrate. Within the gathered experiments, we propose an exchange reaction for the utilization of the used precursors.

To corroborate the QCM-studies, scanning-TEM and EDX-analyses of Topological Insulating nanowires (Bi_2Se_3 and Sb_2Te_3) treated with vapor of the two precursors have been conducted. Figure 2 shows the results of the analyses for a Sb_2Te_3 nanowire treated with 50 pulses of $Se(Et_3Si)_2$. The observations on such nanowire-systems support the results of the previously mentioned QCM-studies.

Hence, care has to be taken by coating of structures with ALD with respect to possible exchange reactions. Especially, the synthesis of core-shell nanostructures by ALD based on V-VI semiconductors might be more challenging compared to other substrates-precursors combinations.

9:15am **AF+AA-MoM-6 Interface Dipole of High k -Y_2O_3 on GaAs(001) Attained using Cycle-by-Cycle ALD and Synchrotron Radiation Photoelectron Spectroscopy*, Wan-Sin Chen,*** National Synchrotron Radiation Research Center, Republic of China*; K Lin, L Young,* National Taiwan University, Republic of China*; Y Cheng,* National Chia-Yi University, Republic of China*; Y Lin, H Wan,* National Taiwan University, Republic of China*; C Yang,* National Tsing Hua University, Republic of China*; C Cheng,* National Chia-Yi University, Republic of China*; T Pi,* National Synchrotron Radiation Research Center, Republic of China*; R Kwo,* National Tsing Hua University, Republic of China*; M Hong,* National Taiwan University, Republic of China

Deposition of high-k dielectrics via atomic layer deposition (ALD) onto semiconductors becomes a norm to prepare a metal-oxide-semiconductor field-effect transistor (MOSFET). One key issue in determining the device performance of a MOSFET is the strength of the interface dipole at the O/S interface. The conventional method to tackle the issue of the interface diploe is using electrical current (I) - voltage (V) measurements, from which the interfacial dipole was calculated by processing the obtained I-V curve using a fit to a theoretical model with a few parameters under assumptions. The approach essentially deals with the bulk properties of the oxide and semiconductor. It becomes rather complicated to access to the “real” interface dipole. Because the interface dipole is an energy-parameterized function, the dipole strength can be directly determined without a presumption by utilizing the photoelectron spectroscopy (PES). Synchrotron radiation PES plays a key role here because it is able to deliver all the energy levels needed to determine the strength of the interface dipole. In this Conference, we will demonstrate the development of the ALD Y_2O_3 on a p-type GaAs(001)-4x6 with different cycles of deposition. The pristine p-GaAs(001)-4x6 surface was grown by molecular beam epitaxy (MBE) in a multi-UHV chamber system.[1] The as-grown sample was then transferred to the ALD oxide reactor for further Y_2O_3 deposition.[2] After each deposition, the sample was moved to National Synchrotron Radiation Research Center (NSRRC) with a UHV portable chamber for SRPES measurements. The photon energy was set at 120 eV to maximize the surface sensitivity. The interface dipole potential has been directly measured by the change of ionization potential (IP) relative to the IP value of the clean p-GaAs(001)-4x6. The change could result in with direction pointing outwardly from the surface (a positive dipole) and inwardly to the surface (a negative dipole). The formula of determining the ionization potential, IP = hn – W, where the width (W) is the energy separation between valence-band maximum (VBM) and the onset of the energy cut-off. We found that the surface dipole of the Y_2O_3/GaAs system is positive in the first few ALD cycles. The dipole strength becomes even greater with further cycles of Y_2O_3 until reaching to the polarization property of Y_2O_3.

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9:30am **AF+AA-MoM-7 Surface Reactions during Three-step ALD of SiC_xN_y using Si_2Cl_6, CH_3NH_2, and N_2 Plasma*, Rafaiel Ovanesyan,*** *N Leick,* Colorado School of Mines*; K Kelchner,* Lam Research Corporation*; D Hausmann,* Lam Research*; S Agarwal,* Colorado School of Mines

High aspect ratio nanostructures in 3D semiconductor devices have necessitated the use of atomic layer deposition (ALD) for the growth of highly-conformal ultra-thin films. In particular, low-temperature (<400 °C) ALD of C containing silicon nitride (SiC_xN_y) is needed for applications such as sidewall spacers and trench liners. Herein, we report on the plasma-enhanced ALD of SiC_xN_y via a novel three-step process using sequential exposures of Si_2Cl_6, CH_3NH_2, and N_2 plasma. The film composition, reactive surface sites, and adsorbed surface species were determined using *in situ* attenuated total reflection Fourier transform infrared spectroscopy, which allowed us to elucidate the C incorporation mechanism. *In situ* four wavelength ellipsometry was used to obtain the growth per cycle (GPC) and the refractive index of the SiC_xN_y films.

Our infrared spectra show that the three-step ALD process deposits a SiC_xN_y film (see Fig. 1) with C and H incorporated primarily as Si-N=C=N-Si and –NH species, respectively. Infrared spectra were also recorded after each step in this three-step ALD process. In the first step, at a substrate temperature of 400 °C, the infrared spectra (see Fig. 2) show that on a post N_2-plasma treated surface, Si_2Cl_6 reacts primarily with $–NH_2$ surface species to form –NH surface species, and most likely $–Si_xCl_{(2x+1)}$ (x = 1, 2) species. In the subsequent cycle, CH_3NH_2 reacts with the $–Si_xCl_{(2x+1)}$ terminated surface to form $Si_2N\text{-}CH_3$ surface species. This surface termination resembles the one that is obtained using aminosilanes as the Si precursor in N_2-plasma-assisted SiN_x ALD. In the N_2 plasma cycle, the N_2 plasma removes the $–CH_3$ surface species, and N=C=N- species are incorporated into the film through the redeposition of C and N species liberated from the surface into the plasma. The N_2 plasma restores the $–NH_x$ (x = 1, 2) surface species allowing for the continuation of the ALD process. The spectra for the Si_2Cl_6 and CH_3NH_2 cycles contain prominent features at ~2110 and 2210 cm^{-1} that we attribute to the conversion of surface carbodiimides (-N=C=NH) to cyanamides (-NH-C≡N). The incorporated C and H species are similar to those observed in SiC_xN_y films deposited using Si_2Cl_6 and CH_3NH_2 plasma ALD. *In situ* ellipsometry shows that the SiC_xN_y ALD process has a GPC of 0.1 ± 0.01 nm, which is higher than other aminosilane ALD processes, and a refractive index of ~1.9. Thus, the primary advantage of the three-step ALD process is that it can provide the positive attributes of the chlorosilane/CH_3NH_2 plasma process; high GPC and high conformality, while maintaining the low wet-etch rates characteristic of aminosilane/N_2 plasma ALD processes.

Figure 1: Infrared spectra of a SiC_xN_y film deposited using 100 Si_2Cl_6, CH_3NH_2, and N_2 plasma ALD cycles at 400 °C.

Figure 2: Infrared absorbance change during the Si_2Cl_6 and CH_3NH_2, and N_2 plasma half-cycles at 400 °C.

9:45am **AF+AA-MoM-8 A Comparative Study on PEALD Grown Nanolaminates on polypropylene: Influence of precursor and plasma variation*, Maximilian Gebhard*,** *F Mitschker, P Awakowicz, A Devi,* Ruhr-University Bochum, Germany

During the last years, the advantages of atomic layer deposition (ALD) grown thin films, like high density and excellent conformity, have attracted a lot of interest from the packaging industry: Degradable goods like food, beverages, pharmaceuticals and advanced electronic devices (OLEDs) show an increased demand for improved protection with respect to harmful gases and vapors like oxygen and water. In this context, inorganic materials like Al_2O_3, SiO_2 and TiO_2 are promising candidates as gas barrier layers (GBLs) and they exhibit superior barrier performance even for extremely thin layers.

Coating of plastic materials, like polypropylene (PP) and polyethylene-terephthalate (PET), without substrate damage is often complicated, as the low melting points of the coated material makes the ALD process development a challenging task. Here, the benefits of low-pressure plasma-enhanced ALD (PEALD) are essential: with an average process temperature close to room-temperature and the generation of highly reactive plasma species, the deposition of strongly cross-linked materials at low temperatures is possible without substrate damage. In addition, processes can be operated faster while conformity of the grown film is ensured as well. Furthermore, a broader variety of precursors can be applied. However, the film growth on plastics differs from that on inorganic substrates (*e.g.* silicon) as different surface termination with respect to chemical species and reactive surfaces sites are present. In addition, plasma species, especially atomic oxygen, are known to etch polymers. While this kind of surface conditioning depends on the applied plasma and is in some cases an occurring but not desired process, surface pre-treatment can be achieved on purpose as well, for example using water plasma. Such kind of pre-treatment of the plastic substrate can affect the nucleation and growth of the subsequently deposited thin film.

Here we discuss the results from a comparative study, investigating the growth of nanolaminates, consisting of alumina and silicon oxide, on PP deposited by means of PEALD. The film growth was monitored using *in-situ* quartz-crystal microbalance (QCM) and we present a first approach to separate the growth and etching contribution during the initial cycles. Furthermore, the mechanical properties of nanolaminates are discussed in terms of adhesion and film stress as well as the influence of water plasma on the oxygen transmission rates (OTR) performance.

10:45am **AF+AA-MoM-12 A Dual Action Optical Sensor Using Metal and Dielectric ALD Layers*, Sean Barry,*** Carleton University, Canada

Tilted fibre Bragg gratings (TFBGs) are a class of optical fibre based sensor that are presently employed for temperature and pressure detection in transportation, building, and other infrastructure applications. The working principle of these sensors is that a Bragg grating in the core both diffracts light modes to the surface of the fibre, and breaks their symmetry. This produces very surface-sensitive modes that can interact with atmosphere surrounding the fibre.

Our recent discovery of a gold metal ALD process has permitted the coating of a TFBG with gold: this allows a surface plasmon resonance (SPR) to exist in the gold, and can sense the surface in two important ways: firstly, the shift from a localised plasmon in gold nanoparticles to a continuous plasmon in a "closed" metal film allows the detection of the thinnest conductive layer of gold. Gold metal grown from (Me_3P) $Me_3Au(III)$ has a growth rate of 0.50 Å/cycle with oxygen plasma and water. The fibre sensor showed that a continuous plasmon formed at 84 cycles, suggesting that the thinnest optically conductive film of gold metal formed at 4.2 nm (which is demonstrably better than a sputtered film, which showed this shift at 6.5 nm).

This ALD gold coated fibre also showed significant sensitivity to the surrounding refractive index (SRI). The SPR can reach several nanometers into the space surrounding the fibre, and the SRI can invoke a shift in the wavelength of the cladding mode. With an ALD grown stack of 50 nm $Al_{-2-}O_{-3}$/50 nm Au^0, the SPR was 150% more sensitive to an external refractive index, and the nature of the surroundings could be interrogated through changing the polarization of the affected modes.

This contribution will discuss the two aspects of sensing that a TFBG can provide, and show the effect of alumina, gold, and an alumina/gold stack on the extent and sensitivity of the SPR.

11:00am **AF+AA-MoM-13 Disentangling Photochromism and Electrochromism by Blocking Hole Transfer at the Electrolyte Interface*, Omid Zandi,*** *Y Wang, J Kim,* University of Texas at Austin*; Z Gao,* Washington University, St. Louis*; S Heo,* University of Texas at Austin*; P Banerjee,* Washington University, St. Louis*; D Milliron,* University of Texas at Austin

Tungsten oxide (WO_3), the most ubiquitous inorganic electrochromic material, has found great applications in switchable smart windows that can significantly reduce energy consumption in buildings. However, the undesirable photochromism of WO_3, which can be activated by natural ultraviolet irradiation, often leads to uncontrolled coloration and serious material degradation via a proton-coupled electron transfer process at the electrode/electrolyte interface. Herein, we report a novel strategy to largely suppress photochromism by depositing a uniform ultra-thin conformal layer of amorphous Ta_2O_5 on a mesoporous WO_3 nanocrystal film via atomic layer deposition (ALD). The substantial valence band offset between WO_3 and Ta_2O_5 effectively blocks hole transfer from WO_3 valence band to the electrolyte, and thus greatly reduces UV-induced darkening without significantly compromising the rapid electrochromic switching kinetics. These results clearly demonstrate that rational design of the band alignment combined with precise nanoscale material engineering, can substantially improve performance of electrochemical systems, just as in solid state electronic devices.

11:15am **AF+AA-MoM-14 Atomic Layer Deposition of Electro-optically Active Ferroelectric Barium Titanate Films*, Edward Lin,*** *E Ortmann,* The University of Texas at Austin*; S Abel,* IBM Research-Zurich*; A Posadas,* The University of Texas at Austin*; J Fompeyrine,* IBM Research-Zurich*; A Demkov, J Ekerdt,* The University of Texas at Austin

The extremely large effective Pockels coefficient makes thin-film barium titanate (BTO) a highly promising candidate for on-chip electro-optical applications integrated on Si(001) [1]. Atomic layer deposition (ALD) allows for scalable growth of epitaxial perovskites on Si(001). In particular, both *a*- and *c*-axis out-of-plane oriented epitaxial BTO films grown on strontium titanate-buffered (STO-buffered) Si(001) were demonstrated using ALD. However, no direct observations of ferroelectricity have yet been reported on ALD-grown BTO films. Herein we report on the growth of electro-optically active BTO films *via* ALD. Epitaxial BTO films were grown on STO-buffered Si(001) at 225 °C, with the epitaxy verified by reflection high-energy electron diffraction and x-ray diffraction. Films up to approximately 10-nm thick were oriented *c*-axis out-of-plane as grown and after annealing up to 650 °C with a temperature change rate of no greater than 10 °C/min. Films became orientated *a*-axis out-of-plane when employing a faster heating/cooling rate. Films greater than 10-nm thick were *a*-axis out-of-plane orientated for all vacuum annealing conditions explored. Electro-optical measurements of BTO/STO/Si heterostructures showed ALD-grown BTO films as thin as 40 nm can exhibit an electro-optical response. The measurements also confirmed an observable remanence and therefore ferroelectricity of the BTO film. The results suggest the feasibility of fabricating BTO-based photonics devices that are monolithically integrated on silicon *via* ALD.

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11:30am **AF+AA-MoM-15 Laser Spike Annealing of ALD VO_2**, ***Alexander Kozen,*** U.S. Naval Research Laboratory*; R Bell,* Cornell University*; B Downey,* U.S. Naval Research Laboratory, usa*; M Currie,* U.S. Naval Research Laboratory*; M Thompson,* Cornell University*; V Wheeler, C Eddy, Jr.,* U.S. Naval Research Laboratory

VO_2 is an interesting thermochromic smart material notable for its first order phase transition at a critical temperature (Tc) of 68˚C. This phase transition is accompanied by major changes in both electrical and optical properties, particularly in the infrared. Due to these properties, and the T_C range, VO_2 has many important applications including variable emissivity sensors, bolometers, and active circuit elements.

Atomic layer deposition (ALD) can deposit thin, conformal VO_2 films at 150˚C uniformly over large areas. However, as-deposited films are amorphous and exhibit poor thermochromic modulation behavior. A high temperature (>500˚C), long (≥1 hr) post deposition anneal is typically required to crystallize the VO_2 into the desired monoclinic phase. This anneal precludes the use of many temperature-sensitive substrates.

Laser spike annealing (LSA) is a transient anneal technique using a high power continuous wave (CW) laser rastered over substrates on short (ms or µs) timescales. Compared to conventional anneals, LSA has the advantage of enabling crystallization of ALD films in short times without exposing substrates to damaging time/temperature regimes. We demonstrate the use of LSA on ~40 nm ALD VO_2 films, transforming them into the desired phase with no prolonged high temperature processing.

Appropriate processing windows for LSA of ALD VO_2 on Si and sapphire substrates were determined. LSA films were compared with conventionally annealed films to identify morphological and structural differences, and determine resulting temperature dependent optical and electrical properties.

We identify a clear relationship between the LSA peak temperature/dwell and the resulting film morphology. High temperatures result in substrate damage and VO_2 ablation, while lower temperatures are not adequate to anneal the VO_2. Similarly, long dwell times result in VO_2 ablation while short dwell times exhibit greater uniformity.

We successfully area annealed ALD VO_2 on c-plane sapphire substrates at temperatures near 550˚C, well below the expected melting temperature of VO_2. The annealing window is limited by competition between formation of VO_2 and V_2O_5 phases. Films exhibit an unusual propeller-like morphology that suggests explosive crystallization.

11:45am **AF+AA-MoM-16 Improving Processability of Poorly Flowing Pharmaceutical Powders by Atomic Layer Deposition**, ***Tommi Kääriäinen,*** University of Helsinki, Finland*; J Nyman,* Åbo Akademi University, Finland*; M Kääriäinen, P Hoppu,* NovaldMedical Ltd Oy, Finland*; N Sandler,* Åbo Akademi University, Finland*; S George,* University of Colorado*; M Ritala, M Leskelä,* University of Helsinki, Finland

Product and process design of oral drug dosage forms, such as tablets, capsules, pellets, granules and inhalation powders, strongly depend on flowability of pharmaceutical powders. Flowability is critically important to determine uniform powder feed into unit processing steps, such as tableting or capsule-filling equipment. Proper flow allows uniform particle packing and a constant volume-to-mass ratio in the final drug product. Proper flow is especially important in mixing and formulation of high potent and low dosage drugs, where the content of active pharmaceutical ingredient is measured in micrograms.

Factors affecting powder flowability are interparticle attractive forces, gravitational forces, as well as design and operating conditions of manufacturing process. Interparticle forces originate from electrostatic interactions and molecular interactions between single particles. For powders to be able to flow, gravitational forces need to dominate over interparticulate attractive forces. Atomic Layer Deposition (ALD) has shown to be a promising coating method to modify surface characteristics of solid pharmaceutical powders and improve flowability.

In this work, we present results of sub-nanometer scale TiO_2 and ZnO ALD layers on poorly flowing acetaminophen drug powder. The depositions were performed on acetaminophen particles at temperatures around 100ºC by using $TiCl_4$ – water for TiO_2 ALD, and DEZ – water for ZnO ALD. Deposition was accomplished using static reactant exposures in a rotary particle ALD reactor. The powder flow properties were determined using a direct flow rate meter measuring a powder mass flowing through a hopper.

Pharmaceutical manufacturing can benefit from conformal ALD coatings. Three ALD cycles of TiO_2 and ZnO ALD coatings on acetaminophen powder have already been found to increase the average flow rate tenfold compared to uncoated powder. Five ALD cycles resulted in slightly higher flow rate. However, the flow rate did not increase further with increasing number of ALD cycles. The flow rate of ZnO coated acetaminophen powder was more than double to flow rate of TiO_2 coated powder. This difference is attributed to the electrical and hydroscopic properties of these two ALD materials.

Surface modification of pharmaceutical powders with sub-nanometer thick ALD films improves flowability. These results illustrate a promising new industrial application area for ALD in pharmaceutical manufacturing. The latest developments in particle ALD focusing on continuous spatial processing of particles will allow high volume industrial powder processing.

Atomic Layer Etching
Room Plaza D - Session ALE-MoM

Atomic Layer Etching Session III (8:00-10:00 am) and Session IV (10:45 am-12:00 pm)

Moderators: Fred Roozeboom, TNO-Holst Centre & Eindhoven University of Technology, The Netherlands, Sumit Agarwal, Colorado School of Mines

8:00am **ALE-MoM-1 Selectivity in Thermal Atomic Layer Etching**, ***Younghee Lee****, S George,* University of Colorado **INVITED**

Selectivity in etching is required to remove one material in the presence of other different materials. Selectivity in atomic layer etching (ALE) is important for advanced semiconductor fabrication. Selective ALE, together with selective atomic layer deposition (ALD), could lead to the maskless fabrication of device structures. This talk will examine the selectivity of thermal ALE by exploring the etching of a number of important semiconductor materials including Al_2O_3, HfO_2, ZrO_2, SiO_2, Si_3N_4, and TiN. The thermal ALE will be conducted using various sequential, self-limiting reactions.

The first part of the talk will examine selective thermal ALE based on fluorination and ligand-exchange reactions.[1] Fluorination is achieved using HF as the fluorine reactant. Different metal precursors provide various ligands that may transfer during ligand-exchange. Etching occurs when the transferred ligands produce stable and volatile metal products that may leave the surface. The metal precursors are tin(II) acetylacetonate ($Sn(acac)_2$), trimethylaluminum (TMA), dimethylaluminum chloride, and $SiCl_4$.[2] These metal precursors provide acac, methyl, and chloride ligands for ligand exchange. Spectroscopic ellipsometry was used to measure the etch rates.

The spectroscopic ellipsometry measurements revealed that HfO_2 was etched by all of the metal precursors. Al_2O_3 was etched by all of the metal precursors except $SiCl_4$. ZrO_2 was etched by all of the metal precursors except TMA. In contrast, SiO_2, Si_3N_4, and TiN were not etched by any of these metal precursors. These results can be explained by the stability and volatility of the possible etch products. Temperature can also be used to obtain selective thermal ALE. The combination of different metal precursors with various ligands and different temperatures can provide multiple pathways for selective thermal ALE.

The second part of this talk will present results for the thermal ALE of TiN using a new etching mechanism. Spectroscopic ellipsometry and x-ray reflectivity analysis showed that the TiN films were etched linearly versus the number of ALE cycles. In contrast, this new method was highly selective and did not etch Al_2O_3, HfO_2, ZrO_2, SiO_2, and Si_3N_4. The etch rates for TiN ALE increased with temperature from 0.06 Å/cycle at 150 °C to 0.20 Å/cycle at 250 °C and stayed nearly constant for temperatures ≥250 °C. The thermal ALE of many other materials should be possible using this new etching mechanism.

[1] Younghee Lee and Steven M. George, *ACS Nano* **2015**, 9, 2061.

[2] Younghee Lee, Craig Huffman, and Steven M. George, *Chemistry of Materials* **2016**, 28, 7657.

8:30am **ALE-MoM-3 Modeling the Chemical Mechanism of Thermal ALE of Alumina by HF and Tin Acetylacetonate*, Simon Elliott,*** Tyndall National Institute, University College Cork, Ireland

Lee and George have established a new platform for the conformal removal of oxide materials with atomic-level control, termed 'thermal atomic layer etch' (ALE) [1]. By-products, intermediates and limiting factors have been deduced from in situ infrared spectoscopy and quartz crystal microbalance measurements [2]. In this study, we use density functional theory (DFT) to further investigate the mechanism of thermal ALE. We focus on the etching of Al_2O_3 by HF and $Sn(acac)_2$ [acac=acetylacetonate], and also consider the viability of alternative reagents and substrates.

By simulating the interaction of HF with an alumina surface, we confirm that H2O is the by-product and that this apparently self-limiting reaction fixes the maximum etch rate that can be achieved. We find that other halides HCl, HBr and HI are also reactive in this part of the ALE cycle.

Further calculations reveal that the ligand-exchange reactions of the Sn $(acac)_2$ co-reagent with a fluorinated surface require thermal activation. A range of by-products are possible. However, brominated and iodated surfaces are inert towards this co-reagent.

The study is extended to screening other substrates by computing the thermodynamics of the overall etch reaction. The computed data show that etching of HfO_2 and ZrO_2 with $HF+Sn(acac)_2$ is more favourable than etching Al_2O_3. The fact that the experimental ALE rate of HfO_2 and ZrO_2 is lower than that of Al_2O_3 [3] emphasises the need to consider not just thermodynamics, but also how kinetics affects residual coverages and hence etch rates during the ALE cycle.

[1] Y. Lee, J. W. DuMont & S. M. George, ECS J. Solid State Sci. Techn. 4,

N5013 (2015); S. M. George & Y. Lee, ACS Nano 10, 4889 (2016).

[2] Y. Lee, J. W. DuMont & S. M. George, Chem. Mater. 27, 3648 (2015).

[3] Y. Lee, C. Huffman & S. M. George, Chem. Mater. 28 7657 (2016).

8:45am **ALE-MoM-4 Integrating Atomic Layer Deposition and Etching to Achieve Selective Growth*, Stacey F. Bent,*** Stanford University **INVITED**

A variety of steps in electronic device fabrication may benefit from selective processing, including those in both the front end and back end of line. Area selective atomic layer deposition (ALD), an approach in which deposition occurs on specific regions of a substrate (active) while other regions (passive) remain free of deposition, has received much attention over the past decade. However, area selective ALD processes typically break down after more than a few nanometers of material is deposited, degrading the selectivity between active and passive regions of the substrate. We have found that combining area selective ALD with chemically-selective etching can significantly enhance selective processing. We introduce a process in which self-assembled monolayers (SAMs) are used to create passive regions of a surface, allowing ALD to preferentially deposit on the remaining active areas. Imperfect selectivity results, however, because the ALD process begins to nucleate on the regions of the surface covered with the SAM. Selectivity is regained when the area selective ALD is combined with selective removal of any residual dielectric film with a mild etchant. Selective growth of more than 60 nm of metal oxide dielectric material has been achieved using this combined deposition/etching process. Strategies to expand this process to cycle between deposition and etching, and to eliminate the SAM, will be discussed.

9:15am **ALE-MoM-6 ALE and ALC: Computational Assessment of Opportunities and Challenges in Nanoelectronic Applications*, Sumeet C. Pandey,*** Micron **INVITED**

Realization of atomic-scale control during processing can catalyze incorporation of ultra-thin materials (low-dimensional) with device functionality on complex three-dimensional topographies. Atomic layer etching and cleans have been cited as potential processes that can help enable a sustainable semiconductor technology roadmap, however, there is a clear need to identify paths to achieving applications in high-density semiconductor manufacturing. We will leverage the literature data and learning from ALD community to evaluate thermal ALE regime against various options for precursor chemistry, process parameters, and feature aspect ratios. The talk will discuss findings relevant to nanoelectronic applications with emphasis on the surface reactions and its control through process conditions and chemistry using first-principles-based multiscale modeling.

9:45am **ALE-MoM-8 Reactor Scale Uniformity Enabled by Atomic Layer Etching*, Chad Huard,*** *S Lanham, M Kushner,* University of Michigan

One of the possible benefits of atomic layer etching (ALE) is improved uniformity at the wafer scale when compared to continuous etching processes. The ability to produce uniform etch rates in spite of non-uniform reactant fluxes stems from the self-limited nature of the reactions used for ALE. Similar to atomic layer deposition (ALD), utilizing self-limited reactions enables step times to be extended until surface coverage is complete and uniform for each of the ALE sub-cycles. Wafer scale non-uniformities in the incoming fluxes therefore should not, in principle, translate into non-uniformities in etch rates. While ideally self-limited reactions in ALE are expected to produce perfectly uniform etch profiles across the wafer, it is not clear what effect the presence of non-self-limited reactions – which are inevitable in conventional plasma equipment – will have on the wafer scale uniformity.

ALE using non-uniform and non-ideal fluxes was computationally investigated using the 3-dimensional Monte-Carlo Feature Profile Model (MCFPM). The etching of silicon trenches was used as an example case. The ALE of silicon was accomplished using a Cl_2 plasma to passivate the surface, and an Ar plasma (with a small RF bias) to remove the passivated layer, while continuous etching was simulated using an Ar/Cl_2 mixture with similar ion energies. The Hybrid Plasma Equipment Model was used to simulate fluxes, energy and angular distributions as a function of radial position on the wafer in an inductively coupled plasma (ICP) reactor. By changing the position of the ICP antenna, the uniformity of reactant fluxes to the wafer was varied.

The simulated etch profiles indicate that changes in the ion flux to the wafer produce a nearly linear change in etch rate for the continuous etching cases, while when operating in ALE mode, there was a much smaller dependence of etch rate on the incoming ion flux. The ability of the ALE process to tolerate non-uniform fluxes is not only dependent on the lack of continuous etching mechanisms (high ALE synergy), but it requires that the system is operated in a regime where a large proportion of the incoming reactant fluxes are rejected by the saturated surfaces. For sub-saturated conditions, the ALE etch rate is also linearly dependent on ion flux, despite having little or no continuous etching.

Work supported by LAM Research Corp., the DOE Office of Fusion Energy Science and the National Science Foundation.

10:45am **ALE-MoM-12 Thermal Atomic Layer Etching of Cobalt Metal Films*, Charles H. Winter,*** *W Waduge,* Wayne State University **INVITED**

Atomic layer deposition (ALD) produces films with sub-nanometer thickness control and perfect conformality because of the inherent self-limited growth mechanism.[1] The opposite of ALD is atomic layer etching (ALE), where films are etched with a layer-by-layer, self-limited mechanism.[2] To date, ALE has been mostly focused on plasma-based processes.[2] However, plasma ALE requires expensive equipment and the energetic plasma ions can damage substrates, films, and equipment. Accordingly, there is an urgent need to develop thermal ALE processes, which use carefully designed, exothermic chemical reactions to achieve etching. The first thermal ALE processes were only reported in 2015 for Al_2O_3,[3] AlF_3,[4] and HfO_2[5] films. Cobalt metal films are widely used to encapsulate copper in microelectronics devices to stop the electromigration of copper.[6] The thermal ALE of cobalt metal would be valuable for the manipulation of cobalt liners and caps, however, the thermal ALE of cobalt metal films has not been reported. Herein, we will describe a thermal ALE process for cobalt metal, which entails treatment of 50 to 100-nm thick cobalt metal films with formic acid, followed by the organic ligand $Me_2NNHC(O)tBu$ (L^1H). The etch rate is about 0.08-0.10 Å /cycle at 180 ° C. Presumably, the formic acid pulses oxidize the surface cobalt atoms to cobalt(II) formate, and then the L^1H pulse reacts with the cobalt(II) formate to afford $Co(L^1)_2$. We recently reported the synthesis and structure of $Co(L^1)_2$, and found that it sublimes at 75 °C/0.05 Torr and undergoes solid state thermal decomposition at 245 °C.[7] Accordingly, $Co(L^1)_2$ should be evolved as a volatile species under the ALE conditions. Additional details of the ALE process will be presented.

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11:15am **ALE-MoM-14 WO_3 and W Thermal Atomic Layer Etching Using "Conversion-Fluorination" and "Oxidation-Conversion-Fluorination" Etching Mechanisms***, **Nicholas Johnson**, S George,* University of Colorado

Atomic layer etching (ALE) of metals is important for the controlled removal of many valuable semiconductor materials such as conductors (e.g. W, Cu), metal gates (e.g. Ta, Ti) and metals in magnetic multilayers (e.g. Co, Fe). However, few reports exist for metal ALE using either plasma or thermal processes. Conventional thermal ALE that has defined recent work on metal oxide [1] and metal nitride [2] materials does not work for metals. New reaction pathways are required to etch metals. This study targets W ALE and examines both WO_3 ALE and W ALE as W oxidation to WO_3 is needed to define self-limiting reactions for W ALE.

WO_3 ALE was demonstrated using an AB exposure sequence with boron trichloride (BCl_3) and hydrogen fluoride (HF). BCl_3 and HF etch WO_3 by a "conversion-fluorination" mechanism. The BCl_3 converts the WO_3 surface to a B_2O_3 layer while forming volatile WO_xCl_y. HF then spontaneously etches the B_2O_3 layer producing volatile BF_3 and H_2O products. WO_3 films were formed by oxidizing W ALD films with an oxygen plasma at 280°C. *In situ* spectroscopic ellipsometry (SE) studies determined that the BCl_3 and HF reactions were self-limiting versus exposure. WO_3 ALE etch rates increased with temperature from 0.55 Å/cycle at 128°C to 4.19 Å/cycle at 207°C. W served as an etch stop because BCl_3 and HF could not etch the underlying W film.

W ALE was performed using a three-step "oxidation-conversion-fluorination" mechanism. This is an ABC exposure sequence that where the W surface is first oxidized to a WO_3 layer and then the WO_3 layer is etched with BCl_3 and HF. SE could simultaneously monitor the W and WO_3 thicknesses and conversion of W to WO_3. Oxidation of the W surface was performed using either O_2 plasma or O_3. SE measurements showed that the W film thickness decreased linearly with number of ABC reaction cycles. The etch rates for W ALE were between 1.2-1.6 Å/cycle at 207°C depending on oxidation reactant and reaction conditions. In contrast, the WO_3 thickness was variable and could either increase or decrease depending on the oxidation conditions.

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[2] Nicholas R. Johnson, et al., "Thermal Atomic Layer Etching of Crystalline Aluminum Nitride Using Sequential, Self-Limiting HF and $Sn(acac)_2$ Reactions and Enhancement by H_2 and Ar Plasmas", *J. Vac. Sci. Technol. A* **34**, 050603 (2016).

11:30am **ALE-MoM-15 Plasma-Enhanced Atomic Layer Etching of TiN and TaN with Organic Masks***, **Nathan Marchack**, J Papalia, R Bruce, S Engelmann, E Joseph,* IBM TJ Watson Research Center **INVITED**

The concept of atomic layer etching (ALE) has garnered significant interest for future technology node patterning applications, owing to its potential for unparalleled control over the vertical dimensions of subtractive etching as well as minimal damage through a set of self-limiting reactions.[1] The continual downscaling of feature sizes and integration of novel materials has already begun to be limited by the complex nature of conventional continuous-wave plasmas, in which etch and deposition reactions occur simultaneously and cannot be fully decoupled from the variation of physical parameters such as power, pressure and gas flows. The ability of ALE to at least partially delineate these competing mechanisms in a plasma could be a powerful tool to overcoming these challenges.

This talk focuses on the plasma-enhanced ALE of TaN and TiN, which often serve as hardmasks for patterning of etch-resistant metals for non-volatile memory applications. These materials also function as the top electrode in memory cells due to their conductive nature, so the ability to generate patterns with low damage at tight pitches becomes increasingly important for future device technology. A plasma-enhanced atomic layer etch (PE-ALE) process utilizing sequential cycles of Cl_2 (deposition) and He/H_2 (etch) chemistries separated by purge steps was used to pattern TiN and TaN lines using an OPL mask at 100nm CD and 200nm pitch. Compared to a continuous wave Cl_2 plasma, the PE-ALE process demonstrated virtually no metal residue on the OPL mask and SiOx stop layer; as well as a powerful knob for tuning the profile and CD of the features by controlling the purge times between cycles.

[1] G. S. Oehrlein, D. Metzler, and C. Li, Atomic Layer Etching at the Tipping Point: An Overview

ECS J. Solid State Sci. Technol. 2015 4(6): N5041-N5053

ALD Applications
Room Plaza ABC - Session AA-MoA

Memory and MIM I (1:30-3:30 pm)/Memory and MIM II (4:00-5:30 pm)

Moderators: John Smythe, Micron Technology, John Conley, Oregon State University, Robert Clark, TEL Technology Center, America, LLC

1:30pm **AA-MoA-1 Atomic Layer Deposited Ta-doped ZrO_2 for DRAM Capacitors***, **Bo-Eun Park**, I Oh, J Park, S Seo, H Kim,* Yonsei University, Republic of Korea

With accelerated scaling down of integrated circuit, it is very challenged to employ DRAM capacitor with high capacitance density and low leakage current. Until now, ZrO_2 has been wide used as a high-*k* dielectric, but oxygen vacancies (V_o) in ZrO_2 have been considered as one of the significant reasons for high leakage current [1]. Doping of higher valent element than tetravalent Zr can be possible solution for reduction of V_o in ZrO_2 films since it introduces excessive O atoms and passivates the vacant position of V_o. Among various high valent element-based materials, Ta could be expected to be a good dopant in ZrO_2, since Ta_2O_5 is a well-known high-*k* material with high dielectric constant (22-60), good dielectric breakdown strength, and thermal and chemical stability [2]. However, previous studies on Ta-doped ZrO_2 films have shown conflicting results on their electrical properties. The reduction of V_o by Ta doping can transform the crystal structure of ZrO_2 from cubic to tetragonal and monoclinic due to atomic arrangement around V_o [3], and the dielectric constants of ZrO_2 significantly depend on the crystal structures [4]. Also, since Ta has limited solubility in ZrO_2, high Ta concentration form new orthorhombic phase of $Ta_2Zr_6O_{17}$ [4].

Therefore, proper control of Ta concentration in ZrO_2 is very important to reduce leakage current related to V_o with maintaining high dielectric constant. In this paper, we investigated Ta-doped ZrO_2 with various Ta concentration by supercycle process of atomic layer deposition (ALD). X-ray photoelectron spectroscopy analysis showed gradual increase of O/(Zr+Ta) with increase of Ta concentration, indicating reduction of V_o concentration in films. The decrease of V_o concentration transformed the crystal structure of ZrO_2 from cubic to tetragonal in X-ray diffraction pattern. The introduction of high dielectric constant of tetragonal ZrO_2 and Ta_2O_5 increase the dielectric constant from 16 up to 29 in C-V characteristics. Simultaneously, the reduction of V_o affects decrease of leakage current density of Ta-doped ZrO_2 from ~10^{-7} A/cm^2 to ~10^{-9} A/cm^2 in I-V characteristics (Table. 2). These results are very interesting because the dielectric constant and leakage current densities of conventional high-*k* dielectrics are usually inversely proportional.

Reference

[1] Shimeng Yu et al., Appl. Phys. Lett. 99, 063507 (2011)

[2] Min-Kyu Kim et al., Thin Solid Films, 542 (2013) 71–75

[3] Stefano Fabris et al., Acta Materialia, 50 (2002) 5171–5178

[4] J. Ferrand et al., ECS Transactions, 58 (10) 223-233 (2013)

1:45pm **AA-MoA-2 High Capacitance 3D MIM Structures Achieved by ALD Deposited TiO_2 for Advanced DRAM Applications***, **Ahmad Chaker**, P Szkutnik, P Gonon, C Vallée, A Bsiesy,* Univ. Grenoble Alpes, CNRS, France

The increase of capacitance density in Dynamic Random Access Memory (DRAM) is major challenge for CMOS advanced technology nodes. Metal-insulator-metal (MIM) structures based on high dielectric oxides (high k) is used in DRAM to increase the capacitance density. Titanium dioxide (TiO_2) is very promising candidate thanks to its high permittivity constant, up to 170, in its rutile crystalline phase. Rutile structure is obtained at low temperature (250°C) by ALD deposition on RuO_2 bottom electrode thanks to the small lattice mismatch with TiO_2. Planar (2D) TiO_2 based MIM structures can achieve capacitance density in the range of 50 nF/mm^2 which falls rather below the ITRS 100 nF/mm^2 preconized density. A way to increase this density is to build 3D capacitor structures, but conformal MIM deposition has to be achieved that exhibits uniform TiO_2 thin (10-20 nm) layer. In this paper, we report a study achieved on tapered silicon 3D substrate used to achieve high-density MIM capacitors (> 100nf/mm^2) which retains excellent electrical properties, comparable to flat (2D) MIM devices.

This paper will also discuss the effect of TiO_2 multicrystalline grain size on the MIM structure electrical properties. Indeed, two rutile TiO_2 layers, grown by ALD in different conditions to exhibit different grain size show that higher dielectric constant along with reduced conductance are obtained when the average grain size is larger. This result will be discussed by analyzing the grain boundaries role in the current transport mechanism.

2:00pm **AA-MoA-3 Seed-layer Effects on the Crystallization and Electrical Characteristics of ALD-grown Ta_2O_5 Thin Films***, **Jae Hyoung Choi**,* Samsung Electronics, Korea, Republic of Korea*; S Kang, S Chung, C Cho, S Oh, Y Kim, K Yoon, H Lim, K Hwang, H Kang,* Samsung Electronics, Republic of Korea

As the design rule of DRAM devices shrinks rapidly, Toxeq. (Equivalent Oxide Thickness) scaling of the capacitor by the development of high-k dielectric materials with permittivity over 50 has been attracted much interest to compensate the significant area reduction and to satisfy the cell capacitance. High dielectric constant over 50 was reported in Ta_2O_5 films of hexagonal crystal structure which was formed by Atomic Layer Deposition (ALD) using Tantalum halide precursors and H_2O reactant, such as $TaCl_5$ and TaF_5 [1, 2]. However, Ta_2O_5 dielectric material has critical demerit of high crystallization temperature over 800℃ on non-noble metal electrode.

In this study, we developed interface engineering inserting seed-layer before Ta_2O_5 film formation for facilitating crystallization during Post Deposition Annealing (PDA). The specific seed-layer effect on the lowering of the crystallization temperature and the leakage current of the capacitor were evaluated as well.

Ta_2O_5 thin films were prepared on TiN metal electrodes by ALD using both amide-type liquid TBTEMT (Tert-Butylimido-Tris-Ethyl-Methyl-Tantalum) and halide-type solid $TaCl_5$ precursors, respectively. As a reactant, O_3 was compared with H_2O. The crystallinity and crystal structure were analyzed by X-ray diffraction (XRD) and transmission electron microscopy.

First, we evaluated the ALD window and decomposition behavior with temperature. Figure 1 shows the ALD behavior of Ta_2O_5 films using TBTEMT and O_3 on Si substrate. Because the temperature window of ALD was observed between 290℃ and 350℃, we chose the temperature of 320℃ for film growth.

XRD patterns of ALD grown Ta_2O_5 films on TiN electrode were shown in Fig. 2. No crystalline Ta_2O_5 phases were observed in the films up to PDA temperature of 700℃. By inserting a seed-layer, however, the crystallization temperature of ALD-Ta_2O_5 film to hexagonal structure was significantly reduced to 575℃.

Figure 3 shows the dependence of Toxeq. of TIT-Ta_2O_5 and RIS-Ta_2O_5 (Top-Ru/Bottom-poly Si electrode) capacitor with Ta_2O_5 thickness. The dielectric constants of Ta_2O_5 films on the seed-layers were approximately 62, 61, respectively, even at the low crystallization temperature of 600℃. This indicates the interfacial engineering using seed-layers is very effective to lower the crystallization temperature of the Ta_2O_5 film without using non-noble metal electrode. Including these results, it will be discussed on the feasibility of the low temperature crystallized Ta_2O_5 films for the candidate of next-generation DRAM dielectric material.

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2:15pm **AA-MoA-4 Electrode Induced Variation in Voltage Nonlinearity of ALD Al_2O_3 and HfO_2 Metal-Insulator-Metal Capacitors (MIMCAPs)***, **Dustin Austin**, K Holden, J Hinz, C Remple, J Conley,* Oregon State University

The nonlinearity of capacitance vs. voltage (C-V) in high-κ MIMCAPs presents a major challenge for analog and mixed signal applications. The curvature in C-V is characterized empirically by the quadratic voltage coefficient of capacitance (αV_{CC}). High-κ dielectrics typically exhibit a positive αV_{CC} (C increases with V). Although a few dielectrics such as SiO_2 and TiO_2 have negative αV_{CC}. The magnitude of αV_{CC} increases with κ and with decreasing thickness, imposing a significant hurdle to increasing capacitance density. In addition, metal electrodes exhibit a secondary influence on αV_{CC}. The influence of metal electrodes increases as thinner dielectric layers are used. By pairing up positive and negative αV_{CC} insulators and relying on the precise thickness control afforded by ALD, it is possible to use the cancelling effect to create highly linear MIIM capacitors. However as the physical mechanisms responsible for αV_{CC} are not fully understood, re-optimizing a device for a new metal or a change in metal thickness, much less meeting future ITRS goals, will require significant trial and effort, leading to extended development time. Despite this, there have only been a few studies on the impact of metal electrodes on αV_{CC}. In this work we investigate the impact of a variety of metal electrodes on αV_{CC} in ALD Al_2O_3 and HfO_2 MIMCAPs.

MIMCAPs were fabricated using TaN bottom electrodes. 10 nm Al_2O_3 and 11 nm HfO_2 was deposited via ALD at 250 °C using H_2O and either TMA or

TEMA-Hf in a Picosun R-200 or R-150, respectively. Ag, Au, Ni, Pd, and Pt were evaporated through a shadow mask to form the top gate.

Plots of normalized capacitance (C/C_0) vs. electric field (E^2) show a similar dependence of αE_{CC} (quadratic electric field coefficient of capacitance) on Ni, Au, and Ag (Fig. 1) for both Al_2O_3 and HfO_2. Most studies have concluded that interfacial oxides dominate the influence of metal electrodes on αV_{CC}. However this cannot fully explain variation between near zero enthalpy of formation metals as they are unlikely to form substantial oxides. The αV_{CC} variation between these metals is likely due to an interaction between the bulk dielectric mechanism and an interfacial effect. One possible bulk mechanism for positive αV_{CC} materials is a decrease in film thickness due to voltage induced compression (Fig. 2). The compressive stress within the dielectric is modulated by the induced tensile stress at the metal interfaces. We see that metals with larger lattice mismatch show increased αV_{CC}. The effect of lattice mismatch and additional results showing effect of dielectric and metal thickness will be presented at the meeting.

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2:30pm **AA-MoA-5 High-Voltage Nanolaminate Metal-Insulator-Insulator-Metal (MIIM) Tunnel Diodes using ALD Al_2O_3 and Ta_2O_5**, *D Austin, M Jenkins, **Konner Holden**, J Conley,* Oregon State University

ALD nanolaminate tunnel barriers have enabled enhancements of low voltage asymmetry ($\eta_{asym} = I^-/I^+$) and non-linearity (f_{NL}) in MIIM tunnel diodes for applications such as rectenna based energy harvesting.[1,2] In this work, we investigate ALD bi-layers of Al_2O_3 and Ta_2O_5 for use in high-voltage applications such as electrostatic discharge (ESD) protection and high-voltage logic.

Nanolaminate Al_2O_3/Ta_2O_5 stacks were deposited on TaN bottom electrodes via ALD. ALD was performed at 200°C in a Picosun R-150 without breaking vacuum using alternating pulses of H_2O and either TMA or tris(ethylmethylamido)(tert-butylimido)tantalum. Al_2O_3:Ta_2O_5 thickness ratios of 1:1, 1:2, 1:3, 1:5, and 1:9 were fabricated, where the Al_2O_3 thickness is fixed at 30 nm. Bias was applied to Al top electrodes (formed by evaporation through a shadow mask).

I-V behavior (Fig. 1) was found to be a strong function of the Al_2O_3:Ta_2O_5 thickness ratio. Under positive bias, the reverse diode current for all devices remains low until the reverse "breakdown" voltage at which current increases rapidly. The reverse "breakdown" voltage increases with the thickness of the Ta_2O_5 layer, from 15 V for 1:1 to 53 V for the 1:9 devices. For small magnitude negative bias, in the range of 0 to -15V, the diode forward current *is higher* for thicker Ta_2O_5 layers, a somewhat counter-intuitive result. Beyond -15 V, the forward current is lower for thicker Ta_2O_5 layers, in line with expectations. Plots of $\log|\eta_{asym}|$ vs. V are shown in Fig. 2. That maximum asymmetry and voltage at which it occurs increases from ~900 at ~19 V for 1:1 to ~10^5 at ~52V for the 1:9 devices.

Multiple changes in slope of the I-V curves at both positive and negative bias reveal a number of competing conduction mechanisms. Overall, conduction and asymmetry are dominated by Fowler-Nordheim tunneling through the Al_2O_3 barrier and defect based conduction through the Ta_2O_5. The trends in conduction and η_{asym} are well explained by the asymmetric barrier (inset Fig. 1) created by the pairing of Al_2O_3 (E_G = 8.7 eV, χ = 1.4 eV, κ = 8.7) and Ta_2O_5 (E_G = 4.5 eV, χ = 3.2 eV, κ ~26). The detailed explanation will be discussed at the meeting.

This work demonstrates that ALD bilayers may be used to effectively engineer the reverse breakdown voltage, maximum asymmetry, and operating range of high voltage MIM diodes. These diodes may be of interest for implementation in back end of the line as well as for large area electronics due to low temperature fabrication.

2:45pm **AA-MoA-6 Capacitance Maximization of Ultra-thin Si-capacitors by Atomic Layer Deposition of Anti-ferroelectric HfO_2 in High Aspect Ratio Structures**, ***Stefan Riedel**, W Weinreich, C Mart, J Müller,* Fraunhofer IPMS, Germany

The increasing number of independent, electrical devices operating in networks intensifies the need for distributed and autonomous power supplies. Therefore, short term storage and buffering of electrical energy for both complete systems as well as individual integrated circuits is required for a multitude of applications. Anti-ferroelectric (AFE) capacitors are an emerging solution for this field of application due to their high energy density, low loss and fast charge and discharge rates.

Perovskite based materials like lead-lanthanum-zirconium-titanate (PLZT) are well known for showing promising energy storage properties [1]. However their scaling potential in thin films especially for three dimensional structures is limited due to the lack of conformal deposition methods. Additionally these materials contain heavy metals raising environmental concerns.

On the other hand HfO_2 based systems have been demonstrated to show both ferroelectric and anti-ferroelectric phases [2] and can be deposited by atomic layer deposition using well established chemistry. Additional HfO_2 is compatible with semiconductor processing enabling both an integration of AFE capacitors directly into semiconductor circuits or as stand-alone silicon based capacitors.

To demonstrate this applicability of AFE HfO_2 we fabricated metal insulator metal capacitors on 3D structured Si substrates. $TiCl_4/NH_3$ based ALD and CVD processes where applied to create metallic TiN electrodes. Silicon doped HfO_2 (Si:HfO_2) was used as anti-ferroelectric. These films were deposited using TEMAHf and 3DMAS as metalorganic precursors and ozone as co-reactant.

The Si:HfO_2 thin films have been characterized by means of XPS, XRR and XRD and electrical properties of these capacitors have been investigated in dependence of the silicon content, deposition temperature and post deposition thermal treatments. A maximum stored energy of >100 µJ/cm² could be achieved, which is sufficient to integrate these capacitors as buffer for low power integrated circuits.

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[2] T. S. Böscke, J. Müller, D. Bräuhaus, et al., Appl. Phys. Lett. 99, 102903 (2011)

3:00pm **AA-MoA-7 Ferroelectricity in Ternary HfO_2-ZrO_2-La_2O_3 Mixed Oxide Grown by ALD**, ***Anna Chernikova**, M Kozodaev, A Markeev,* Moscow Institute of Physics and Technology, Russian Federation

Recently discovered ferroelectric (FE) properties of HfO_2 based thin films attracted much attention. The novel FE material is considered as promising candidate to replace perovskites in new generation of high density non-volatile memory concepts: FeFET, FeRAM [1-3] and even more challenging FTJ [4]. Notable feature of FE HfO_2 is complete compatibility with semiconductor fabrication process. Particularly, ALD is successfully applied to its growth. According to the previous works, FE in such films is caused by the presence of orthorhombic ($Pca2_1$) polar phase. Although numerous factors (thickness, annealing temperature, electrodes materials, etc.) were previously shown to affect stabilization of $Pca2_1$ phase, there is still strong focus to essentially promote FE (i.e. remnant polarization value P_r) of HfO_2 by doping with other elements [5,6]. Particularly, La doping of HfO_2 was already applied to achieve high P_r and promising endurance behavior, while ALD (including plasma enhanced PEALD) could be successfully utilized to ensure the required low level of doping [7]. At the same time since La doping usually increases the crystallization temperature of HfO_2 its integration to the BEOL process of FeRAM could be challenging and some ways to avoid this rise of crystallization temperature have to be found.

In this work, the first attempt to obtain FE in ternary HfO_2-ZrO_2-La_2O_3 oxide was made**.** The strategy was to combine the advantages of La doping with lower crystallization temperature of $(HfO_2)_x(ZrO_2)_y$ system. For this purpose metal-insulator-metal (MIM) structures based on 10 nm thick $(La_2O_3)_x(HfO_2)_y$ as well as $(La_2O_3)_x(HfO_2)_y(ZrO_2)z$ were entirely grown by PEALD. TiN as a desired material in semiconductor industry and simultaneously well-known feasible electrode for HfO_2 based FE was utilized for MIM structures formation. As grown as well as annealed in wide temperature range stacks were investigated in terms of crystalline structure, FE response and endurance characteristics. Stabilization of $Pca2_1$ in $(La_2O_3)_x(HfO_2)_y(ZrO_2)z$ and robust FE response of fully PEALD grown TiN/$(La_2O_3)_x(HfO_2)_y(ZrO_2)z$/TiN stacks were confirmed after annealing at relatively low temperature and dependence of FE response on annealing temperature was elucidated in details.

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[7] Chernikova A.G. et al. Appl. Phys. Lett. 108, 2016, 242905

3:15pm **AA-MoA-8 A Study on the Oxygen Source and Annealing Temperature Effects of Atomic Layer Deposited Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ Thin Films**, ***Si Joon Kim***, *D Narayan, J Lee, J Mohan,* University of Texas at Dallas*; S Summerfelt,* Texas Instruments*; J Kim,* University of Texas at Dallas

Ferroelectric random access memory (FRAM) has several advantages such as fast read/write cycle time, non-volatile data retention, low voltage/power operation, and simplified process flow. Texas Instruments reported the use of 70-nm-thick $Pb(Zr,Ti)O_3$ (PZT) film to make FRAM devices using 1.5 V 130 nm CMOS technology [1]. This conventional PZT ferroelectric (FE) material has the primary problem which is the difficulty in scaling down. Recently, FE properties in very thin doped HfO_2 have been identified [2]. However, although most studies use an atomic layer deposition (ALD) process for doped HfO_2 film deposition, there is no report of the effect of oxygen sources on the FE properties.

In this study, FE properties of 10-nm-thick $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films deposited on the TiN bottom electrode by ALD (Cambridge Nanotech Savannah S100) using TDMA-Hf (Hf-precursor), TDMA-Zr (Zr-precursor), and ozone or water (oxygen sources) have been investigated. The wafer temperature was set to 250°C during the HZO deposition and annealing processes were performed for 60 s at 300-500°C in an N_2 atmosphere using rapid thermal annealing after TiN top electrode deposition. Then, a conventional photolithography/etching process was performed to form a precise area of capacitors (diameter of 50-100 μm). The polarization-electric field hysteresis curves of the ozone- and water-based HZO samples were measured at 20 kHz after wake-up field cycling. A pulse write/read test was also performed to extract the real FE switching polarization. The ozone-based HZO sample annealed at 400°C showed large remanent polarization ($2P_r$, 46 μC/cm^2), large switching polarization (P_{sw}, 45 μC/cm^2), and low FE saturation voltage (1.5 V) compared to those ($2P_r$ of 42 μC/cm^2, P_{sw} of 38 μC/cm^2, and FE saturation voltage of 2.0 V) of the water-based HZO sample annealed at 400°C. Furthermore, the effect of the annealing temperature on the FE polarization of the ozone- and water-based HZO samples was examined. Both HZO samples annealed at 500°C exhibited a relatively high FE saturation voltage and also have high leakage current properties compared to the 400°C annealed HZO samples. Our investigations showed that the annealing temperature and oxygen source have a significant influence on the FE properties of HZO films.

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4:00pm **AA-MoA-11 Thickness Dependence of Polarization Response in $(Hf,Zr)O_2$**, ***Sean Smith***, *M Rodriguez, D Henry, M Brumbach, J Ihlefeld,* Sandia National Laboratories

$(Hf,Zr)O_2$ is an exciting recently discovered ferroelectric that can be deposited as a thin film by atomic layer deposition and has sparked interest in $(Hf,Zr)O_2$ FRAM and other thin film ferroelectric devices. $(Hf,Zr)O_2$ is unusual because its ferroelectric response is due to a metastable phase most commonly seen as a thin film and its polarization response has been shown to increase with decreased thickness -- at size scales that are unusual for conventional ferroelectrics. Still, like more traditional ferroelectrics, properties are expected to degrade at some point, as the thickness approaches that of a single unit cell. The surface limited growth of atomic layer deposition is a natural fit for producing the very thin films needed to investigate this thickness regime. We observe an increase in remanent polarization with decreasing thickness, from 16 μC/cm^2 for 20 nm films up to 20 μC/cm^2 for 15 nm films before the ferroelectric response drastically falls off for thinner films, dropping to 7 μC/cm^2 for 10 nm films,. We will discuss these results in the context of developing highly scaled (<20 nm) $(Hf,Zr)O_2$ ferroelectric thin film memory devices. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:15pm **AA-MoA-12 ALD as a Primary Contributor Towards Enabling Key Materials in the Memory Roadmap**, ***John Smythe,*** Micron Technology **INVITED**

Atomic layer deposition methods for dielectrics and metals have been widely reviewed in the literature for over a decade. Though there are exceptions, cost and complexity have largely limited adoption in more than a few high volume applications. The transition from proof of concept to robust implementation can illuminate the need for alternative precursors, reactants and hardware in various combinations. Think of the following scene: Engineers stand at the white board and draw a sketch depicting the next amazing memory cell. After some reflection, a common phrase shortly thereafter is some version of, "How are we going to make the structure with the required materials characteristics?" This talk will explore a selection of cases to explore the nature of past, present and future transitions related to the memory space.

4:45pm **AA-MoA-14 Plasma-Enhanced Atomic Layer Deposition of Oxygen Deficient TaOx Thin Films for Resistive Switching Memory Applications**, ***Konstantin Egorov***, *D Kuzmichev, Y Lebedinskii,* Moscow Institute of Physics and Technology, Russian Federation*; C Hwang,* Seoul National University, Korea*; A Markeev,* Moscow Institute of Physics and Technology, Russian Federation

The plasma-enhanced atomic layer deposition (PEALD) process using $Ta(OC_2H_5)_5$ as a Ta precursor and plasma-activated hydrogen as a reactant for the deposition of TaOx films with a controllable concentration of oxygen vacancies (VO) is reported herein. The VO concentration control was achieved by varying the hydrogen concentration of the hydrogen-argon mixture inthe plasma, allowing the control of the leakage current density in the tantalum oxide films within the range of five orders of magnitude compared with the TaO_5 film grown via thermal ALD using the identical Ta precursor and H_2O.

The detailed chemical analysis and AFM topography were given for different growth temperatures and amount of ALD cycles. The saturation of growth rate for Ta-precursor pulse and reactant gas (H_2O and H_2/Ar plasma with different H_2 concentration) pulse time was studied too. Temperature-dependent current-voltage measurements combined with Poole-Frenkel emission modelling demonstrated that the bulk trap depthdecreases with the increasing hydrogen concentration, which could be attributed to the increase of the VO concentration. The change of VO quantity in the PEALD TaOx films grown under different hydrogen concentrations was confirmed by the *in-situ* X-ray photoelectron spectroscopy (XPS) measurements of the Ta4*f* core and valence band spectra. The comparison of the XPS-measured non-stoichiometry and the secondary ion mass spectrometry analysis of the hydrogen content allowed this study to conclude that the non-stoichiometry is largely related tothe formation of Ta-VO sites rather than of Ta-H sites.

Such oxygen-deficient TaOx layers were studied for application as a VO reservoir layer in a resistance switching random access memory stack (Ta_2O_5/TaOx) where the actual switching occurred within the stoichiometric Ta_2O_5 layer.The bilayer memory stack showed reliable resistance switching up to ~10^6 switching cycles, whereas the single-layer Ta_2O_5 memory showed only several hundred switching cycles.

5:00pm **AA-MoA-15 Monitoring Resistive Switching Properties of ALD Grown Al_2O_3/HfO_2 Nanolaminate ReRAM Structures by *iin-situ* Reducing Plasma Treatments**, ***Marceline Bonvalot***, *B Eychenne, P Gonon,* LETI-LTM, France

Metal oxide resistive random access memories (RRAM) are considered as strong candidates in novel memory and logic device applications, thanks to low power consumption, fast switching speed and easy down scaling below 20 nm. It is widely accepted that this soft breakdown is induced by the formation or rupture of a conductive filament (CF) based on oxygen defect migration upon voltage application. However, other mechanisms such as electrochemical reactions or Joule heating may also play a role in the switching. From the technological point of view, HfO_2 is undoubtly one of the most mature dielectric oxides under investigation for this purpose. One major issue that needs to be addressed before HfO_2 RRAM devices can be successfully implemented concerns the adequate control of their performance, in terms of variability and reliability of the switching parameters. To address this issue, Al_2O_3 has been used as an intercalation layer material in the HfO_2 dielectric oxide. Indeed, Al_2O_3 has a large band gap and a strong oxygen affinity. It also favors higher thermal stability of amorphous HfO_2 and thus impedes HfO_2 recrystallization potentially induced upon cycling, providing improved endurance.

Al_2O_3-HfO_2 bilayer structures have been deposited by ALD on Si/Ti/TiN bottom electrodes and capped with patterned Pt top electrodes using a shadow mask and a PVD process. Thickness values of each layer have been adjusted so as to maintain a 10 nm overall dielectric thickness.

We have observed that as deposited Al_2O_3-HfO_2 structures do not exhibit any memory effect. This is attributed to the defect free ALD Al_2O_3 layer which can sustain high electric fields without any breakdown. Subsequent reducing plasma treatments have then been applied in situ during the ALD Al_2O_3 growth in order to tune up a significant amount of oxygen vacancies which have been quantified by XPS analyses for several durations to plasma exposure (between 60 and 200 seconds). These treatments have proven to be necessary to trigger reversible switching in Al_2O_3-HfO_2 RRAM structures. Our results suggest that the formation energy of oxygen defects to a threshold concentration is too large to allow the CF formation. However, when preexisting in the insulating material, these oxygen vacancies can easily migrate along the applied electric field without significantly damaging the insulating matrix. Our results also indicate that both SET voltage (V_{SET}) and RESET voltage dispersion (ΔV_{RESET}) can be significantly reduced by appropriate plasma exposure durations. All these results will be presented and discussed in the light of current knowledge on conductive filament propagation in the dielectric material.

5:15pm **AA-MoA-16 Properties of ALD Ferroelectric Si-doped HfO_2 Characterized with Noncontact Corona-Kelvin Metrology**, ***Dmitriy Marinskiy***, Semilab SDI; *P Polakowski,* Fraunhofer IPMS, Germany; *A Findlay, P Edelman, M Wilson, J Lagowski,* Semilab SDI; *J Metzger, R Binder,* GLOBALFOUNDRIES, Germany; *J Müller,* Fraunhofer IPMS, Germany

The recent discovery of ferroelectricity in Si-doped HfO_2 thin films opens an attractive possibility for new ferroelectric FET's based on HfO_2 already integrated in IC technology [1].

We report a pioneering application of rapid feedback noncontact corona-Kelvin metrology for characterization of the ferroelectric (FE) behavior of Si-doped HfO_2. The 10nm films with Si mol% of 3.5, 4.6, and 11.3 were deposited using a halide based ALD process on 300mm Si wafers. Based on previous studies, which showed enhanced ferroelectric behavior for capped layers, the films were covered with 10nm PVD-TiN and spike annealed at 800°C . For corona-Kelvin measurements, the top TiN was removed by SC1 etching. On sister wafers MIM capacitors were prepared for standard measurement.

In the corona-Kelvin method, corona deposits charge-bias pulses (ΔQ_C) on the dielectric. The induced change of surface voltage (ΔV) is measured with a Kelvin probe and capacitance is obtained as $C=\Delta Q_C/\Delta V$. Present results demonstrate that large charge bias provides a means for poling of the ferroelectric films similar to voltage biasing of MIM capacitors. Sequential small charge pulses are used for acquiring the Q-V and C-V characteristics that monitor the ferroelectric property again in good agreement with standard MIM polarization characteristics and permittivity derived from C-V.

Distinctly different properties are revealed in films with small and large Si doping. Based on structural analysis, the sample with 11.3% Si stayed amorphous after the anneal, while the samples with lower amount of silicon showed a distinct amount of orthorhombic, ferroelectric phase of HfO_2. The 11.3% Si film was found to be non-ferroelectric as demonstrated by linear Q-V and lack of hysteresis. For the two low Si films, a large Q-V hysteresis loop was measured after large positive corona charge poling (Q_C of $30\mu C/cm^2$). In the hysteresis loop the coercive positive and negative fields were identified at about ± 1.2MV/cm for the 3.5% film and 1.0MV/cm for the 4.6% Si film.

For large positive charging the Fowler-Nordheim electron tunneling from TiN to HfO_2 conduction band was measured, showing a large effect of Si-doping manifested by the linear tunneling field decrease with %Si. This offers a possibility of %Si monitoring in HfO_2 with an estimated sensitivity of about 0.1mol%.

The corona-Kelvin technique facilitates whole wafer mapping of ALD film properties. Differences in maps that correlate with processing were observed showing promise for the technique as a fast, inline ALD and post deposition process monitor.

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ALD Fundamentals
Room Plaza F - Session AF-MoA

ALD Fundamentals: Characterization (1:30-3:30 pm)/Mechanisms and Surface Science (4:00-5:00 pm)

Moderators: Mikko Ritala, University of Helsinki, David Emslie, McMaster University, Simon Elliott, Tyndall National Institute, University College Cork

1:30pm **AF-MoA-1 FTIR and NMR Analysis of ALD Al_2O_3 on poly-L-lactone Acid Powder and Electrospun Fibres**, ***Laura Svärd***, *T Virtanen, M Putkonen, E Kenttä, H Rautkoski, P Heikkilä, P Simell,* VTT Technical Research Centre of Finland, Finland

Atomic layer deposition (ALD) is a coating technique capable of producing uniform material layers on complex surfaces. Although the ALD growth is extensively studied on inorganic substrates, less attention is being paid coating of polymeric materials. In addition to traditional polymeric 2D materials, it is interesting to study the growth and structure of films 3D substrates, such as electrospun fibres. Electrospinning is a process utilizing high voltage electric field to produce non-woven polymer fibres with diameters ranging from dozens of nanometres to several microns. In this study ex-situ NMR (nuclear magnetic resonance), is used to characterize the beginning ALD film growth on polymeric substrates.

In this study [1], we have used poly-L-lactic acid (PLLA) as a polymeric material in a form of a powder and electrospun fibres. Electrospinning was performed from commercial poly-L-lactic acid (Purasorb PL24), dissolved in $CHCl_3$ and DMF. The 1-500 cycles of Al_2O_3 films were made with Picosun R-200 ALD reactor from TMA (trimethylaluminium) and H_2O or O_3 at 80°C. Al_2O_3 coated PLLA powder was analysed by using solid state ^{27}Al NMR spectroscopy, in combination with NMR relaxometry, with aim to characterize the possible infiltration of the precursors inside the PLLA. Due to its quadrupolar nature ^{27}Al nucleus is extremely sensitive to changes in its local environment. It has also a high magnetic moment and a 100 % natural abundance, thus enabling the detection of very thin coatings. The effect of penetrated precursors inside PLLA particles to the proton longitudinal relaxation of PLLA was also studied. Additionally, coated materials were analysed with ATR-FTIR.

When electrospun PLLA fibres were coated with 500 cycles of TMA + O_3 and analysed with ATR-FTIR, we detected clear Al_2O_3 stretches. Spectra of parallel measurements were identical indicating the homogeneity of the deposited material. Furthermore, there was a new stretch (1614 cm^{-1}) in the spectrum with Al_2O_3 coating lacking from the spectrum of uncoated electrospun PLLA. The new stretch is probably from polymeric material reacting with the ALD precursors during the deposition. Further studies are needed with NMR, ATR-IR and in-situ QCM to elucidate the structure, growth and reactions between the ALD precursors and polymer more thoroughly.

[1] The research has received funding from the Academy of Finland, project ID 288212.

1:45pm **AF-MoA-2 Bulge Testing of Freestanding ALD Thin Film Membranes**, ***Oili Ylivaara,*** VTT Technical Research Centre of Finland, Finland; *P Törmä,* HS Foils, Finland; *I Stuns, J Saarilahti, R Puurunen,* VTT Technical Research Centre of Finland, Finland

Thin films made by atomic layer deposition (ALD) are ideal to be used as freestanding membranes in microelectromechanical system (MEMS) devices, as self-saturated surface reactions in ALD enable uniform and conformal film growth with precise thickness control. In applications, were ALD films are used as functional layers, thin film mechanical properties play in a crucial role as those enable design of reliable device structure. Here, the ultimate tensile strength (UTS), describing materials' ability to withstand external loads, is measured using bulge testing [1, 2] by pressurizing the membrane until the point where membrane breaks. The UTS is determined from the maximum breakage pressure. Studied ALD Al_2O_3 and TiO_2 films were grown on 380 µm thick double side polished RCA-cleaned (100) silicon wafers and targeted film thickness was about 100 nm. The films were grown in a top-flow ALD reactor, Picosun^{TM} R-150, using temperature range from 110 to 300 °C. Freestanding ALD membranes were fabricated using isotropic xenon difluoride (XeF_2) etch process, which is purely chemical process, using silicon as sacrificial material. As UTS may depend on the membrane fabrication process, some of the freestanding membranes were fabricated also using deep reactive ion etching (DRIE). Through wafer etching, using DRIE, requires additional hard mask, as in XeF_2-process, photoresist withstands through wafer etching and no additional hard mask is required. This work continues the mechanical property characterization [2-6] started for ALD Al_2O_3 and TiO_2 on residual stress, elastic modulus, hardness and adhesion, and helps to deepen the knowledge about the influence of the process conditions (temperature) to mechanical properties of ALD thin films.

Acknowledgements: This work has been carried out within the Finnish Center of Excellence in Atomic Layer Deposition (ref. 251220) of the Academy of Finland.

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2:00pm **AF-MoA-3 Infiltrated Zinc Oxide in Polymethylmethacrylate: An Atomic Cycle Growth Study**, ***Leonidas Ocola,*** Argonne National Laboratory*; A Connolly,* Vassar College*; D Gosztola,* Argonne National Laboratory*; R Schaller,* Argonne National Laboratory, Northwestern University*; A Yanguas-Gil,* Argonne National Laboratory

We have investigated the growth of zinc oxide in a polymer matrix by sequential infiltration synthesis (SiS). The atomic cycle-by-cycle self-terminating reaction growth investigation was done using photoluminescence (PL), Raman and X-ray photoemission spectroscopy (XPS). Results show clear differences between Zn atom configurations at the initial stages of growth. Mono Zn atoms (O-Zn and O-Zn-O) exhibit pure UV emission with little evidence of deep level oxygen vacancy states (V_O). Dimer Zn atoms (O-Zn-O-Zn and O-Zn-O-Zn-O) show strong UV and visible PL emission from V_O states 20 times greater than that from the mono Zn atom configuration. After 3 precursor cycles the PL emission intensity drops significantly exhibiting first evidence of crystal formation as observed with Raman spectroscopy via the presence of longitudinal optical phonons. We also report a first confirmation of energy transfer between polymer and ZnO where the polymer absorbs light at 241 nm and emits at 360 nm, which coincides with the ZnO UV emission peak. Our work shows that ZnO dimers are unique ZnO configurations with high PL intensity, unique O_{1s} oxidation states, and sub-10 ps absorption and decay, which are interesting properties for novel quantum material applications.

- Use of the Center for Nanoscale Materials, an Office of Science user facility, was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357, with the EXAFS data being collected at 9-BM-B. Work also supported by the University of Chicago Materials Research Center (MRSEC) IRG3-Engineering Quantum Materials and Interactions Contract #2-60700 – 95.

2:15pm **AF-MoA-4 Study on Atomic-Layer-Deposited Al_2O_3 Dielectric Films with a New Small Angle X-Ray Scattering Method**, ***Chao Li,*** *F Shahriarian, M Goorsky,* University of California Los Angeles

The porosity and pore size distribution of dielectric films deposited by atomic layer deposition (ALD) is important to understand their optical, mechanical and electrical properties. Advances in the development of X-ray generators and optics have made in-house small angle X-ray scattering (SAXS) experimentation suitable for the determination of sizes and shapes of pores (in the scale of sub-nanometer to several hundred nanometer) in thin films, which can be realized through the simulation of pore scattering based on distorted wave Born approximation. Previously, SAXS was widely applied to low-k dielectric films, with pore scattering determined with offset θ:2θ scans using conventional 1-dimensional (1D) configuration of X-ray diffractometer. However, challenge still exists in estimating the diffuse scattering from surface roughness that also contributes to total diffuse scattering measured with offset θ:2θ scans. In this study, we propose a new 1D SAXS method in which the scattering from surface roughness was determined by the simulation of X-ray reflectivity (XRR) longitudinal scan with parameters of RMS surface roughness σ, lateral correlation length ξ, and Hurst parameter h obtained from atomic force microscopy measurement, along with layer densities and compositional grading determined by specular XRR simulation. This new SAXS method was validated with scanning electron microscope using a single-layer porous InP sample, and was utilized to reveal the effects of ALD parameters on pore size distribution of single-layer Al_2O_3 dielectric films. Two Al_2O_3 single layers were deposited on Si substrates with different parameters of ALD that is a good candidate for dielectrics films in various applications, due to the self-limiting nature of chemical reactions resulting in the precise control of film thickness and large-area uniformity. Both of them have amorphous structures. It is indicated by the new SAXS method that the #1 Al_2O_3 film is porous with a mean pore size of 19 ± 1.8 nm along the out-of-plane direction, while there are no pores in the #2 Al_2O_3 film. This correlates with the specular XRR showing a lower density (2.95 ± 0.01 g/cm^3) of the #1 Al_2O_3 film than that (3.01 ± 0.01 g/cm^3) of the #2 Al_2O_3 film. In addition, 2-dimensional (2D) glancing incidence SAXS (GISAXS) measurements also suggest the absence of pore scattering for the #2 Al_2O_3 film while the #1 Al_2O_3 film to be porous, agreeing with the new 1D SAXS method. Besides, a mean pore size of approximately 2 ± 0.2 nm along the in-plane direction of the #1 Al_2O_3 film was also suggested by 2D GISAXS.

2:30pm **AF-MoA-5 Evaluating Mechanical Properties of Free-standing ALD Al_2O_3**, ***Junmo Koo,*** Korea University, Republic of Korea*; S Lee, T Kim,* Korea Advanced Institute of Science and Technology, Republic of Korea*; J Shim,* Korea University, Republic of Korea

Recently, atomic layer deposition (ALD) has been widely used in various fields due to its unique characteristics. Film thickness and composition can be precisely manipulated by controlling the number of ALD cycles in the atomic scale. In addition, ALD can produce large area thin films without pinholes or defects even in complex structures such as nano-trenches and three-dimensional porous media.[1] ALD Al_2O_3 is one of the most actively used materials in various fields such as gate dielectrics, memory and capacitors, encapsulation of organic displays and solar cells, and chemical protection.[2] For this reason, understanding the mechanical properties of ALD Al_2O_3 is expected to be of great help in developing robust and reliable devices.

A number of studies have been conducted to determine the mechanical properties of ALD Al_2O_3 using a variety of methods including nano-indentation and bulge testing.[3] However, many of these methods are performed with the ALD film bonded to the substrate, where it is difficult to completely eliminate the influence of the substrate properties. In particular, the stiffness and roughness of the substrate are known to have a significant effect on the Young's modulus and hardness measurements of the films.[4] In this study, we have evaluated free-standing ALD films completely separated from the wafer.[5] We have successfully measured the Young's modulus, tensile strength and elongation of ALD Al_2O_3 thin films (~ 130 nm in thickness) deposited at temperatures of 80-250 °C. In this presentation, we will discuss in detail the recent progress and results of our research.

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2:45pm **AF-MoA-6 Secondary Electron Yield of Nano-oxide Thin Films Measured by Spherical Collector with Pulsed Electron Irradiation**, ***Baojun Yan,*** *S Liu, K Wen,* Institute of High Energy Physics of Chinese Academy of Sciences, China

As a solid-state detector, electron multipliers coated with high secondary electron yield (δ) materials have the potential to provide a significant improvement over existing devices. Nano-oxide thin films, such as aluminum oxide (Al_2O_3) and magnesium oxide (MgO), with high δ were deposited via atomic layer deposition technique. The δ of nano-oxide thin films were measured by spherical collector with pulsed electron irradiation in high vacuum condition. The influences of incident electron energy (100 eV ~ 1 KeV), incident electron angle (0° ~ 85°), sample thickness (3 nm ~ 100 nm) and annealing temperature (25°C ~ 200°C) on δ have been investigated in this study and the time evolution of δ also has been investigated under the pulsed electron irradiation. The mechanism of improving the δ of the insulating material has been discussed.

3:00pm **AF-MoA-7 Electrical Characterization of Platinum Thin Films Deposited by Plasma-Enhanced ALD and Magnetron Sputtering***, **Martin Winterkorn**, H Kim, K Kaplan, J Provine, T Kenny, F Prinz,* Stanford University

Platinum is widely used in sensing applications such as thermistors, bolometers or thermal accelerometers due to its desirable thermal, electrical and chemical properties, including a high temperature coefficient of resistance (TCR), low 1/f noise, high melting point and chemical inertness. With the ability to synthesize ultra-thin pinhole-free layers with high conformality, Atomic Layer Deposition of platinum enables an even wider range of usages and fabrication processes. However, ALD of platinum also has several disadvantages compared to traditional deposition techniques, most notably low growth rate, high precursor cost and incorporation of carbon impurities into the film from unreacted precursor ligands. In this work, we compare the properties of platinum thin films from plasma-enhanced ALD (PEALD) and magnetron sputtering in an intermediate thickness regime of around 30 nm, deposited on flat thermally oxidized Si substrates.

Particular characterization and optimization effort has been put on electrical properties as those are of prime importance for sensing applications. A resistivity close to the bulk value (10.6 µΩcm) indicates a low density of impurities and other scattering sites, which correlates with better stability and higher TCR.

Sputtered films were prepared in a multipurpose sputtering system by Kurt J. Lesker Company, which is capable of both DC and RF magnetron sputtering with variable plasma power, Argon gas pressure, substrate temperature and substrate bias. Due to the large number of process parameters, a non-factorial design-of-experiments approach was used to optimize the deposition conditions for low resistivity. A summary of the first-order dependencies found is shown in Table 1. A maximum substrate temperature of 270°C was used to be comparable to the non-annealed ALD films.

PEALD of platinum was accomplished by sequential introduction of remote O_2 plasma and trimethyl(methylcyclopentadienyl)platinum(IV) precursor, performed in an Ultratech / Cambridge Nanotech Fiji ALD reactor. A variation of this base recipe with additional cycle-by-cycle H_2 and O_2 plasma treatment has shown to significantly improve film adhesion as tested by tape lift-off. Both films were deposited at 270°C and post-deposition, rapid thermal annealed at various temperatures for 5 minutes in a N_2 ambient. Figure 1 shows the film resistivities as a function of anneal temperature, with 270°C indicating no anneal. The overall findings are summarized in Figure 2. Further characterization of film morphology using AFM and TEM as well as resistivity stability is currently underway.

3:15pm **AF-MoA-8 A Facile Control of Major Carriers on Atomic Layer Deposited SnO_x Thin Film by using Various Oxygen Reactants***, **Jung-Hoon Lee**,* Hanyang University, Republic of Korea*; J Park, J Park,* Hansol Chemical, Republic of Korea*; J Park,* Hanyang University, Republic of Korea

Oxide semiconductor materials have attracted attention for application in thin film transistors (TFT), solar cells, gas sensors, and lithium batteries. A great number of experimental studies have been conducted for a n-type semiconductor such as ZnO, In--$_2$O$_3$, InGaZnO, ZnSnO, but p-type materials such as Cu_2O, NiO, SnO are rarely studies due to their stability. However, since needs of p-type materials are increased in electronic device for p-n junctions, complementary metal-oxide semiconductors (CMOS). SnO is one of good candidate for p-type material because it has high mobility and wide band gap, which can be used to fabricate transparent device.

In our study, SnO_x thin film was deposited by thermal atomic layer deposition (ALD) method using N,N'-tert-butyl-1,1-dimethylethylenediamine stannylene as a precursor, Ozone and Water as a reactant. Both processes using ozone, water show surface limit reaction behavior as increase precursor temperature with constant purge time 10s during processes. Growth rate is different a lot; it can be caused from different surface functional group state derived from different reactant. Absorbance and refractive index of SnOx thin films are investigated using ultraviolet-visible spectroscopy (UV-VIS) and spectroscopic ellipsometry (SE), respectively. SnOx using ozone and water have 3.60-3.17, 2.24-2.30 eV of optical band gap and ~2.0, ~2.6 refractive index, which are correspond to SnO_2. SnO, respectively. SnO exhibit p-type characteristic confirmed by Hall measurement and has carrier concentration about 10^{18}. Furthermore, we can optimize SnO, SnO_2 processes and use them for TFT, p-n diode, CMOS application

4:00pm **AF-MoA-11 Activation of Metal Amidinate ALD Precursors on Surfaces and Implications for Film Growth***, B Chen,* University of California, Riverside*; Y Duan,* University of Delaware*; Y Yao,* University of California, Riverside*; J Coyle, S Barry,* Carleton University, Canada*; A Teplyakov,* University of Delaware*; **Francisco Zaera**,* University of California, Riverside

Finding good metallorganic compounds with clean chemistry for the growth of metal films has proven challenging. Amidine ligands have shown some promise for this application because they are stable and form volatile complexes with most metals. Unfortunately, although the clean displacement of amidine ligands from metal complexes on solid surfaces should be facile, most studies carried out to date on the use of metal amidinates for metal film growth have pointed to the incorporation of significant amounts of impurities, a sign of extensive decomposition of the ligand upon activated adsorption.

Here, we discuss a potential reason for this behavior, namely, the fact that the metal amidinate complexes form dimers or tetramers, and that those adsorb on surfaces via side bonds with nitrogen atoms and cannot be fully decoupled unless using the higher temperatures that also favor ligand decomposition.

Specifically, the gas-phase structure of three copper amidinate compounds, copper(I)-N,N'-di-sec-butyl-acetamidinate (**1**), copper(I)-N-sec-butyl-2-iminopyrrolidinate (**2**), and copper(I)-N-tert-butyl-5,5-dimethyl-2-iminopyrrolidinate (**3)**, and their initial adsorption on silicon oxide surfaces were characterized by a combination of experimental measurements and density-functional theory (DFT) calculations. Liquid-injection field desorption ionization mass spectrometry (LIFDI-MS) data proved that the dimer and tetramer structures that these compounds adopt in solid phase are retained upon vaporization into the gas phase (dimers for the first and third compounds, a tetramer for the second). Results from DFT calculations of the relative energies of formation of the monomers, dimers, and tetramers, confirmed the experimental results. Adsorption on the surface of silicon oxide films was determined, based on additional DFT calculations, to lead to the binding of the copper amidinates preferentially as dimers; although the monomers form stronger bonds to the silicon surface because they bind directly through their copper atom, this cannot fully compensate for the large energy required to break the dimers apart. N 1s x-ray photoelectron spectroscopy (XPS) data were used to corroborate both the presence of the dimers on the surface with the second (**2**) precursor and the threshold for their surface decomposition around room temperature. The behavior of the third compound is somewhat more complex, with some decomposition possibly happening immediately upon adsorption at 100 K.

Results from additional studies will be presented to analyze the role of the nature of the solid substrate in defining the precursor activation chemistry.

4:15pm **AF-MoA-12 Surface Chemistry during Atomic-Layer Deposition of Pt Studied with Vibrational Sum-frequency Generation***, **Vincent Vandalon**, A Mackus, W Kessels,* Eindhoven University of Technology, Netherlands

The reaction mechanism of Pt atomic-layer deposition (ALD) using $MeCpPtMe_3$ as precursor and O_2 as co-reactant was investigated with vibrational broadband sum-frequency generation (BB-SFG) spectroscopy. Pt nanoparticles and ultrathin films synthesized by ALD have a wide range of potential applications because of the chemical stability, catalytic nature, and high work function of Pt. Moreover, the Pt ALD process can be considered as a model system for noble metal ALD. Insight into the growth mechanism of these noble metal ALD processes is essential for extending the operating conditions or for enabling new applications. However, to gain fundamental understanding of the growth mechanism, an analysis technique is needed which can directly study the surface chemistry during ALD.

Vibrational BB-SFG spectroscopy is excellently suited for in-situ studies of the surface chemistry governing ALD because of its inherent interface selectivity, submonolayer sensitivity, and short acquisition times. It is a nonlinear optical technique which uses the mixing of picosecond visible and femtosecond mid-IR pulses to probe the vibrational response of surface groups. The unique nature of BB-SFG spectroscopy allows the in-situ investigation of the surface chemistry on both reflective (i.e. Pt metal) and transparent substrates without any modifications to the setup.

Although the Pt ALD process serves as a model system, several questions about the underlying reaction mechanism remain. For example, it is not clear which species of hydrocarbons are present on the surface. In this work, direct evidence for the presence of CH_3 groups during ALD will be presented. Moreover, a contribution assigned to species containing C=C bonds was observed, originating from the MeCp ligand. This assignment was confirmed in a series of experiments exposing different surfaces (Pt and SiO_2) to either the $MeCpPtMe_3$ precursor or to CH_3-C_5H_7, a molecule similar to the MeCp ligand. For ALD at 250 C, both the CH_3 and the C=C groups were observed on the surface after the precursor half-cycle and both were removed in the subsequent O_2 half-cycle. The relative CH_3 and C=C coverage after the precursor half-cycle was studied from 80 C up to 300 C. The CH_3 coverage showed a monotonic decrease with temperature whereas the C=C coverage was fairly constant. Furthermore, the reaction kinetics during the precursor half-cycle were studied, revealing that the saturation of C=C groups occurred ~ 3 times faster than that of the CH_3 groups. Both the temperature trend and the reaction kinetics are evidence for the dehydrogenation of some of the hydrocarbon species on the Pt surface during ALD.

4:30pm **AF-MoA-13 Mechanistic Study of the Atomic Layer Deposition of Titanium Dioxide Films from Ethylcyclopentadienyltris(dimethylamido)titanium and Ozone or Water***, **Joseph Klesko**, R Rahman, A Dangerfield, C Nanayakkara, T L'Esperance,* University of Texas at Dallas*; C Dezelah, R Kanjolia,* EMD Performance Materials*; Y Chabal,* University of Texas at Dallas

A plethora of Ti precursors are widely available. However, many generate corrosive reaction byproducts (e.g. Ti halides), suffer from low thermal stability (e.g. alkylamides like $Ti(NMe_2)_4$), or exist as solids and consequently increase the risk of particle incorporation into the growing film (e.g. alkoxides like $Ti(OMe)_4$). Heteroleptic cyclopentadienyl-based Ti precursors have increased thermal stability over their homoleptic alkylamide or alkoxide analogues.[1] Herein, a mechanistic study is presented of the ALD of titanium dioxide films grown from ethylcyclopentadienyltris(dimethylamido)titanium (TIECTA) and either ozone or water.

TIECTA was selected because it is a liquid, halogen-free precursor that is thermally-stable under inert conditions. A comparison analysis of the ALD processes between ozone and water as co-reactants was performed. In both cases, TIECTA initially reacts with the OH-terminated Si(111)-SiO_2 substrates at 150 °C and remains thermally stable up to 350 °C. Using spectroscopic ellipsometry and X-ray photoelectron spectroscopy (XPS), an ALD window was found to be approximately 250–300 °C with a deposition rate of ~1 Å/cycle with ozone, while with water there is an apparent deposition rate of approximately 0.6 Å/cycle with no obvious ALD window. *In-situ* Fourier transform infrared spectroscopy (FTIR) revealed a clear ligand exchange for the ozone process, with the formation of intermediate Ti-formate (1614 cm^{-1}) and -carbonate (1580 cm^{-1}) species upon ozone exposure,[2] and CH_x absorption after TIECTA exposure. In contrast, ligands associated with the water process were difficult to measure, preventing the formulation of an extact mechanism. XPS further showed that films grown within the ALD window using ozone contained no detectable carbon after 5 s of argon ion sputtering, while films grown with water at 300 °C contained ≤3 at.% carbon.

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4:45pm **AF-MoA-14 The Role of Surface Chemical Functionality in the Initial Stages of Deposition for Copper and Silver Precursors***, **Andrew Teplyakov,*** University of Delaware

Copper and silver deposition onto solid substrate forms a foundation for multiple applications, from catalysis to microelectronics and photonics. The key practical issue in the deposition process is the formation of the interface between the metal deposited and the substrate material. The control over the formation of this interface in chemical deposition schemes depends on the possibility to tune the chemical reactions leading to the deposition. This in turn depends on the actual surface functionalities available and their distribution on the surface. Thus, understanding and controlling these reactions is of paramount importance for producing the desired interfaces.

Chemical interactions of several copper and silver deposition precursor molecules with functionalized silicon, silica, ZnO, and carbon (ordered pyrolytic graphite, HOPG) surface will be discussed targeting specifically the chemistry of adsorption and decomposition depending on the precursor ligands and oxidation states of the metal. The study considers surface chemical functional groups available on the surfaces of these different materials and the mechanistic understanding is supported by microscopic (atomic force microscopy, scanning electron microscopy, transmission electron microscopy) and spectroscopic (X-ray photoelectron spectroscopy, time of flight secondary ion mass spectrometry, and infrared spectroscopy) methods supported by the density functional calculations. The work with copper deposition precursors targets $Cu(acac)_2$, $Cu(hfac)_2$, and Cu(hfac)VTMS. The more challenging and far less investigated reactions of silver precursor molecules are mostly focused on trimethylphosphine(hexafluoroacetylacetonato)silver(I). These molecules possess very different reactivities with respect to different surface functionalities and substrates; however, understanding the mechanisms of surface reactions allows one to direct the deposition to prepare surface metallic nanostructures and thin films with well-defined interfaces between the metals deposited and underlying substrates.

5:00pm **AF-MoA-15 Reaction Mechanism of ALD Zirconium Oxide using Alkylamido-Cyclopetadienyl Zirconium Precursors***, **Jae-Min Park**, T Mayangsari, S Kim, Y Kim,* Sejong University, Republic of Korea*; W Han, B Yoo, W Koh,* UP Chemical Co., Ltd., Republic of Korea*; W Lee,* Sejong University, Republic of Korea

Zirconium oxide thin films are used as the high dielectric constant material in dynamic random access memory (DRAM) devices. ALD technique has been used because of good step coverage, precise control of film thickness, and high film quality, and alkylamido-cyclopetadienyl zirconium compounds, such as $CpZr(NMe_2)_3$, are used as the zirconium precursor. As the aspect ratio of the DRAM capacitor continue to increase to >50 in the state-of-art DRAMs, however, the zirconium precursor with higher reactivity and thermal stability is requested for improving step coverage [1]. In the present work, we investigate reaction mechanism of ALD zirconium oxide using different alkylamido-cyclopetadienyl zirconium compounds and ozone. Density functional theory calculation is used for expecting the characteristics of the precursors with different structures and ligands. The deposition kinetics and the reaction mechanism were investigated for different precursors by in-situ QCM and FTIR. The physical and electrical properties of the deposited films were also characterized.

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5:15pm **AF-MoA-16 Elucidation of Distinct Electric Characteristics of ALD Oxides on Highly Ordered GaAs(001) and $In_{0.53}Ga_{0.47}As(001)$ Surfaces using Synchrotron Radiation Photoelectron Spectroscopy***, **Yi-Ting Cheng**,* National Chia-Yi University, Republic of China*; W Chen,* National Synchrotron Radiation Research Center, Republic of China*; K Lin, L Young, Y Lin, H Wan,* National Taiwan University, Republic of China*; T Pi,* National Synchrotron Radiation Research Center, Republic of China*; M Hong,* National Taiwan University, Republic of China*; C Cheng,* National Chia-Yi University, Republic of China*; J Kwo,* National Tsing Hua University, Republic of China

The frequency dispersion at accumulation in the capacitance-voltage (CV) curves has long been noted to behave differently between n- and p-type (In)GaAs MOS capacitors. In Fig. 1 (a)-(c), the dispersion is greater in n-GaAs(001) than that in p-GaAs, while greater in p-$In_{0.53}Ga_{0.47}As(001)$ than that in n-InGaAs. This is irrespective of the atomic-layer deposited (ALD) oxides.[1,2] We have solved the puzzles by investigating the surface electronic structure of as-grown MBE GaAs(001)-4x6 and $In_{0.53}Ga_{0.47}As(001)$-4x2, and later using the noble metals as the probed adatoms to simplify the atom-to-atom interaction. The characterization method is synchrotron radiation photoelectron spectroscopy, which is a powerful tool to probe the charge environments of the surface atoms prior to and after the ALD oxide depositions, namely the interfacial electronic characteristics. We always kept the samples under UHV throughout the experiments. The Pauling electronegativity of As, Ga, Ag, and Au is 2.18, 1.81, 1.93, and 2.54, respectively. Intuitively, the contact of As and Au atoms would result in a charge transfer from As to Au. The induced peak of As 3d core level should appear in a higher binding energy (BE), the ordinal energy position of the contacted As atoms. However, we found that the induced As 3d component actually lies at *lower* BE as shown in Fig. 2. In other words, the III-V surfaces show high Pauling electronegativity. This unique property alone is still unable to resolve the issue of different dispersion behavior in between GaAs(001)-4x6 and InGaAs(001)-4x2. We further notice that the surface electronic structure is not entirely the same in them. The As atoms in the top As-In-As rows on $In_{0.53}Ga_{0.47}As(001)$-4x2 are enriched in charge due to surface reconstruction,[3] while those in the faulted terrace of the GaAs(001)-4x6 are deficient in charge.1

Now, it becomes clear that if the surface As atoms are not properly passivated, they will serve as charge trappers to the ones accumulated at the oxide/(In)GaAs interface, namely, electrons in n-GaAs and holes in p-InGaAs MOS. Indeed, upon deposition of 10-cycles TMA and H_2O precursors onto a GaAs(001)-4x6 surface, a great percentage of the un-bonded surface As atoms were still observed in Figs. 3-4. In Figs. 5-6, the case is similar for 10-cycles tetrakis(ethylmethylamino) hafnium (TEMAHf) and H_2O onto a InGaAs(001)-4x2 surface. We will illustrate how the ALD precursors react with (In)GaAs surface atoms in an atomic scale.

[1] T.W. Pi, *et. al.*, *Nanotechnology* **26**, 164001 (2015).

[2] T.D. Lin, *et. al.*, *Appl. Phys. Lett.* **100**, 172110 (2012).

[3] T.W. Pi, *et. al.*, *Appl. Phys. Lett.* **104**, 042904 (2014).

Atomic Layer Etching
Room Plaza D - Session ALE+AF-MoA

Atomic Layer Etching Session V (1:30-3:30 pm)/ALD Fundamentals: Process Development (4:00-5:45 pm)

Moderator: Mike Cooke, Oxford Instruments Plasma Technology

1:30pm **ALE+AF-MoA-1 *In situ* Spectroscopic Methods for Atomic Layer Etching and Atomic Layer Deposition*, Yves Chabal,*** *J Klesko, A Dangerfield, J Veyan,* University of Texas at Dallas **INVITED**

As a relatively new technique, Atomic Layer Etching requires a fundamental understanding of the surface chemical processes that govern its operation. Most reported ALE processes are based on halogenation reactions followed by ion or noble gas atom bombardment, but there have recently been promising thermal ALE developments based on sequential fluorination and ligand exchange reactions. In all cases, knowledge of the fluorinated surface species and resulting surface composition after bombardment or exchange reactions is helpful to derive a mechanistic understanding of the surfaces. Such knowledge requires *in situ* characterization, in particular chemical bonding information that can be derived from vibrational spectroscopy.

We have developed reactors that can be used both for ALD and ALE, in which *in situ* IR spectroscopy is performed either in transmission for semiconductor substrates or reflection for metaling substrates, to examine gas phase or plasma-induced processes. We have also developed an ultra-high vacuum cluster tool in which IR spectroscopy, X-ray photoemission and Low Energy Ion Scattering can be performed on substrate subjected either to gas phase exposures or plasma treatment (remote plasma). Examples will be presented, taken mostly from ALD studies, which illustrate how mechanistic information can be derived from *in situ* IR spectroscopy, including the interaction of plasmas with oxides, nitrides and metal alloy films and the role of TMA in either stabilizing interfaces or enhancing surface reactions in ALD processes.

A schematic drawing of UHV cluster tool with in situ IR spectroscopy, XPS and LEIS is shown below.

2:00pm **ALE+AF-MoA-3 An *in situ* Optical Diagnostic Study of the Process Conditions that Affect the Etch per Cycle in ALE of SiO_2*,*** *S Agarwal,* ***Ryan Gasvoda,*** *N Leick,* Colorado School of Mines*; A van de Steeg,* Eindhoven University of Technology, Netherlands*; R Ovanesyan, J Klein,* Colorado School of Mines*; R Bhowmick, E Hudson,* Lam Research Corp.

With the advent of 3-D architectures in semiconductor devices combined with shrinking device dimensions, precise patterning requirements pose new challenges for conventional plasma etching. One recently proposed technique to address the limitations of continuous plasma etching is atomic layer etching (ALE), which can simultaneously enable directional control, etch selectivity, and atomic-level removal rates. ALE has been extensively studied for a variety of materials including Al_2O_3, HfO_2, Si, and silicon-based dielectrics. In this study, we have explored the atomistic-level details of an ALE process for SiO_2 based on a CF_x deposition step using a C_4F_8/Ar plasma, which is followed by an ion-assisted Ar plasma activation step to release the fluorine in the CF_x film for SiO_2 etching.

Specifically, we used *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and *in situ* four-wavelength ellipsometry during ALE of SiO_2 to monitor the surface composition, and the net SiO_2 and CF_x film thickness, respectively. Infrared spectra recorded after the CF_x deposition half-cycle (spectrum in blue in Fig. 1) predominantly shows an increase in CF_x (x = 1, 2, 3) stretching vibrations at ~1230 cm$^{-–1}$, but it also shows very weak C-O-Si and SiF_x (x = 1, 2, 3) stretching vibrations at ~1110 and ~970 – 1000 cm^{-1}, respectively. Given that the latter two vibrational bands appear as weak features, this indicate that a very thin mixing layer is formed at the SiO_2-CF_x interface compared to continuous etching of SiO_2.

After exposing the CF_x film on SiO_2 to an Ar plasma for 10 s, the spectrum in dark green in Fig. 1 clearly shows the simultaneous removal of SiO_2 and CF_x during Ar^+ activation. Further exposure to Ar plasma continues the etch of SiO_2 until the CF_x layer is completely removed as seen in the next four spectra. The last 10 s of Ar plasma exposure (red spectrum in Fig. 1) shows continued SiO_2 etching even after the removal of CF_x layer, which indicates that there is an additional source of etchant in the reactor. Sequential ALE cycles also show an increase in the etch per cycle as a function of cycle number (Fig. 2). This increase occurs even though the infrared spectra confirm that the deposition step remains reproducible from cycle to cycle as also seen in the inset in Fig. 2. Therefore, the increase in the etch per cycle occurs due to the Arplasma half-cycle as Ar^+ liberate CF_x radicals from the reactor walls that participate in the etching process. This chamber wall effect manifests as an increase in the etch per cycle since CF_x film accumulates on the chamber walls and, therefore, more F is available for etching in later cycles.

2:15pm **ALE+AF-MoA-4 New Innovative Etching Approaches for Future Generation by Controlling the Surface Reaction at Atomic-Level*, Masanobu Honda,*** *T Katsunuma,* Tokyo Electron Miyagi Ltd., Japan **INVITED**

A new technology has been developed using the Atomic Layer Etching (ALE) and Atomic Layer Deposition (ALD) concepts. It has been applied to self-aligned contacts (SAC) and patterning processes, for the sub 7nm technology generation.

In the SAC process, ultra-high selectivity of SiO_2 etching towards SiN is required, for which we have developed Quasi-ALE technique for SiO_2 etching. We were able to significantly improve the trade-off between the etching ability of SiO_2 on the micro slit portions and SiN selectivity. Quasi-ALE precisely controls the reaction layer thickness of the surface, by controlling the radical flux and ion flux independently, and hence enables etching at lower ion energies.

On the other hand, in the patterning processes, the shrinking of critical dimensions (CD) without loading is mandatory. Therefore, we developed a new process flow that combines ALD technique and etching. With this method, we were able to achieve CD shrinking at atomic-layer level precision for various patterns, without causing CD loading. In addition, we were also able to uniformly control the CD shrinkage amount across the whole wafer. This is because this technique takes advantage of the deposition step which is independent of the pattern density and the location on the wafer by self-limited reactions.

As discussed earlier, the fine processing technology will become more important for future generation. In recent years, to meet the highly complex requirements imposed by device fabrication processes, alternative process was developed for thin layer etching [1]. We have made several improvements on this new approach and applied it to various etching processes [2]. In the presentation, the newly improved approach will also be introduced in addition to Quasi-ALE and CD shrinking technique without causing CD loading.

1. N Posseme, O Pollet and S Barnola 2014 Alternative process for thin layer etching: Application to nitride spacer etching stopping on silicon germanium Applied Physics Letters105 051605

2. Sonam D Sherpa and Alok Ranjan 2017 Quasi-atomic layer etching of silicon nitride J. Vac. Sci. Technol. A 35 01A102

2:45pm **ALE+AF-MoA-6 Controlled Layer-by-Layer Etching of ALD Grown Ta_2O_5 Thin Films*, Anil Mane,*** *J Elam,* Argonne National Laboratory

Precisely controlled layer-by-layer etching processes for metal oxide films are required to enable the fabrication of 3D-microelectronic devices such as semiconductor memories, logic, and MEMS. Ta_2O_5 is a high-k dielectric and is useful in flash memory as well as resistive random access memory (RRAM) devices. Here we developed a precisely controlled layer-by-layer etching process for Ta_2O_5 thin films using alternating exposures to MoF_6 and H_2O vapors. For example, etching of ALD Ta_2O_5 thin films deposited using either $TaCl_5$ or TaF_5 and H_2O can be perform in either a one-step, chemical vapor etching manner (CVEt) or in a layer-by-layer self-limiting controlled manner (ALEt). We used in-situ quartz crystal microbalance (QCM) measurements to monitor the deposition and etching of the Ta_2O_5 layers (Figure 1). Next, the etched Ta_2O_5 thin films were analyzed by spectroscopic ellipsometry to determine the thickness and refractive index. These ex-situ measurements confirmed the findings from our in-situ QCM studies. Here we will discuss the details of the self-limiting ALD growth and etching of Ta_2O_5 Thin films.

3:00pm **ALE+AF-MoA-7 Atomic Layer Etching Mechanism of 2D MoS_2 Layers***, **Ki Seok Kim**, K Kim, Y Ji, G Yeom,* Sung Kyun Kwan University, Republic of Korea

The single MoS_2 monolayer has a $S_{(top)}$-Mo-$S_{(bottom)}$ crystal structure that is consisted of a three-atom-thick covalent bonds between Mo and S atoms; thereby, the ALE mechanism using Cl as the adsorption species and Ar^+-ion as the desorption species can be quite different from other two-dimensional (2-D) materials with one-atom-thick materials such as graphene. We have investigated that the MoS_2 ALE mechanism from bilayer MoS_2 to monolayer MoS_2 using controlled Cl radical adsorption and Ar^+-ion desorption as a function of Ar^+-ion desorption time with a monoenergetic Ar^+-ion energy of 20 eV. The result showed that Cl atoms are adsorbed on top S atoms and trapped between top S atoms and Mo atoms by van der Waals force during the Cl radical adsorption. The reults also showed that the monolayer MoS_2 is sequentially removed from the top S atoms by S-Cl, Mo by Mo-Cl, and bottom S atoms by selective sputtering. XPS data showed no change of chemical composition and no structural damage on the exposed 2nd MoS_2 layer after one-cycle ALE. In addition, the MoS_2 FET fabricated with the monolayer MoS_2 obtained after the one-cycle MoS_2 ALE of a bilayer MoS_2 exhibited the similar electrical charteristics as those fabricated with a pristine monolayer MoS_2, therefore, nearly no electrical damage on the MoS_2 layer was ocurred by the MoS_2 ALE process. It is believed that the ALE technique used in the experiment can be applicable to all the layered TMD materials including MoS_2 for next generation nano-devices.

3:15pm **ALE+AF-MoA-8 ALD & Quasi-ALE Patterning Application in EUV Contact Etch***, **Hongyun Cottle**, D O'Meara, A Metz,* Tokyo Electron Limited*; P Biolsi,* TEL Technology Center, America, LLC*; S Nakamura, T Yang,* Tokyo Electron Limited*; M Honda,* Tokyo Electron Miyagi Ltd., Japan*; S Morikita,* Tokyo Electron Limited

Continued pitch scaling of semiconductor devices to 7nm node and beyond utilizing conventional 193i based multiple patterning techniques is rapidly driving up cost, complexity, and variability control. EUV patterning can be used to mitigate or delay the challenges of pitch scaling through multiple patterning, but introduces new challenges of its own. EUV lithography introduces new types of resists that are thinner and less etch resistant compared to conventional 193nm resists. Interactions of polymers with plasma etch environments can lead to large changes of the polymer material properties and the three-dimensional nanostructures they pattern. Mask deformation during such etch process can lead to changes in nanoscale topography of device features, often with undesirable consequences, such as increased LER and LWR, tip-to-tip degradation, and line wiggling. Plasma etch faces a significant challenge to optimize its process window to enable high yields with EUV patterning.

This paper presents the synergetic combination of ALD & Q-ALE in EUV contact mask etch to overcome the above-mentioned EUV lithography changelings. ALD application at mask open level improves incoming LWR/LER and defines what can be transferred to final etch product. Q-ALE mask open improves EUV photoresist etch selectivity by greater than three-fold while maintaining critical feature dimensions, such as elliptical contact minor vs major axis CD ratio. By utilizing a direct current superposition (DCS) technology, EUV photoresist can also be treated to improve not only its etch resistant, but also LER and LWR. These unique processes (ALD vs. Q-ALE vs. DCS) can be applied independently or in combination utilizing Tokyo Electron advanced etchers. Through their accumulative effects, these processes offer a wide range of etch capabilities to enable EUV lithography to 7nm and beyond.

Reported is the structural characterization pre and post-etch detailing LER and LWR improvement, and shrink ratio control. In addition, a mechanistic model will be proposed based on thin film compositional analysis and process trend data.

4:00pm **ALE+AF-MoA-11 Boron Nitride Growth at Room Temperature Using Electron Enhanced Atomic Layer Deposition (EE-ALD)***, **Jaclyn Sprenger**, H Sun, A Cavanagh, S George,* University of Colorado - Boulder

Electron-enhanced atomic layer deposition (EE-ALD) can drastically reduce the temperatures required for film growth. This temperature reduction occurs because electrons can desorb surface species by electron stimulated desorption (ESD) to create very reactive "dangling bonds". Precursors can then adsorb efficiently on the dangling bonds. EE-ALD lowers the thermal budget and enables the deposition of thin films on thermally sensitive substrates. EE-ALD has been demonstrated previously for the deposition of polycrystalline GaN [1] and amorphous Si [2] at room temperature.

BN film growth by EE-ALD was performed at room temperature on Si (111) substrates using alternating doses of borazine ($B_3N_3H_6$) and low-energy electrons. Borazine is a single-source precursor for BN deposition. *In situ* ellipsometry was performed during the BN EE-ALD. These ellipsometry measurements yielded a linear growth rate of ~0.45 Å/cycle for electron energies of 100 eV with an electron current of 100 μA for 60 s. This *in situ* growth rate was confirmed by *ex situ* spectroscopic ellipsometry. A BN film with a thickness of 90 nm was deposited after 2000 EE-ALD cycles (see supplemental Figure 1).

Film composition was studied with *ex situ* XPS (see supplemental Figure 2). The BN composition is consistent throughout the film with a B/N ratio of 1.3/1. The films are pure with C and O concentrations of only <3 at.% in the bulk of the film. A thin, self-passivating surface oxide resulting from atmospheric exposure is present. In addition, *ex situ* FTIR transmission was performed on the BN films. These FTIR measurements yielded an absorption peak at ~1370 cm^{-1} that is consistent with hexagonal BN.

Doubling the electron emission current used for BN film growth from 100 μA to 200 μA with exposure times of 60 s yielded slightly lower film growth rates. However, these films had a higher measured index of refraction. This suggests that an electron current of 100 μA may be sufficient to remove all the surface hydrogen in the electron beam. The fairly flat BN thickness spatial profiles are also consistent with self-limiting hydrogen desorption. The higher electron current of 200 μA for 60 s does appear to increase the film density.

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4:15pm **ALE+AF-MoA-12 Catalyzed Atomic Layer Deposition of Silicon Oxide at Ultra-low Temperature using Alkylamines***, **Tirta Rona Mayangsari**, J Park, L Yusup, J Gu,* Sejong University, Republic of Korea*; J Yoo, H Kim,* JUSUNG Engineering, Republic of Korea*; W Lee,* Sejong University, Republic of Korea

The dielectric spacer in multipatterning process such as self-aligned double patterning (SADP) or self-aligned quadruple patterning (SAQP) has been adopted to increase the density of line pattern with only single exposure. Deposition of the dielectric spacer directly on the photoresist patterns instead of the hardmask patterns would reduce several process steps. For this purpose, ultra-low temperature deposition of the spacer film is highly required to avoid the distortion of the underlaying photoresist patterns. Atomic layer deposition (ALD) processes of SiO_2 dielectric thin film at ultra-low temperature have been studied by using pyridine catalyst [1] or O_2 plasma [2]. Catalyzed ALD of SiO_2 is especially suitable for the cost-effective SADP or SAQP process flow, because it can avoid the damages of the underlying photoresist patterns by O_2 plasma. However, in the catalyzed ALD process using pyridine, the generation of salts is still an issue as a result of reaction between the catalyst and ALD reaction byproducts, HCl [3]. To resolve this issue, catalyst having less reactivity with HCl is needed. In the present study, we simulated the reaction of various catalysts with HCl as well as the interaction between catalysts and precursors by density functional theory (DFT) calculation.

Lewis-base amine catalysts with different alkyl ligand and hydrogen concentration were studied, and silicon chlorides with different numbers of silicon and chlorine atoms were investigated. The length and the energy of hydrogen bond between catalyst and water molecule were calculated for each catalysts to expect the catalytic activity, and the energies of the formation and desorption of the catalyst-HCl salt were also calculated. The effects of molecular structures of catalysts and silicon precursors on the catalytic activity and the salt formation were confirmed by in-situ FTIR analysis. Finally, the growth rate, the chemical composition, and the step coverage of the deposited films were analyzed for different combinations of catalyst and silicon precursor.

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4:30pm **ALE+AF-MoA-13 Low Resistance ALD TiN from Low Temperature Thermal N_2H_4 + $TiCl_4$*, Steven Wolf,*** *M Kavrik, J Park,* University of California San Diego*; R Holmes, D Alvarez, J Spiegelman,* RASIRC*; A Kummel,* University of California San Diego

Titanium nitride (TiN) has been extensively studied in semiconductor devices because of its ideal thermal, mechanical, and electrical properties and its ability to act as a metal diffusion barrier [1]. ALD TiN has previously been performed using a wide range of Ti precursors including halides (i.e. TiI_4, $TiCl_4$) and metal organics (i.e. TDMAT, TEMAT), as well as nitrogen sources (thermal/plasma NH_3, N_2/H_2, etc). Metal halide precursors are preferred over metal organic grown films that typically contain high levels of carbon and oxygen contamination; this contamination has been correlated with an increase in TiN film resistivity [2]. Plasma enhanced-ALD TiN has been shown to achieve optimal growth rates with lower contamination at temperatures below 350°C, but the film and underlying substrate can suffer from plasma induced damaged [1,3]. In this study, low temperature thermal ALD TiN from anhydrous N_2H_4 and $TiCl_4$ was performed on a SiO_xN_y substrate, and the deposited films were studied using x-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), and atomic force microscopy (AFM). In addition, the resistivity of thin TiN films was measured using a modified four-point probe measurement, in which 30nm thick Ni dots with 150µm diameter and 250µm spacing were deposited on top of ALD TiN films.

SiO_xN_y substrates underwent an ex-situ degrease procedure with acetone, methanol and water before being loaded into vacuum. A 275°C UHV anneal was performed to remove surface hydrocarbon. Subsequent cycles of TiN ALD at temperatures between 275°C and 350°C were performed resulting in an estimated 3nm thick film with a Ti/N ratio of ~3/4 with chlorine comprising ~10% in the normalized XPS spectrum. Uniform deposition with subnanometer RMS roughness was seen from STM and AFM measurements. After depositing Ni dots and performing a modified four-point probe measurement, film resistivity was estimated at ~176 µΩ-cm. In conclusion, the thermal low-temperature TiN ALD using anhydrous N_2H_4 and $TiCl_4$ was performed and the subsequent low impurity TiN film's chemical, topographical and electrical properties were characterized.

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4:45pm **ALE+AF-MoA-14 Study of the Isotropic Behavior of AZO Conductivity Deposited by Atomic Layer Deposition - Effect of Film Thickness*, Benoit Dugrenil,*** Microoled - CEA Leti, France*; S Guillamet, M Thomschke,* Microoled Company*; M Tournaire, B Aventurier, L Mollard, T Maindron,* CEA-Leti, France

Keywords: ALD, TCO, transparent electrode, OLED, anisotropic conductivity

Al-doped ZnO (AZO) is one of the most recently studied Transparent Conductive Oxides (TCO), especially because of its numerous attractive properties as electrode in OLED, OPV or OTFT. Atomic Layer Deposition (ALD) allows a precise control of AZO performances versus deposition temperature, doping ratio and thickness. Conventional AZO measurements using four-point probe setup or Hall effect (fig 1 a) are mainly representative of the combination of vertical and lateral conductivity of the film. However, when those TCO have to be integrated into an OLED stack as transparent electrode, carrier injection is made in the vertical direction (fig 1 b). We believed that AZO is an anisotropic material, particularly because of its growth as nanolaminate, i.e. alternating ZnO bulk layers with Al_xO_y interlayers in ALD mode.

In this work, we want to study the anisotropy of the electrical conductivity of AZO films, as depicted in figure 1 a and 1 b. Furthermore, as the AZO film thickness impacts the electro-optical characteristics, its influence on the vertical conductivity needs to be highlighted.

We firstly investigated the major differences between very thin films (approximately 10 nm), and thicker AZO (60 nm, 110 nm) deposited on 200 mm silicon and silicon oxide wafers, respecting exactly the same growth conditions. The resistivity decreases from ~ 100 mΩ.cm for very thin films to 3 mΩ.cm when the thickness is increased above a hundred of nanometers. Identical variations have been measured for the square resistance and are consistent with other studies [1]. These trends are known and can be attributed to the growth parameters like preferential orientation, nucleation delay and ionized impurities scattering [2, 3].

In a second step, the same AZO recipes were deposited onto structured TiN layers, where the TCO films can be evaluated in the OLED configuration, as an anode (fig 1 b). In order to correlate the AZO behavior in both configurations and function of the deposited thicknesses, attention will be carried out on crystalline profile using XRD measurements and onto electro-optical characteristics of the OLED.

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5:00pm **ALE+AF-MoA-15 Growth Behaviour and Stability of Atomic Layer Deposited MoO_3 by $Mo(CO)_6$ and H_2O/O_3 Precursors*, Perttu Sippola,*** Aalto University, Finland*; Z Zhu,* Beneq Oy*; T Sajavaara,* University of Jyväskylä, Finland*; H Lipsanen,* Aalto University, Finland

Molybdenum trioxide has been shown to be a lucrative material e.g., for catalysis [1] and electrochromic applications [2]. This applicability can be credited to the multitude of oxidation states and polymorphs of the compound. Despite MoO_3 complex chemistry, ALD presents a promising and efficient way of growing amorphous MoO_3 thin films. Still, mainly the *in-situ* growth and annealing behavior has been studied. [3] Therefore, we present a growth, structure and chemical analysis of as-deposited MoO_3 ALD thin films.

MoO_3 thin films were deposited on silicon with Beneq TFS-500 using $Mo(CO)_6$ and H_2O/O_3. The effect of precursor doses to the growth behavior and physical properties was studied immediately after the ALD with ellipsometry and later with XRR. Moreover, chemical and elemental analysis with ATR-FTIR and ToF-ERDA, respectively, were performed.

With ellipsometry, the ALD-window of the process was determined to be approximately in the range of 165-175 °C. Thus, deposition temperature of 170 °C was selected. The pulse time saturation of 55 °C heated $Mo(CO)_6$ was studied to take place around 2 s. The overlapping H_2O/O_3 pulsing time ratio in seconds was varied from 0/2-3/2. The O_3-only precursor yielded GPC of 0.65 Å/cycle and for the H_2O added pulses GPC was 0.75 Å/cycle. The ATR-FTIR spectra showed that unlike the other samples, the 2/2 mixture did not had an emphasized band at ~3650 cm^{-1} which is usually attributed to the presence of –OH groups.

The further studies suggest that prolonged storage of the samples in ambient conditions produced structurally differing surface layer on top of the original MoO_3 thin films. The XRR analysis showed a surface layer of 6 nm with a density of 2.8 g/cm^3 on average while the underneath MoO_3 layer showed density of 4.3 g/cm^3. Also, the refractive index value reduced on average from 2.03 to 1.90 between the fresh and aged samples. Moreover, the ToF-ERDA elemental depth profile results revealed that the C (2.5 at.%), H (14 at.%) and N (3.1 at.%) impurities are concentrated to the surface in the thin films. Still, the average O/Mo ratio was 3.1, being very close to stoichiometric.

Due to the presence of the parasitic surface layer, valid differences on the structural and elemental constitution of the different samples could not be identified. Therefore, this research concludes that the $Mo(CO)_6$ and H_2O/O_3 ALD thin films are not chemically stable in ambient conditions without further in-line-processing such as surface passivation.

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5:15pm **ALE+AF-MoA-16 Characterization of Al_2O_3 and HfO_2 Grown on Metal Surfaces with Thermal and Plasma Enhanced Atomic Layer Deposition*, Haiping Zhou,*** *Y Fu, M Mirza,* University of Glasgow, UK

Atomic layer deposition (ALD) is potentially a very suitable deposition technology to grow ultra thin films with excellent thickness control, good conformity on high aspect ratio structures, and less defects. Al_2O_3 and HfO_2 are well-established high-k materials to replace SiO_2 in transistor and capacitor applications. To grow high quality ALD films with low leakage current, high breakdown electric field and dielectric constant, it is important to understand the impact of both plasma enhanced ALD (PEALD) with O_2-plasma and thermal ALD with H_2O on the interface between ALD film and substrate surface, and also the impact of the interface on the quality of ALD films.

We present the electrical and chemical characterizations of Al_2O_3 and HfO_2 films directly grown on Au, Ti and TiN surfaces. Metal Insulator Metal (MIM) capacitors with 10nm of Al_2O_3 or 10nm of HfO_2 as a dielectric layer were realized. Our results show that (1) the Al_2O_3 film grown by TMA metallic precursor and O_2-plasma has the highest breakdown electric field of 6.74 MV/cm, and the lowest leakage current of 8.6e-8 A/cm^2 at 2 MV/cm, which indicate that this 10nm of Al_2O_3 layer is high quality dielectric film with low pin-hole density and defects; (2) the HfO_2 film grown by TEMAH metallic precursor and H_2O has the lowest breakdown electric field of 3.95 MV/cm, and the highest leakage current of 7.6e-7 A/cm^2 at 2 MV/cm, which indicate that this 10nm of HfO_2 film has more pin-holes and defects; (3) the Al_2O_3 film grown by TMA and H_2O, and the HfO_2 film grown by TEMAH and O_2-plasma have the breakdown electric fields of 6.56 and 4.28 MV/cm, and the leakage currents of 2.40e-7 and 2.33e-7 A/cm^2 at 2 MV/cm, respectively; (4) both the Al_2O_3 and HfO_2 films grown by the PEALD with O_2-plasma show better qualities than that grown by the thermal ALD with H_2O; (5) the Al_2O_3 and HfO_2 with O_2-plasma processes do not show plasma-induced damage based on the tests of Van der Pauw (VdP) samples made from InGaAs-InAlAs layer structure with channels buried ~ 30 nm from the surface.

To further investigate, understand and optimize the ALD processes, Auger energy spectroscopy (AES) and high-resolution scanning Auger microscope (SAM) are used to analyze the chemical compositions and distributions in the interface between the ALD films (Al_2O_3 and HfO_2 grown with O_2-plasma and H_2O) and the metal surfaces (Au, Ti and TiN) without exposing the ALD films to air.

Emerging Materials
Room Plaza E - Session EM+AA-MoA

Organic-Inorganic Hybrid Materials & MLD (1:30-3:30 pm)/Catalysis and Fuel Cells II (4:00-5:30 pm)

Moderators: Sang In Lee, Synos Foundation, Yongfeng Mei, Fudan University, China, Ville Miikkulainen, University of Helsinki

1:30pm **EM+AA-MoA-1 Unique Inorganic-Organic Hybrid Materials by ALD/MLD as Enablers of Next-generation Applications?*, Maarit Karppinen,*** Aalto University, Finland **INVITED**

The combined ALD/MLD approach has the capacity to yield unique functional hybrid materials, consisting of finely-tuned combinations of inorganic and organic components and possessing a property palette that may reach properties even beyond those directly derived from the component inorganics and organics. These materials are formed through different bonding schemes and may be amorphous or crystalline, isotropic or organized into different superlattice structures. Our recent works[1-9] have demonstrated e.g. exciting coordination-network or MOF-type crystal structures, attractive heat and Li-ion conduction properties, and various luminescence phenomena, relevant to next-generation applications in e.g. flexible heat harvesters, photoconverters, microbatteries, sensors or catalysts.

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2:00pm **EM+AA-MoA-3 Atomic/molecular Layer Deposition of Luminescent Inorganic-Organic Hybrid Erbium Pyridine Dicarboxylate Thin Films*, Lukas Mai,*** Ruhr-University Bochum, Germany*; Z Giedraityte,* Aalto University, Finland*; M Schmidt, D Rogalla, S Scholz, A Wieck,* Ruhr-University Bochum, Germany*; M Karppinen,* Aalto University, Finland*; A Devi,* Ruhr-University Bochum, Germany

Erbium containing thin film materials are often used in amplifiers, detectors or LEDs because of the specific luminescence of Er^{3+} at ~1500 nm.[1] In fact, the absorption coefficient of Er^{3+} ions is too low for practical utilization. In order to enhance the luminescence, either the concentration of the erbium ions can be decreased or an organic molecule, which is sensitizing the Er^{3+}, can be used.[2] To introduce a sensing organic molecule into a thin film to produce an inorganic-organic hybrid material, exhibiting a low erbium concentration and a defined stoichiometry, the atomic/molecular layer deposition (ALD/MLD) technique is the method of choice. Here, for a complete reaction, the reactivity of the two precursors toward each other must be sufficient.[3] For the ALD of erbium oxide thin films, tris(N,N'-diisopropyl-2-dimethylamido guanidinato)erbium(III) or [Er(DPDMG)$_3$] shows high potential, as the all-nitrogen coordinated complex exhibits a high reactivity toward oxygen functionalities.[4] In addition, it was shown that 3,5-pyridine dicarboxylic acid (3,5-PDA) can be used organic precursor in an ALD/MLD processes as a sensing ligand for the excitation of europium.[5]

Here, the successful combination of [Er(DPDMG)$_3$] and 3,5-PDA in an ALD/MLD process is presented.[6] The usage of the guanidinate precursor resulted in high growth rates compared to common rare earth precursors, such as β-diketonates ([Er(THD)$_3$]). Furthermore, we investigated the typical ALD characteristics, including surface saturation for the applied precursors, linearity of thickness vs. cycles and an ALD window between 250 °C and 265 °C, proving a true ALD/MLD process (Figure 1). From Rutherford-Backscattering (RBS) experiments, nearly stoichiometric erbium 3,5-pyridine dicarboxylate ([Er_2(3,5-PDC)$_3$]) was found to be deposited. The thin film structure was confirmed by FT-IR spectroscopy, indicating the reaction between the precursors takes place by deprotonation of 3,5-PDA and subsequent coordination of the nitrogen functionality toward the erbium-ion. From UV-Vis investigation (Figure 2, left), a strong absorption at 270 nm was detected and assigned to the absorption of the organic molecule. Furthermore, by direct excitation of different electronic states of the erbium ions, a sharp photoluminescence emission at 1535 nm arises (Figure 2, right). Here, intensity could be increased with decreasing erbium concentration.

The obtained results show the distinct advantage of using a well-developed inorganic precursor such as [Er(DPDMG)$_3$] in combination with different organic molecules for ALD/MLD processes in order to produce novel materials that can be precisely tailored for various applications.

2:15pm **EM+AA-MoA-4 Molecular Layer Deposition of Manganese-Ethylene Glycol Hybrid Films*, David Bergsman,*** *J Baker, N Yang, C MacIsaac, A Strickler, M Lillethorup, S Bent,* Stanford University

Manganese oxide films have shown potential as earth abundant catalysts for various reactions, including the oxygen evolution and reduction reactions (OER and ORR, respectively), the reduction of hydrogen peroxide, and as a promoter for the Fischer-Tropsch reaction. Because of this, many methods have been developed for depositing manganese-based materials, including incipient wetness impregnation and atomic layer deposition (ALD). However, in recent years, there has been increased effort towards the nanostructuring of materials, driven in part by the desire to increase surface-to-volume ratios, tune reaction site chemistry, and improve catalyst stability. One promising method for depositing nanostructured manganese films is hybrid organic-inorganic molecular layer deposition (MLD). By combining a metal precursor typically associated with atomic layer deposition and an organic counter reactant monomer associated with MLD, films of catalytically relevant materials can be grown with a carbon-based component that can be easily removed, allowing for further nanostructuring.

Here, we discuss the deposition of a hybrid organic-manganese film using MLD and the precursors bis(ethylcyclopentadienyl)manganese and ethylene glycol. As-deposited films are characterized using a combination of spectroscopic ellipsometry (SE), Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy (XPS) to verify the self-limiting nature of this layer-by-layer process and the successful reaction of the precursors. Time-resolved SE suggests that the organic component of the films is unstable in air over a time frame that can be controlled through the addition of a blocking layer or through chemical and temperature treatments. Characterization of the stabilized and degraded films with atomic force microscopy, scanning electron microscopy, x-ray reflectivity, and XPS show the extent of organic degradation and removal. Finally, the results of testing the manganicone films for use as a catalyst, including the OER/ORR reaction, will be discussed.

2:30pm **EM+AA-MoA-5 Synthesis, Characterization, and Electrochemistry of Molybdenum-1,2-Ethanedithiol Hybrid ALD Films***, **Callisto MacIsaac**, R Closser, J Schneider, T Hellstern, D Bergsman, S Bent,* Stanford University

Hybrid atomic layer deposition-molecular layer deposition (ALD/MLD) is a self-saturating, layer-by-layer, gaseous technique for depositing thin, conformal thin films that involves both the typical metal-containing precursors used in ALD and the organic linkers of MLD. The combination of ALD and MLD chemistries enables the creation of hybrid materials that incorporate the properties and benefits of the parent materials, with the opportunity to create new electrical, magnetic, and catalytic properties. The exploration of novel gas-phase chemistries and unique new types of inorganic-organic thin films is therefore of interest both for the fundamental chemistry and for potential wide-ranging applications.

One such application is the production of hydrogen, a clean, energy-dense fuel that can be formed by the electrochemical splitting of water. Platinum is considered the ideal catalyst for the hydrogen evolution reaction (HER) due to its low overpotential; however, it is costly and scarce. One promising substitute for platinum is MoS_2, a cheap but highly active and stable alternative whose catalytic properties are well-known. However, the HER activity of crystalline MoS_2 is limited to the exposed edge sites of the MoS_2 sheets, since the basal planes are chemically inert. This has led to the investigation of a variety of novel MoS_2 nanoarchitectures ranging from nanowires, supported nanoparticles, and 3D patterned networks in an effort to increase the number of the active edge sites relative to what is present in MoS_2 sheets. Here, we introduce a novel material that incorporates the –S-Mo-S- chemical moiety of MoS_2, yet has organic linkers that create a porous matrix for these MoS_2-like domains, as an alternative HER catalyst. Further, these organic linkers can be removed using sulfurization to introduce catalytically active edge sites.

This work investigates in detail a novel hybrid ALD-MLD process from the precursors $Mo(CO)_6$ and 1,2-ethanedithiol, with a focus on the film growth behavior and structure. Fourier transform infrared spectroscopy, X-ray diffraction, X-ray reflectivity, Raman spectroscopy, variable angle spectroscopic ellipsometry, and X-ray photoelectric spectroscopy are utilized to characterize the resultant material. This work further details proof-of-concept experiments using the Mo-ethanedithiol hybrid films as a catalyst for HER. The results show that the catalyst is active for HER, with a lower overpotential at 10mA/cm^2 and a higher current density on a geometric basis compared to flat MoS_2. The study offers insight into the possibility of other organic-inorganic materials with similar properties that can be deposited in an ALD-regime.

2:45pm **EM+AA-MoA-6 Ultrahigh Elastic Strain Energy Storage in Metal-Oxide-Infiltrated Polymer Nanopillars Generated by Infiltration Synthesis***, **Chang-Yong Nam**,* Brookhaven National Laboratory*; K Dusoe,* University of Connecticut*; A Stein, X Ye, K Kisslinger,* Brookhaven National Laboratory*; S Lee,* University of Connecticut

Infiltration synthesis is a type of inorganic-organic hybridization technique derived from atomic layer deposition, where the material precursors infiltrate into polymer medium, generating unique organic-inorganic hybrids. Here, we report the generation of an organic-inorganic hybrid nanostructure having an exceptional ability to store elastic strain energy, whose mechanical modulus of resilience for a given density exceeds what is observed in most engineering materials. Lithographically patterned polymer nanopillars with ~300 nm diameter and 1 µm height from a negative-tone resist SU-8 were subjected to the infiltration synthesis of AlO_x using trimethylaluminum (TMA) and water as precursors, creating unique composite nanopillars in which an interpenetrating polymer-AlO_x hybridized matrix extended down to ~50 nm below the surface. We performed the mechanical testing of the produced hybrid nanopillars by using an in-situ nanomechanical testing system based on a scanning electron microscope. The hybrid nanopillars after 16 cycles of AlO_x infiltration exhibited a high yield strength (500 MPa) which was accompanied by an unusually low Young's modulus (7.5 GPa) in uniaxial nanocompression tests, a unique combination of strength and modulus that has never been observed. The resulting apparent modulus of resilience, a parameter that quantifies the ability of storing elastic energy, was over 16,000 kJ/m^3, the highest among the known values. Consequently, this is translated into the specific modulus of resilience higher than most engineering materials. The infiltration-synthesized composite nanopillars combine the exceptional, tunable mechanical resilience with the compatibility with lithographic techniques, promising potential applications in micro- and nanoelectromechaical systems which require ultrahigh-elastic components for advanced actuation and sensor devices.

3:00pm **EM+AA-MoA-7 Kinetics of Vapor Phase Infiltration: Fitting Theory to Experimental Measurements***, C Leng, **Mark Losego**,* Georgia Institute of Technology

Vapor phase infiltration (VPI) is an emerging processing technology for infusing polymers with inorganic constituents to create new organic-inorganic hybrid materials with novel electrical, chemical, and/or physical properties. These new materials can have applications as chemical barriers, filtration media, or photolithographic hard masks. Here, the focus is to have a better knowledge of the diffusion and reaction kinetics during this vapor phase infiltration process with the goal of understanding how both polymer structure and processing conditions can maximize the depth of inorganic infiltration. In this study, we use the model system of poly(methyl methacrylate) (PMMA) films exposed to trimethylaluminum (TMA) gaseous precursors. A basic kinetics model has been developed to describe the diffusion and reaction processes in VPI and has been fit to experimental data. From spectroscopic ellipsometry we are able o track total infiltration based upon film swelling and changes in refractive index. At a process temperature of 60°C, films are found to initially swell with the square root of time, suggesting that kinetics are dominated by Fickian-like diffusion behavior. A maximum film swelling of 60% is measured at any exposure time exceeding 1000 minutes. Using these swelling curves as a proxy for infiltration amount, we calculate effective diffusion coefficients for TMA in PMMA at 60^o C to be on the order of 10^{-15} cm^2/s, with faster diffusion in PMMA films of lower molecular weight. At higher temperatures (160^o C), swelling is less significant, but refractive indices of infiltrated films increase by 2% to 3%. We interpret the decrease in swelling as a result of faster chain relaxation when processing above the glass transition temperature of the polymer. To determine whether polymer films infiltrated and swollen below T_g can also undergo similar polymer relaxation behaviors, a systematic study of post-annealing was carried out at 150^o C. In these instances, the amount of swelling decreases by approximately half and refractive index increases but to a lesser degree than those from the initial high process temperatures. The results of this study will be put in context with other ongoing research in the field to help build a phenomenological model that can be used to better design vapor phase processing schemes to form organic-inorganic hybrid materials.

3:15pm **EM+AA-MoA-8 Vapor Phase Infiltration for Doping Conducting Polymers***, W Wang, F Yang,* CIC nanoGUNE, Spain*; C Chen, Y Qin,* Chinese Academy of Sciences, China*; **Mato Knez**,* CIC nanoGUNE, Spain

Vapor phase infiltration is a top-down strategy that is based on the ALD process and allows fabrication of organic-inorganic hybrid materials by incorporation of metal organic precursors into polymeric substrates. The growth of inorganic clusters or particles in the subsurface area of a polymer allows modifying some of the physical properties of the polymer greatly. While related earlier work investigated the improvement of mechanical properties of polymers applying the infiltration route, here we describe a novel approach, namely a single precursor infiltration process to dope polyaniline (PANI) or the polythiophene P3HT. The infiltration was performed with various precursors typically used in ALD processes. The conductivities were assessed with four-point probe measurements and showed significant enhancement by up to 6 orders of magnitude, confirming the efficiency of the infiltration process. Furthermore, we found that the thermal and temporal stability of the thus doped polymers were significantly enhanced in comparison to their traditionally wet-chemically doped counterparts. For example, conductivities of infiltration-doped PANI outperformthe conductivity of HCl-doped PANI if exposed to elevated temperatures (150 °C) in vacuum. In the case of P3HT, the infiltration-doped polymer maintains the gained conductivity even after exposure to ambient conditions for more than 30 days. The chemical changes resulting from the infiltration of the two polymers were characterized by FTIR and Raman spectroscopy and will be discussed. SEM micrographs showed that the morphologies of the samples did not alter after the infiltration process, being one of the most important arguments for doping conductive polymers in the presented way.

4:00pm **EM+AA-MoA-11 Catalysts Modified by ALD for Harsh Biomass Conversion Processes***, **Steven Christensen**, K Hurst, M Griffin, D Vardon,* National Renewable Energy Laboratory

Black liquor, fast pyrolysis, and bio-coke are terms that denote some of the challenges encountered from the feedstock, processes, and unwanted products of catalytic biomass conversion that ALD techniques can address. Catalysts developed for the petroleum industry often deactivate and degrade when applied to biomass applications. Furthermore, biomass can offer chemicals and fuels that cannot be derived from petroleum feedstock and therefore new catalyst formulations and properties are required. Research of catalytic materials for biomass conversion at the National Renewable Energy Laboratory is using ALD to reduce metal leaching, improve de-oxygenation catalysis, and tailor catalysts with novel properties. An overview of the challenges for biomass processing and strategies for how ALD catalysts can be designed to solve these problems will be presented. The production of bio-nylon precursors and catalytic fast pyrolysis of bio-oil will be used as examples. Advanced catalysts from ALD look to have an exciting future to help enable new technologies for this industry.

4:15pm **EM+AA-MoA-12 Effects of Alumina Incorporation by Particle Atomic Layer Deposition on Sintering and Microstructure of Yttria-Stabilized Zirconia (8YSZ)***, **Christopher Bartel**, R O'Toole, M Kodas, A Drake, A Horrell,* University of Colorado - Boulder*; R Hall,* ALDNanoSolutions, Inc.*; C Musgrave, A Weimer,* University of Colorado - Boulder

Yttria-stabilized cubic zirconia (YSZ) is the most-common electrolyte material for solid oxide fuel cells (SOFC) due to its reasonable oxygen-ion conductivity and chemical stability across a wide range of environments. To achieve suitable ionic conductivity, YSZ electrolytes must be near theoretical density; this necessitates high sintering temperatures, often exceeding 1450 °C. This high sintering temperature limits the viability of low-cost one-step sintering during manufacturing and thus increases the cost of SOFC fabrication. Previous researchers have successfully lowered the required YSZ sintering temperature through incorporation of aluminum oxide (Al_2O_3) particles with the YSZ. While this technique has proven to be successful in reducing the sintering temperature, the presence of particulate Al_2O_3 inclusions in densified parts reduces the homogeneity of the electrolyte which may have deleterious effects on operation. In this work, we report on the use of atomic layer deposition (ALD) to precisely and conformally coat individual YSZ particles with the desired amount of Al_2O_3. Constant-rate-of-heating (CRH) experiments were conducted using a horizontal push-rod dilatometer to extract the activation energy of sintering in the initial stage and also gain mechanistic insights into the active diffusion mechanisms as a function of ALD film thickness. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to characterize the as-deposited thin Al_2O_3 films and the effects of the Al_2O_3 films on grain growth and microstructure during densification. Al_2O_3 incorporation by ALD is shown to have unique phenomenological effects on the densification of YSZ as compared with conventional Al_2O_3 incorporation using particle-based approaches.

4:30pm **EM+AA-MoA-13 Low-Temperature ALD Cobalt Sulfide for High-Efficient Hydrogen Evolution Textiles***, **Donghyun Kim**, J Park, H Kim,* Yonsei University, Republic of Korea

Hydrogen energy is promising energy source, because it is sustainable and renewable green energy alternatives for fossil fuels and coal. The key component for producing hydrogen in water is the catalyst for hydrogen evolution reaction (HER).

To increase HER efficiency, maximizing surface area for reaction is important factor. Complex structure is widely used to meet this requirement. For example, conducting substrate based on nanowire, nickel foam, or carbon nanotube would serve as electron transfer template. However, these conventional substrates for HER limit its applicable area such as flexible devices. To overcome the limit, conducting textile could be adequate substrate for HER. Textile is intensively used as form of fabric, and it can be applied from clothes to massive energy storage system.

Up to now, the noble metal including Pt is considered as the best electrocatalyst for HER with low overpotential, tafel slope and high exchange current density. However, the noble metal is extremely expensive so that catalyst based on earth-abundant materials with high-efficiency are required. Transition metal chalcogenides (TMCs) have attracted attention owing to its superior catalytic properties. Due to the electron configuration of TMCs, outermost *d* orbitals of TMCs make electron transfer easy. Especially, metallic TMCs including cobalt sulfide, vanadium sulfide, 1T-molybdenum sulfide shows superb electrochemical properties due to their high conductivity which promotes transport of electrons.

In this study, the cobalt sulfide (CoS_x) was synthesized using atomic layer deposition (ALD). ALD is the self-limited process based on surface reaction so that the CoS_x could be deposited with excellent uniformity, precisely controlled thickness in large area. The characteristics of deposited ALD CoS_x were analyzed using XPS and XRD. The morphology and thickness of the film were observed using SEM and AFM and finally, the electrocatalyst based on cobalt sulfide could be synthesized. It showed low tafel slope (~ 41 mV/dec) comparable to the value of Pt, and low overpotential. Also, conducting textiles could be utilized as template for HER catalyst due to the low-temperature process of ALD. As the result, the ALD CoS_x can be considered as the promising electrocatlayst for HER as promising candidate for replacement of Pt.

4:45pm **EM+AA-MoA-14 Atomic Layer Deposition of Platinum: An Avenue to the Scalable Synthesis of Ultra-low-loading Fuel Cell Catalysts?***, A Goulas,* Delft IMP B.V., Netherlands*; F Grillo, A Dokania,* Delft University of Technology, Netherlands*; D Valdesueiro,* Delft IMP B.V., Netherlands*; H Van Bui,* Delft University of Technology, Netherlands*; **Bart van Limpt**,* Delft IMP B.V., Netherlands*; J Moulijn, J van Ommen,* Delft University of Technology, Netherlands

We present an approach for tailoring the growth of platinum nanostructures on commercially-available carbon black powder (Vulcan XC72) based on atomic layer deposition (ALD) in an atmospheric-pressure fluidized bed reactor. By varying the number of ALD cycles, the metal loading could be effectively controlled in the 2 – 10 wt.% range. The expansion of the ALD processing window into lower deposition temperatures, enables us to steer the Pt growth towards highly-dispersed nanoparticles with narrow size distributions.

Although one does not simply control the NP size by the number of ALD cycles, here, by using atmospheric-pressure ALD in a fluidized bed reactor we could use the temperature as another knob to tailor the size distribution. In particular, by employing low deposition temperatures we could achieve narrow size distributions while maximizing the inter-particle distance.

5:00pm **EM+AA-MoA-15 Pd-Ag Bimetallic Nanograin-Decorated Nylon Nanofibers: Efficient Catalytic Reduction of 4-Nitrophenol***, K Ranjith, A Celebioglu,* Bilkent University, Turkey*; H Eren,* Delft University of Technology, Netherlands*; N Biyikli,* Utah State University*; **Tamer Uyar**,* Bilkent University, Turkey

Reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride catalyzed by both monometallic and bimetallic nanostructures through hydrogenation process is of utmost interest. By constructing the bimetallic functionality on a support or template has attracted much attention over the points of catalytic interaction and stability. We demonstrate an effective synthesis process of creating the Pd-Ag bimetallic functionality on the Nylon nanofibers by combining the atomic layer deposition (ALD) of Pd nano grains followed by the solution chemical reduction of Ag ions to form the Pd-Ag bimetallic nanograin alloys. Through the ALD process, the size, density and monodispersivity of the Pd nanoparticles were controlled and reflected as nucleation sites for the loading of Ag ion with controllable ratio. The evolution of the catalytic activity through the reduction of 4-nitrophenol to 4-aminophenol improved on constructing the bimetallic functionality which betters the selectivity of p-nitrophenol adsorbate to the catalytic surface as predicted by Brønsted−Evans−Polanyi (BEP) relation. Different composition ratio of the Ag ion with the bimetallic functionality with ALD Pd nano grains initiates the understanding of the electronic and geometric effect exhibited by the role of Ag ion at the Pd interface. Additionally, Pd nanograins act as nucleation platform for the Ag ion loading, which reveal the absence of sole decoration of Ag ions on the nylon fiber surface. The reduction rate was significantly higher for the Pd-Ag bimetallic alloys loaded nylon fibers relative to the Ag and Pd decorated Nylon fibers which evidence the electronic promotion of Pd ions through the Ag ion which results in the improved catalytic behavior. This observation attributes to the simultaneous effect of (i) enhancive surface area for the interaction through the template form, (ii) supportive high interactive crystallographic facets for the catalytic reduction, and composition of the bimetallic nanostructures. The template based catalyst shows the use of recoverable and reusable performance without obvious loss on catalyst and activity after 3 consecutive cycles.

5:15pm **EM+AA-MoA-16 Size-Selective Catalysts with an Ultra-Thin Porous Shell Prepared by Molecular Layer Deposition***, **Zeyu Shang**, X Liang,* Missouri University of Science and Technology

Heterogeneous catalysts are widely used due to many advantages, including the ease of separating the catalysts by filtration after reaction. However, heterogeneous catalysts usually cannot selectively convert specific molecules in a reactant mixture to only desired products. Size-selective catalysis is an important concept for improving the selectivity of heterogeneous catalysts. In most previous studies, unsupported and nonporous substrates supported metallic nanoparticles were encapsulated in relatively thick porous structures to realize the size-selectivity of heterogeneous catalysts by the size discrimination effect of the porous shell. However, the catalytic activity of the catalysts greatly decreased due to mass transfer limitations brought by relatively thick shells and the contact areas between the porous shells and active sites. In our study, we deposited an ultra-thin porous oxide shell on high surface area substrate-supported Pt nanoparticle catalysts, using molecular layer deposition (MLD), followed by oxidation to remove the organic components in hybrid organic/inorganic MLD films. The encapsulated catalyst showed very high selectivity in catalyzing hydrogenation reactions of n-hexene over cis-cyclooctene. However, there was a decrease of the catalytic activity due to contact areas between the porous shell and metallic nanoparticles. To reduce the contact areas, we introduced gaps between the Pt nanoparticles and porous shells using a sacrifical layer of self-assembled monolayers (SAMs) on the Pt nanoparticles, before the deposition of a MLD layer. This novel nanostructured catalyst showed much higher activity, as compared to the catalyst that had been directly coated with the MLD layer.

ALD Fundamentals

Room Plaza Exhibit - Session AF-MoP

ALD Fundamentals Poster Session

AF-MoP-1 Template-Free Vapor-Phase Growth of Patrónite (VS_4) by Atomic Layer Deposition*, **Matthew Weimer**, R McCarthy,* Argonne National Laboratory*; J Emery, M Bedzyk,* Northwestern University*; F Sen, A Kinaci, M Chan, A Hock, A Martinson,* Argonne National Laboratory

Transition-metal dichalcogenides (TMDC) have received particular attention due to their layered structure and range of bandgaps. Recently, 2D vanadium disulfide, VS_2, has been considered for a wide range of applications, enabled by thin film growth methods. A sub-set of transition-metal sulfides is those that possess disulfide (S_2^{-2}) moieties. Recently, facile routes to sulfide minerals based on S_2^{-2} dimers, pyrite (FeS_2), cattierite, (CoS_2), and vaesite (NiS_2) have been realized, which allows for investigation in a range of applications. Owing to the difficulties in control over V oxidation state and V:S stoichiometry, films of patrónite, VS_4, with the intriguing quasi-one-dimensional chain structure, have only be accessed by templated growth on graphene and graphene oxide surfaces in a non-self-limiting fashion. Despite challenges to control stoichiometry in the V:S system, template-free growth of VS_4 thin films is demonstrated for the first time. A novel ALD process enables the growth of phase pure films and the study of electrical and vibrational properties of the quasi-one-dimensional transition metal sulfide. Self-limiting surface chemistry during ALD of VS_4 is established via *in situ* quartz crystal microbalance and surface chemistry is studied with quadrupole mass spectrometry between 150 to 200 °C. The V precursor, unconventionally, sheds all organic components in the first half-cycle, while the H_2S half-cycle generates the disulfide dimer moiety, S_2^{-2}, and oxidizes V^{3+} to V^{4+}. A suite of x-ray analysis establishes VS_4 crystallinity and phase purity, a self-limiting growth rate of 0.33 Å/cy, modest roughness (2.4 nm), expected density (2.7g/cm^3), and low elemental impurities. Phase pure films enable a new assignment of vibrational modes and corresponding Raman activity of VS_4 that is corroborated by density functional theory (DFT) calculations. Finally, at elevated growth temperatures, 225 °C and above, a change in the surface mechanism provides a self-limiting synthetic route to a second vanadium-sulfur phase, V_2S_3.

AF-MoP-2 Novel Approach to Deposit Carbon Doped Silicon Oxide Film with High Carbon Content via Thermal ALD*, **Haripin Chandra**, K Cuthill,* Versum Materials, Inc*; M MacDonald, G Sanchez,* Versum Materials, Inc.*; A Mallikarjunan,* Versum Materials, Inc

Carbon doped silicon oxide (SiOC) films are used in the semiconductor industry for many applications such as low-k dielectrics, etch stop, and advanced patterning. The established technology for depositing highly-doped, carbon-containing silicon oxide is plasma enhanced CVD (PECVD). The PECVD technique, however, faces a big challenge in meeting the conformality requirements for next generation devices. In an accompanying paper in this conference [Wang, Chandra et al.], atomic layer deposition of SiOC using aminosilane precursors and ozone as the oxidant was studied; the results showed that carbon doping is possible with the ozone process, but it is limited to < 200 °C depositions. This paper describes a novel way of depositing ALD silicon oxide-based films with high carbon content without use of strong oxidants at 300-500 °C. The process utilizes thermal ALD of chlorosilane-based precursors and ammonia to deposit a carbon-doped silicon nitride intermediate, which is then converted to carbon-doped silicon oxide through hydrolysis. Films that are rich in Si-NH_x bonding from low temperature deposition are susceptible to hydrolysis to form SiO_x-based films. The SiOC films deposited using our approach demonstrate excellent etch resistance in dilute hydrofluoric acid and carbon content higher than 20 at. % by XPS. We will discuss the impact of precursor structure (Si-C/Si ratio) on carbon content and feasibility of the overall approach on a 300-mm platform.

AF-MoP-3 A New Reducing Co-Reagent and Challenges in Thermal Atomic Layer Deposition of Electropositive Metal Films*, **Kyle Blakeney**, C Winter,* Wayne State University

Powerful reducing agents are needed to deposit electropositive metals such as Ti, Ta, Mn, and Al by thermal atomic layer deposition (ALD). The ideal reducing co-reagent is volatile, thermally stable, highly reactive, efficient at stripping away metal precursor ligands, and produces volatile and stable reaction products. We have been exploring novel compounds as potential reducing co-reagents for ALD of metal and element films. The organic compounds CHD and DHP enabled Ti deposition via $TiCl_4$, although growth rates were quite low.[1] Borane-dimethylamine ($BH_3(NHMe_2)$) has been used in the low temperature thermal ALD of Ni, Co, Fe, Cr, Cu, Cu/Mn alloy and possibly Mn metal films.[2] $BH_3(NHMe_2)$ was also evaluated for Au and Ag metal ALD.[3] However, film growth using this co-reagent is highly dependent on the substrate. Formic acid and tert-Butylamine have enabled Co deposition, however these co-reagents are likely unsuitable for very electropositive metals.[4] Herein, we demonstrate the use of a new volatile and thermally stable proprietary reducing co-reagent for ALD of metal films provided by BASF. An ALD film growth study using $Ti(NMe_2)^4$ (TDMAT) as the metal precursor established a growth rate of 0.28 Å/cycle within an ALD window of 150-180 °C with similar growth rates on both metal and dielectric substrates. Films grown between 170-180 °C had high resistivities of about 10 Ω·cm. To prevent oxidation as much as possible, a metal carbide capping layer was deposited in situ before XPS analysis. Although the capping layer contained little oxygen, after sputtering the Ti films were largely oxidized with low amounts (<5 at. %) of C and N. Due to the highly oxophilic nature of Ti, trace oxygen in the carrier gas or ALD reactor may be responsible for oxidizing the growing Ti film. Due to the popularity of alkylamide ALD precursors, the observed film growth using the reducing agent and a titanium alkylamide precursor implies great potential for ALD processes of metals and elements.

1. J. P. Klesko, C. M. Thrush, C. H. Winter, Chem. Mater. 27 (2015) 4918–4921

2. L. C. Kalutarage, S. B. Clendenning, C. H. Winter, ECS Trans. 64 (2014) 147–157

3. M. Mäkelä, T. Hatanpää, K. Mizohata, K. Meinander, J. Niinistö, J. Räisänen, M. Ritala, M. Leskelä, Chem. Mater. 29 (2017) 2040–2045

4. M. M. Kerrigan, J. P. Klesko, C. H. Winter, 16th International Conference on Atomic Layer Deposition, Dublin, Ireland, July 24-27, 2016

AF-MoP-4 Volatile Rare Earth Metal Alkoxides for ALD precursors*, **Atsushi Sakurai**,* ADEKA Corporation, Japan*; N Sugiura,* ADEKA Corporation*; M Hatase, A Nishida, A Yamashita,* ADEKA Corporation, Japan

Rare earth metal oxides have been widely investigated to prepare higher-k gate insulator layers especially on Ⅲ-Ⅴ channel surfaces with a low interface trap state density for future CMOS devices1). ALD rare earth oxide processes could be used to produce gate insulator layers in advanced 3D structures such as those found in future multi-gate and gate-all-around devices. Furthermore, thermal ALD may be preferred for such applications in order to achieve a gentler deposition process than with plasma-enhanced ALD and minimize undesired damage to other areas in CMOS devices. Combining a metal alkoxide precursor and H_2O coreactant could lead to new thermally reactive ALD processes for metal oxide films proceeding through the formation of a metal hydroxide-terminated surface and volatile alcohol by-products. Despite considerable research, however, it has proven challenging to identify rare earth metal alkoxide precursors with sufficient volatility to be applied to practical ALD/CVD processes2).

Based on our precursor chemistry development work, we will present details on monomeric rare earth metal alkoxide precursors with attractive volatility, thermal stability, and reactivity for the deposition of ALD oxide films.

[1] Yiqun Liu, et al, Applied Physics Letters 97, 162910 (2010),

[2] W.A.Herrmann, et al, Angew.Chem.Int.Ed.Engl., 34, p.2187 (1995)

AF-MoP-5 Enabling Smooth and Conformal Film Growth via Separate Surface Treatment during Atomic Layer Deposition of Cobalt*, **Jeong-Seok Na**,* Lam Research Corp.

As devices continue to scale down to N7 technology node and beyond, there have been extensive efforts to replace the current tungsten metal with alternative metals due to reduction in current-carrying cross-section, increase in electron scattering, and fill challenge of current tungsten or copper process in narrow trenches. Cobalt is considered a promising candidate because of its low electron mean free path and high melting point associated with resistance to diffusion (i.e., electromigration), especially, in source/drain metal electrodes and local/back-end interconnects in logic devices. The CCTBA cobalt precursor is useful due to its ability to produce pure cobalt films; however, it has an intrinsic instability issue, causing dimerization or polymerization with time. In this study, two new cobalt precursors have been investigated to achieve pure cobalt film with good step coverage and smooth morphology. Cobalt film growth behavior and film properties are affected by precursor design with different precursor stability and volatility. Precursor A is less volatile and more stable, producing slow film growth and smooth film morphology but relatively high carbon impurities. In comparison, precursor B is more volatile and less stable, producing fast film growth with rough film morphology by CVD process. However ALD process enabled improved controllability in film nucleation, step coverage, and morphology by separate surface treatment and low process temperature. Pure and crystalline ALD Co films were obtained with film resistivity at approximately 12 µohm-cm at 25nm, which is comparable to that of CCTBA. Cobalt gapfill behavior within small features using ALD cobalt process has also been studied. Detailed results including film characterization and gapfill performance will be presented.

AF-MoP-6 Comparative Study of ALD SiO_2 Films, ***Andy Zauner,*** Air Liquide R&D, France; *J Girard,* Air Liqude Advanced Materials, France

SiO_2 is a widely used and studied dielectric material for electronic and optical applications, such as in spacer defined multi-patterning, shallow trench isolation (STI), liners, and antireflection coatings.

ALD is a very appropriate deposition technique to be used for those applications due to its extreme good thickness control, uniformity and conformity. In the case of spacer-defined multi patterning, ALD's low deposition temperatures (below 100 °C) allow direct deposition on organic materials like photoresist or SiC films. While for other application, allowing more elevated deposition temperatures, high temperature ALD films might be beneficial due to modified film quality (e.g. etch resistance).

For throughput reasons fast deposition rates, i.e. high growth per cycle (GPC), are important. As presented in previous work, the GPC of a bis-substituted silane, such as SAM.24, can be outperformed while moving to precursors having more Si atoms in their molecular backbone (e.g. aminodisilanes).

A spectacular increase in GPC is achieved with Si rich precursors such as New SAM. Both, at low (~70°C) and at high (~300 °C) deposition temperatures the GPC is more than doubled as compared to the reference compound, SAM.24. The observed decrease of the GPC with increasing deposition temperature is well explained by the reduced number of –OH bonds at elevated temperature [1].

In this study the self-limiting growth rate of different precursors is studied at elevated deposition temperatures (250 °C-450 °C). In addition to the precursor / process parameters, material properties of the resulting films, including thickness uniformity, etching rates, and stoichiometric composition, are presented in this paper.

[1] G. Dingemans, C. A. A. van Helvoirt, M. C. M. van de Sanden, and W. M. M. Kessels, ECS Transactions, 35 (4) 191-204 (2011)

AF-MoP-7 B_2O_3 ALD for Advanced Doping Applications: The Roles of Free Radical Precursors and Surface Composition, *A Pilli, J Jones,* ***Jeffry Kelber,*** University of North Texas; *F Pasquale, A LaVoie,* Lam Research Corp.

ALD of B_2O_3 on Si is the subject of extensive investigation for ultra-shallow Si doping applications. Effects of oxidation chemistry on Si surface composition, precursor coverage and substrate reactivity, however, remain largely unexplored. X-ray photoelectron spectroscopy (XPS) studies of BCl_3 and $B(OCH_3)_3$ interactions with O_2, $O(^3P)$ radicals or H_2O have been carried out at Si surfaces over a temperature range of room temperature to ~ 400 K, under controlled ultra-high vacuum conditions. These experiments monitor the effectiveness of various oxidants over this temperature range, as well as effects on Si surface oxidation and precursor wetting of the surface. The effects of oxidant on Si surface oxidation, and resulting precursor surface coverage, will also be discussed.

Acknowledgements: Work at UNT was supported by a grant from Lam Research.

AF-MoP-8 High-aspect Ratio Anodic TiO_2 Nanotube Layers: Unprecedented Ability of ALD to add a Functionality, ***Raul Zazpe***, *J Přikryl, H Sopha, L Hromadko, J Macák,* University of Pardubice, Czech Republic

Self-organized anodic TiO_2 nanotubular structures have received substantial attention within past 12 years. Their semiconductive nature, high surface area, unique architecture and chemical stability coupled with a low cost fabrication made these structures very popular and efficient in a wide range of applications.

However, the potential of TiO_2 nanotube layers for a range of advanced devices, in particular when considering all possible tubular shapes and geometries, has not at all been exploited. One of the major issues to extend the functional range of nanotube layers is to coat homogenously tube interiors by a secondary material (potentially until the complete tube filling) to create novel devices. Efforts based on electrochemical deposition, chemical deposition and spin-coating led only to limited success in low aspect-ratio nanotube layers with a narrow range of materials.

The presentation will therefore focus in detail on the unique ability of ALD to attain continuous, conformal and homogeneous coating of secondary materials within high aspect-ratio TiO_2 nanotube layers. The deposited materials strongly influence optical, electrical, thermal and mechanical properties of TiO_2 nanotube layers. Experimental details and some very recent results will be presented and discussed [1, 2, 3, 4].

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AF-MoP-9 PEALD Ga_2O_3 as Dielectric Interlayer on GaN, ***Mei Hao,*** *R Nemanich, S Chowdhury,* Arizona State University

GaN based transistors remain one of the most promising next generation power devices due to the large band gap (3.4 eV), high saturation velocity and high breakdown field. While oxygen terminated GaN surfaces have often been used as a starting surface for dielectric layer growth, these dielectric layer structures suffer from a range of defects and impurities. However, studies have suggested that an ordered O-Ga-O layer could provide an excellent low defect starting surface for dielectric layer growth. In this study we have employed plasma enhanced ALD (PEALD) to prepare Ga_2O_3 layers on GaN and determined the band alignment using photoemission spectroscopy. Ga_2O_3 is a transparent material with 4.1 to 4.9 eV band gap. The PEALD growth of Ga_2O_3 is achieved in our laboratory using gallium acetylacetonate ($Ga(acac)_3$) precursor and an O_2 plasma as oxidizer. $Ga(acac)_3$, also referred to as $Ga(C_5H_7O_2)_3$, has a melting point of 197 °C and is non-pyrophoric. The PEALD system is connected by UHV transfer to an x-ray and UV photoemission system (XPS and UPS), which is used to determine saturation coverage and layer thickness in addition to band alignment. The results establish that the Ga_2O_3 growth window starts from 150 °C, saturated coverage of $Ga(acac)_3$ is achieved in 0.4 s, complete oxidation occurs with an O_2 plasma exposure time of 8 s and a N_2 purge time of 60 s was employed. Within the growth window a growth rate of 0.4 Å per cycle was determined using X-ray diffraction (XRD) and photoemission indicated a uniform growth per cycle. The band gap of PEALD Ga_2O_3 derived from the XPS energy loss spectra was 4.1 eV. The results indicated nearly flat bands for the GaN and a valence band offset of 0.1 eV for the oxidized GaN surface.

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AF-MoP-10 Effect of Deposition Temperature and Plasma Condition on Film Quality of TiO_2 Deposited by Plasma-Enhanced Atomic Layer Deposition, ***Munehito Kagaya,*** Tokyo Electron Limited, Japan; *S Iwashita,* Tokyo Electron Yamanashi Limited, Japan; *Y Suzuki, Y Sakamoto,* Tokyo Electron Limited, Japan; *A Uedono,* University of Tsukuba, Japan; *T Mitsunari,* Tokyo Electron Limited, Japan; *N Shindo, M Yamasaka, N Noro, T Hasegawa,* Tokyo Electron Yamanashi Limited, Japan; *T Moriya,* Tokyo Electron Limited, Japan

Plasma-enhanced atomic layer deposition (PEALD) has been widely used as a technique to obtain a conformal thin film at relatively low deposition temperature. Although the fundamental study on PEALD of oxide films has been extensively reported, the effect of process parameters on the quality of PEALD-grown TiO_2 has not been investigated well. In this work, we report the effect of deposition temperature and plasma condition on the film quality of TiO_2 deposited by PEALD. TiO_2 film was deposited on silicon wafers at 60, 100, and 120^{o}C. An N-containing organometallic precursor was used as a Ti precursor and oxidized with Ar/O_2 plasma at high and low mean ion energies. The plasma was generated via capacitively coupled plasma with an RF frequency of 450 kHz. The wet etching rate (WER) of the TiO_2 films was evaluated using diluted HF (0.5 wt%) at room temperature. While the WER of the TiO_2 films was almost constant under a high ion energy condition, it was highly dependent on the deposition temperature under a low ion energy condition (Fig. S1). The results of X-ray photoelectron spectroscopy show that the concentration of nitrogen impurity correlated well with the WER (Fig. S2). An N 1s peak was assigned to the protonated ligand of the precursor. These results indicate that one of the determining factors of the WER of PEALD-grown TiO_2 films is the amount of impurity, which is incorporated in the films by redeposition of reaction-product fragments during plasma oxidation. The temperature and ion energy dependences of the WER might be caused by a change of the desorption probability of redeposited fragments. Thermal desorption is predominant under a low ion energy condition, so more reaction-product fragments are released from the film surface with increasing temperature. On the other hand, when the ion energy is high, ion bombardment on the film surface is pronounced due to the existence of highly energetic ions. Therefore, the desorption probability might be dominated by the ion bombardment rather than the deposition temperature.

AF-MoP-11 Atom Probe Tomography of Platinum and Ruthenium Atomic Layer Deposition Films*, **Daniel Potrepka**, B Hornbuckle,* U.S. Army Research Laboratory*; N Strnad,* University of Maryland

Atom Probe Tomography provides the opportunity for 3D nanoscale compositional characterization. Using electric field or laser pulses single atom removal can be achieved in a controllable manner. The sample specimen can then be reconstructed from atom and position-sensitive detection. Atomic Layer Deposition (ALD) Pt 60 nm thick was performed at 300 °C onto TiO_2 by a plasma-enhanced oxygen process using a 99% pure Trimethyl(methylcyclopentadienyl)platinum(IV) precursor. Rapid thermal anneal was performed at 700 °C, 1 min in an ambient O_2 flow. After x-ray diffraction analysis to characterize the Pt orientation and sheet resistance measurements, sharpened atom probe samples were prepared by focused ion beam techniques. ALD Ru 10 nm thick was deposited at 100 °C onto Si pre-sharpened tips with a plasma-enhanced hydrogen process using the ToRuS^{TM} precursor. Atom Probe Tomography was then performed in a CAMECA LEAP$^{®}$ 5000 system to investigate purity levels and overall chemical distribution of the prepared films.

AF-MoP-12 Nitrogen Doped Al_2O_3 Films with High Doping Uniformity and Low Film Roughness Grown by Plasma Enhanced Atomic Layer Deposition*, **Hong-Yan Chen**, H Lu,* Fudan University, China

The nitrogen doped Al_2O_3 (AlON) film exhibits superior chemical, electrical, and interfacial stability than that of the undoped one, which is widely used in nanoscale devices. However, a homogenous nitrogen doping profile in AlON film cannot easily to be obtained through the conventional way by annealing the Al_2O_3 film in the NH_3 environment. Another common way of Al_2O_3/AlN multi-layer growth will greatly increase the film roughness. In this work, AlON film with high doping uniformity and low film roughness has been prepared by plasma enhanced atomic layer deposition (PEALD) using a novel manner. The precursors NH_3 and O were introduced simultaneously during PEALD of Al_2O_3 at 200 ^{o}C. Through controlling the NH_3:O_2 ratio, the refractive index (*n*) value of the film can be regulated from 1.63 (Al_2O_3) to 2.05 (AlN). As the O_2/NH_3 ratio increases from 5 to 20 %, the *n* value of the obtained film drops quickly. It indicates that the composition of the obtained film quickly changes from AlN to Al_2O_3 when a small amount of O_2 is introduced into the chamber. The reason is that the reactivity of the O_2 is much higher than that of the NH_3. Results show that the O_2/NH_3 ratio should be maintained at a very low level (<5 %) for realizing a higher nitrogen doping level of the AlON film. Benefited from the growth method demonstrated in this work, the nitrogen can be doped evenly in the entire film. Moreover, the atomic force microscopy shows that the root mean square roughness value for ~20 nm thick AlON film is determined to be ~0.15 nm, which is almost in dependent of the nitrogen doping level. These findings of this work offer a way for growing AlON films with high doping uniformity and low film roughness.

AF-MoP-13 Study on the Gate Sidewall Spacer Silicon-Nitride ALD Process at Low Temperature by High Density Multiple ICP Sources*, **Ho-Hyun Song**, H Chang, Y Seol,* KAIST, Republic of Korea

Plasma sources, such as CCP(Capacitively Coupled Plasma), ICP(Inductively Coupled Plasma), etc., have been widely used for fabrication processes in the semiconductor, flat-panel display, and solar-cell industries. In next-generation semiconductors, the necessity of high concentration nitride film deposition due to decrease of gate line-width and low temperature process using high density plasma with good step coverage at high aspect ratio have been required.

We have developed 7-coil multiple ICP sources(for 300 mm wafer), generating high-density & uniform nitrogen plasma by delivering high power(~10 kW) at low temperatures(300 ~ 550 K). Using this source, a silicon nitride film was deposited on a 300 mm wafer by PE-ALD(Plasma Enhanced Atomic Layer Deposition) method. We also have conducted PE-ALD process experiments at low temperature conditions(300 ~ 550 K) and have analyzed the properties of deposited silicon nitride films. In order to analyze the characteristics such as composition ratio according to the depth of the thin film, we performed SIMS and XPS analysis. Through this study, it has been confirmed that the silicon nitride film, deposited by our sources, was very similar to that of the general LP-CVD process, and also the good step coverage was confirmed. We also have repeated the same experiment and the same analysis for SiCN thin film deposition.

AF-MoP-14 Effect of Revolution and Rotating Substrate for ALD SiO_2 Film at Low Temperature Using SDP System*, **Jin-Hyuk Yoo**, B Cho,* JUSUNG Engineering, Republic of Korea

We report in this article low-temperature SiO_2 thin film ALD system for next-generation semiconductor devices which can have circle map controllability and provides a very uniform and conformal thin film.

In this study, we present a newly developed SDP^{TM} (Space-Divided Plasma) ALD system with a wide range of map controllability by both revolution and rotating the substrate, and dividing the area of Source/ Purge/ Reactant (Plasma)/Purge.

We have investigated the characteristics of SiO_2 thin film composition by O_2 plasma for reactant and BDEAS for Si source at low process temperature ranging from 50℃ to 100℃. We have realized thickness map controllability and CD map adjustment at a real device, while showing high productivity. We have used an ellipsometer, TEM, AFM, XPS to evaluate thin film characteristics. The result shows the uniformity less than 0.3%, step coverage more than 95% at aspect ratio of 60:1. This SiO_2 film is better on wet etch rate & breakdown voltage compared to HTO (High-Temperature Oxide).

AF-MoP-15 Breakthrough Trace Element Analysis for Challenging ALD Film Precursors*, **Lisa Mey-Ami**, J Wang, H Gotts, F Li,* Air Liquide - Balazs NanoAnalysis

It is necessary to adequately characterize the analytical purity of ALD precursors with the appropriate techniques in order to avoid device failure and enhance production yield. However, the high concentration of parent element in the precursor samples poses molecular interference challenges using inductively coupled plasma – mass spectrometry (ICP-MS). For example, in a cobalt precursor, ^{59}Co^{16}O interferes with determining trace levels of ^{75}As. In addition, in a zirconium sample, ^{91}Zr^{16}O interferes with determining ^{107}Ag. Several ICP-MS instruments in our laboratory are used jointly to determine trace levels of elements present in challenging precursor materials. A dynamic reaction cell quadrupole based ICPMS (DRC ICP-MS) filters out argon associated molecular ion interferences using an ion-molecule collision reaction. A high resolution double-focusing ICP-MS (HR ICP-MS) employs a magnetic sector field to eliminate or reduce the effect of interferences by baseline-separating mass interference from analyte signals . A triple quadrupole ICP-MS (QQQ ICP-MS) uses a combination of reaction gases to eliminate molecular ion interferences. The challenging precursor compounds have been investigated using all three ICP-MS instruments and the analysis data obtained will be discussed.

AF-MoP-16 New Technology Advances of Electromechanical Valve Technology for Precision-Controlled Millisecond Pulsed Delivery in ALD/ALE Applications*, **Patrick Lowery**,* HORIBA*; H Nishizato,* Horiba Stec, Japan*; J Dick, T Hoke,* HORIBA

Atomic Layer Deposition (ALD) and Atomic Layer Etch (ALE) processes currently require <50 msec time constants for flow pulse width time constants. Currently, these applications are being served by combinations of various technologies such as pneumatic valves, solenoid valves and mass flow controllers (MFC's) which utilizing either solenoid or piezoelectric actuators. Newer ALD and ALE process requirements will push flow time constants to around 5msec in certain applications. However, the currently utilized technologies are not suited for such high duty cycle applications, or cannot capture or meter flow at these time constants without significant error. Pulsed mechanical valves do not have full control capability to deliver precise mass pulses with repeatable dynamic response; therefore, many ALD/ALE processes cannot fully capture process parameters such as cumulated mass flow as function of ALD layer thickness. This presentation will focus on new technologies that are being developed using both new piezoelectric and solenoid technology, with fast flow metering capability for full feedback process-controlled pulse delivery along with metering capability with sub 20 millisecond resolution and beyond.

AF-MoP-17 Band Alignment at the Interface of Atomic Layer Deposition Al_2O_3 and Ga-Polar GaN under Ultraviolet/Ozone Treatment*, K Kim, J Ryu, J Kim, S Cho, D Liu, J Park, I Lee,* University of Wisconsin-Madison*; B Moody,* HexaTech. Inc.*; W Zhou,* University of Texas at Arlington*; J Albrecht,* Michigan State University*; **Zhenqiang Ma**,* University of Wisconsin-Madison

Exploring the band alignment at the interface of dielectric/III-nitride under different surface treatments is fairly important in understanding the interface charge behaviors and improving the III-nitride-based electronic device design, performance, and reliability. The energy band alignment of Ga-polar GaN interfaced with atomic layer deposition (ALD) Al_2O_3 was characterized by ultraviolet/ozone (UV/O_3) treatment. The UV/O_3 treatment and post-ALD anneal effectively varied the band bending, the valence and conduction band offsets, and the interface dipole at the ALD Al_2O_3/GaN interface. In addition, the UV/O_3 treatment affected the surface energy of GaN and the growth quality of ALD thin film. The eventual energy band alignment at the ALD Al_2O_3/GaN interface was determined by screening the polarization bound sheet charges in GaN with the positively charged surface states formed by the trapped charges in the Al_2O_3 thin film. X-ray photoelectron spectroscopy and capacitance-voltage measurements were used for the experiments. The “best” interfaces can be realized under the optimal UV/O_3 treatment conditions. This study of UV/O_3 treatment on the band alignment will be effective for achieving high performance transistors, light-emitting diodes, and photovoltaics.

AF-MoP-18 Raman Spectrum Characterization of Ti-based ALD Thin Films Treated with Ultra-high Vacuum Annealing*, **Chengchun Tang**, X Jia, C Gu, J Li,* Institute of Physics, Chinese Academy of Sciences, China

Ti-based thin films such as TiO_X, TiN_X and TiC_X prepared by atom layer deposition (ALD) exhibit extraordinary optical and physical properties. With a combination of two or three Ti-based ALD thin film, the properties of the compounds can be combined together or be enhanced. Most often, ultra-thin ALD raw films are hard to be characterize by normal XRD or Raman because ALD thin films are intrinsically amorphous, which is very inconvenience for detecting the composition and banding state of ALD thin films. Here we introduce an ultra-high vacuum annealing (UHVA) process to treat Ti-based ALD thin film for realizing Raman spectrum characterization. The results indicate that UHVA is a nondestructive method for increasing the crystallization of ALD thin film, which can be used for the pretreatment of Raman detection and help to analyze composition related electrical and mechanical properties.

The ~30nm thick Ti-based thin films are prepared by ALD at temperature from 150 to 450°C. With increasing deposition temperature, their surface roughnesses are increased from 2nm to 20nm and their metal-like conductivities are changed from 2.72×10^{-3}S/m at 150°C to 8.65×10^{4} S/m at 450°C by seven orders. After UHVA process, Raman measurement results show clearly the change process of the composition and banding state of Ti-based thin films. A well conductive TiNx with two peaks at 203 cm^{-1} and 392 cm^{-1} is stable during the whole ALD process. There are a lot of nonconductive TiO_X with a peak at 517 cm^{-1} formed at lower temperature than 250℃. When the reactor temperature increase to larger than 250℃, there are little TiO_X formed and the conductivity increases dramatically and hard TiC_x appeared, which is revealed by the mountain peak at 609 cm^{-1}, and an increased film modulus also prove it indirectly. The conclusions from Raman spectrum of UHVA Ti-based thin films are well consistent with their physical properties.

AF-MoP-20 Complete Analytical Characterization of Surface, Interfacial and Bulk Layers of ALD Films: The Path to Improved and Reliable Deposition Processes*, **Yagnaseni Ghosh**, C Langland, W Rivello, F Li,* Air Liquide - Balazs NanoAnalysis

As Atomic Layer Deposition (ALD) becomes the ubiquitous deposition technique for emerging semiconductor, micro-electronics and energy conversion fields, it is becoming critically important to characterize the topology, morphology, crystallinity, chemical composition, depth profile, and mechanical properties at the surface, bulk, and interface of the films to optimize the ALD and ALE processes. Using an exhaustive suite of modern analytical techniques and instrumentation, we have carried out complete characterization of various ALD films used in the microelectronics and nanotechnology arenas for their chemical, physical, mechanical and optical properties. The films characterized are oxide films for dielectrics, nitride films for diffusion barriers, and metal films for metallization. The benefit of these comprehensive studies is that the data enables process engineers to identify problems associated with yield loss, improve and control the ALD process, and ultimately make higher quality and more reliable ALD films. The comprehensive studies will be discussed and the representative results will be presented.

AF-MoP-21 Sequential Exposures of N_2H_4 + BCl_3 on Copper, HOPG and $Si_{0.7}Ge_{0.3}$ Surfaces*, **Steven Wolf**, M Breeden, M Edmonds, K Sardashti, M Clemons,* University of California San Diego*; E Yieh, H Ren, S Nemani,* Applied Materials*; D Alvarez,* RASIRC*; A Kummel,* University of California San Diego

Boron nitride (BN) has recently gained attention due to useful thermal and mechanical properties, chemical stability, wide bandgap, and ability to be deposited on a range of metallic and semiconducting surfaces. BN can be deposited as a low-k diffusion barrier on interconnects, such as copper, as an insulating/diffusion barrier layer in MOSFET architectures, or on 2D semiconductors, such as graphene, due to their similar structures. Previous studies have shown that ALD with triethylborane and ammonia occurs at temperatures between 600°C-900°C on sapphire and Si [1], but above this range, the process was not self limiting. George *et al.* showed lower temperature (~500K) ALD was possible with BCl_3 and NH_3 on ZrO_2 nanoparticles, but large exposures were needed [2]. Recent work has shown low temperature ALD hexagonal BN, but with an activated N_2/H_2 plasma [3]. In this study, low temperature sequential pulses of anhydrous N_2H_4 and BCl_3 were dosed on copper, HOPG, and $Si_{0.7}Ge_{0.3}$(001) surfaces. The deposited films were characterized using x-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM) and atomic force microscopy (AFM).

The self-limiting and saturating BN ALD with N_2H_4 and BCl_3 was demonstrated on atomic hydrogen cleaned $Si_{0.7}Ge_{0.3}$(001) at a sample temperature of 350°C. Additional exposures of both N_2H_4 and BCl_3 saturated the respective N 1s and B 1s signals, as monitored in XPS, confirming the ALD process on $Si_{0.7}Ge_{0.3}$(001). AFM of 60 cycles ALD BN/$Si_{0.7}Ge_{0.3}$(001) along with C-V and I-V measurements indicated a uniform, pinhole-free film of BN was deposited. On Cu substrates, BN films were similarly deposited with low contamination, but AFM measurements showed an increase in RMS surface roughness after deposition, consistent with the precursors etching the surface. On HOPG, STM measurements indicated nucleation of N_2H_4 on step edges; however, subsequent exposures etched the surface near the step edge after the initial nucleation. By using reactive anhydrous N_2H_4, the plasma-less BN ALD was accomplished with lower temperatures and smaller exposures on $Si_{0.7}Ge_{0.3}$(001); however, evidence of precursor etching on copper and HOPG was observed.

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AF-MoP-22 Plasma Enhanced ALD of BN, B-doped SiN and B-doped TiN*, **Moo-Sung Kim**,* Versum Materials Korea, Republic of Korea*; X Lei,* Versum Materials, Inc*; S Yang,* Versum Materials Korea, Republic of Korea

Plasma enhanced ALD has been widely used for depositing various nitride films, and BN and B-doped SiN (SiBN) can be potentially used as low k spacer, and B-doped TiN (TiBN) can be used for increasing work function of TiN. In this study, we have investigated PEALD of BN, B-doped SiN and B-doped TiN with various precursors. We used a novel boron precursor, di-sec-butylaminoborane (DSBAB), and commercially available tris(dimethylamino)borane (TDMAB) as the boron sources. BN films deposited with both boron precursors and N_2 plasma showed stoichiometric compositions with low carbon and oxygen impurities. We found BN depositions with these boron precursors showed different ALD windows. ALD window of BN with DSBAB and N_2 plasma was 200C~350°C, while BN ALD window with TDMAB and N_2 plasma was 300C~400°C. The BN GPC was in the range of 0.1 – 0.14 Å/cy for both precursors. PEALD B-doped SiN films were studied with bis(tertiary-butylamino)silane (BTBAS) and di-iso-propylaminosilane (DIPAS) as silicon precursors and N_2 plasma. Boron was incorporated into SiN using super cycles, for example, BNx1 subcycle + SiNx10 subcycles. As shown in Fig.1, boron content could be upto ~13 at. % in the resutling B-doped SiN film with very low carbon and oxygen impurities for both boron precursors, but step coverage and SiN deposition rate improvements were not observed, while Al-doped SiN showed significant improvements of step coverage and SiN deposition rate, as we presented last year [1]. We also studied B-doped TiN (TiBN) with tetrakis(dimethylamino)titanium (TDMAT) as titanium precursor. Boron could be incorporated up to 10 at% into TiN with very low carbon and oxygen impurities. Step coverage of TiBN was excellent with all boron contents, ~100% as shown in Fig.2. Resistivity of BTiN was increased sharply with increasing boron content.

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AF-MoP-23 Scale-Up of Atomic Layer Deposition on Powders in Fixed Bed Reactors

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Atomic Layer Deposition (ALD) is an established technique to coat surfaces in a wide range of applications, e.g. in microelectronics or biomedical applications. Recently it was also used for synthesis or modification of heterogeneous catalysts[1]. Our work focusses on synthesizing and modifying heterogeneous catalysts in the form of powders[2]. A highly versatile ALD setup, consisting of a quartz crystal microbalance (QCM), a thermal magnetic suspension balance and a large fixed bed reactor, was built for developing ALD processes and scale-up of catalyst synthesis[3].

A special version of the IsoSorp® from Rubotherm[4] was used as a fixed bed reactor, holding a volume of 1.5 mL, which allows us to monitor the mass gain *in situ* on our high-surface area powders in real time. Combined with a quadrupole mass spectrometer (QMS) suitable process parameters of the reaction can be determined and used for a scale up of the process in a fixed bed reactor with a 20 times bigger volume. As proof of concept ALD of phosphorus oxides (PO_x) on vanadium oxide powder was executed using trimethyl phosphite (TMPT) as a precursor and oxygen/ozone as reactant. Preliminary tests in the balance were performed and show a self-limiting mass gain in each half cycle (Fig. 1 in SI). Knowing the ALD window and dosing times we successfully transferred this process to a large fixed bed reactor. The per cycle grown phosphorus amount was determined in an experiment in which the fixed bed was separated into eight fractions by quartz wool and every consecutive cycle a partition was removed and analyzed.

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AF-MoP-24 Measurement and Control of Stress of ALD Films and Nano-laminates Measured by Interferometry

Ritwik Bhatia, Ultratech

Traditional applications of ALD, typically in the microelectronics industry, have been skewed towards thin (sub 20nm) films. However, as the ALD application space has grown, so have the applications with thicker (≥ 100nm) ALD films – examples include encapsulation for OLEDs , optical filters, etc. Further, many of these applications involve deposition on "soft" substrates like polymers and biological materials. ALD films are typically tensile and have an intrinsic tensile stress of the order of 100MPa. The combination of thick tensile films with soft substrates leads to problems related to de-lamination, cracking of substrate and/or cracking of film. While some work has been done in the field of stress measurement [1,2,3], there is a need for a better understanding of the origin of film stress and how it can be controlled.

In this work, stress is measured via interferometry – which measures very small changes displacement of the substrate surface. Local curvature change is inferred from displacement and stress is calculated using Stoney's equation. The high sensitivity of the technique allows stress measurement for thinner films which is useful to understand the evolution of stress as a function of film thickness/added layers in a nano-laminate.

This work focuses on stress of metal oxide films. We will discuss the impact of precursor and oxidant on intrinsic film stress of single component ALD films like Al_2O_3, TiO_2, ZrO_2 etc. Figure-1 shows the topography change induced by a 108nm Al_2O_3 film deposted at 190°C, and Figure-2 shows the corresponding stress (338MPa). We will also discuss the effect of film composition on stress by growing multi-component films as nano-laminates or as doped films.

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AF-MoP-25 Temperature Dependent Kinetics of ALD Reaction: SiN PEALD Study

***Triratna Muneshwar**, K Cadien,* University of Alberta, Canada

Precursor (or Reactant) surface reaction in ALD fundamentally consists of (i) physisorption, (ii) desorption, and (iii) chemisorption events, occurring simultaneously at the substrate. The physisorption rate depends upon the instantaneous precursor partial pressure, whereas both desorption and chemisorption rates depend upon the substrate temperature (Tsub). Hence, in a true-ALD process the precursor dose Φpre and Tsub are not independent variables and the self-limiting surface reaction is a function of (Φpre, Tsub) combination. This is contrary to the conventional approach adopted in ALD process development, wherein the temperature window is determined at a fixed Φ (Φpre and Φreac) and respective saturation curves are derived at a fixed Tsub. A first-principle analytical model illustrating this combined effect of Φpre and Tsub on self-saturation of ALD surface reactions is presented. For SiN PEALD process, the experimental results are shown to be in good agreement with model calculations. Furthermore, we show that SiN PEALD growth is self-limiting at Tsub = 100 °C and 150 °C with a constant GPC of 0.034 nm/cycle, and the minimum precursor dose necessary for surface saturation increases with Tsub (i.e. 0.10s at 100°C and 0.30s a 150 °C). In agreement with model calculations, the non-ideal saturation at Tsub > 200 °C is explained from the increase in the desorption rate that restricted surface saturation under experimental conditions.

AF-MoP-26 Process Development and Characterization of the Atomic Layer Deposited MoS2

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The two-dimensional transition metal disulfide gradually attracted widespread attention due to its semiconductor band gap and its fascinating electrical and optical properties. Compare with the other deposition methods, like physical vapor deposition (PVD) or chemical vapor deposition (CVD), Atomic Layer Deposition(ALD) has the advantage of excellent step coverage, uniformity and thickness controllability. We synthesized large-scale and thickness-controllable MoS_2 films on SiO_2/Si substrate by ALD at 150°C with molybdenum hexcarbonyl and hexamethyldisilathiane (HMDST). HMDST is introduced to make the process free from high toxic sulfur precursors such as H_2S and CH_3SSCH_3. X-ray photoelectron spectroscopy (XPS), X-ray reflection (XRR), atomic force microscopy (AFM) are used to characterize the chemical composition, thickness and roughness of the MoS_2 films. The as-grown MoS_2 film is amorphous due to the low growth temperature. We further demonstrated the effects of post-deposition annealing on the MoS_2 films by different temperature, time and ambient respectively. Post-deposition annealing at high temperature in sulfur vapor efficiently improves the film properties including the crystallinity and chemical stoichiometry and reduces the impurity contents in the films. This work opens up an attractive approach to synthesize high quality 2D materials.

AF-MoP-27 Low Energy Ion Scattering (LEIS) Analysis of ALD Deposited GaSb Films on SiO_2

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GaSb is a promising candidate for a III-V channel material for future metal-oxide-semiconductor field-effect transistors (p-MOSFETs) due to its high hole mobility. In this study, GaSb films were grown on SiO_2 in a Pulsar 2000 reactor, using $GaCl_3$ and $Sb(SiMe_3)_3$ precursors at 110 °C. Samples were removed after 1 – 100 ALD cycles to study the growth behaviour by means of low energy ion scattering (LEIS). Prior to the LEIS analysis in a UHV chamber, atmospheric contaminations were removed by exposing the samples to atomic oxygen. In LEIS, noble gas ions are scattered off the sample surface, and the surface elemental composition is determined quantitatively by measuring the energy and number of the backscattered ions. As ions scattered in the second or deeper atomic layers are efficiently neutralized and lose additional energy by electronic and nuclear stopping, their contribution to the total spectrum is easily distinguished from top atomic layer scattering. This leads to an extreme surface sensitivity of just one atomic layer, while additional information about deeper layers up to a depth of about 10 nm is contained in the tails of the peaks.

We show how the different pieces of information contained in a LEIS analysis are optimized by varying the species and energy of the primary ions. As only target atoms heavier than the incoming ions are visible in a backscattering setup, 3 keV He^+ ions are used to obtain the full elemental spectrum of the sample surface, including any unexpected contaminations. As the LEIS analysis is sensitive to the topmost atomic layer, the point of layer closure is accurately determined by the disappearance of the Si signal from the substrate.

Ne^+ ions on the other hand offer increased mass resolution and enhanced sensitivity to heavier elements, which makes a Ne analysis ideally suited to accurately quantify the Ga/Sb coverage and ratio as a function of ALD cycle number.

Ions scattered in deeper layers experience an additional energy loss proportional to their penetration depth. Evaluating this sub-surface signal allows the accurate determination of layer structures and layer thickness. We show how growth curves are extracted from LEIS spectra acquired using 7 keV He^+ ions.

The entirety of this information makes LEIS an ideal tool to study the early stages of film growth, which is crucial to understand and optimize the deposition conditions. For instance, variations in the Ga and Sb surface fractions over the course of the deposition process are detected (Fig. 1). These fine nuances in the sample surface composition would go unnoticed with other, less surface sensitive techniques that integrate over several monolayers.

AF-MoP-28 Alternative Plasma Gas Chemistries for Plasma Enhanced Atomic Layer Deposition and the 2016 PEALD Publication Review*, Plasma-ALD Guy,* www.plasma-ald.com

Plasma-enhanced atomic layer deposition (PEALD) has been an active research area for several decades. Replacement of thermal ALD molecular co-reactants with highly reactive plasma generated radicals offers multiple potential advantages in film selection, film properties, and process requirements. Most PEALD studies have utilized a small set of plasma gases including O_2, N_2, NH_3, and H_2. However, a number of studies have chosen plasma gases outside this primary set. Alternate oxygen source plasma gases include H_2O vapor, N_2O, and CO_2. Deposition of carbides and sulfides have utilized CH_4 and H_2S plasma gases, respectively. Fluorine doping has been accomplished through addition of CF_4 to the plasma gas mix. Admixing D_2 to the plasma gas has provided insights into the surface reaction mechanism. We will discuss these interesting examples of "outside the box" PEALD applications.

Additionally, we will continue our tradition of annual reviews of the PEALD literature. Although publications from as early as 1991 can be said to have used a PEALD-like process, the popularity of the technique really begins to grow starting in the early 2000s. As can be seen in the plot below[1], the annual number of PEALD publications has grown substantially increasing from single digits in 2001 to over 240 in 2015. So far, 213 PEALD publications from 2016 have been identified. We will analyze the trends in PEALD literature including film composition, hardware, precursors, and region focusing on 2012 through 2016.

1. www.plasma-ald.com database

AF-MoP-29 Characterization of Ultra-thin ALD Coating in Mesoporous Silicon Layers*, Andras Kovacs,* *U Mescheder,* Furtwangen University, Germany

One-dimensional photonic crystals (1D PC) have been fabricated using electrochemical etching process and used for characterization of ultra-thin ALD coatings in mesoporous layers, especially in the low mesoporous range. Rugate filters with pronounced peak position were fabricated with sinusoidal current density profile, with pore sizes in the low mesoporous range (4–10 nm), aspect ratio up to 3000 and specific surface area up to 700 m²/cm³. The sinusoidal current profile causes a sinusoidal pore size variation in the layer depth. The spectral shift of the main peak is an indicator for surface processes in the nanostructured layer. Material transformation (e.g. oxidation) of the substrate material causes blue shift and pore coating red shift of the peak position which is a result of the corresponding refractive index change of the individual layers and pore coatings. Simulation results show that even ultra-thin pore coatings in the sub-nm range, i.e. very small pore size reduction can be analyzed with this optical device and spectroscopic measurement method. Ultra-thin HfO_2 layers were deposited on the nanostructured 1D PC surface using alternating dose sequences of hafnium precursor (TEMAH) and H_2O combined with N_2 purge processes. The thermal ALD coating process was carried out at 300°C with and without TEMAH precursor dose sequence to investigate the influence of the material transformation of the huge specific substrate surface especially in the first process cycles. Experiment results using native silicon-based rugate filters and the applied ALD process sequences show that the blue peak shift, i.e. the surface transformation (oxidation) process is dominant in the first process cycles (smaller than 8 cycles) both with and without precursor dose sequence. The saturation effect of the blue shift in the case of the pure H_2O dose process indicates that the surface stabilization after approximately 8 cycles is completed. The red peak shift, an indicator of the effective HfO_2 coating process was observed after 8 process cycles. After this first process phase the red shift is continuously increasing, i.e. the thickness of the coating layer increasing and the pore size is decreasing till the complete pore sealing of the smallest pores and further HfO_2 coating of the top layer. The effective coating thickness and pore size reduction is defined by the combination of the surface stabilization and coating process. The applied silicon-based 1D PC and spectral measurement delivers rapid information about the material transformation, effective pore coating and pore size reduction of the mesoporous layer.

AF-MoP-30 Hydrogen Impurities in Al_2O_3 Thin Films using TMA and Heavy Water as Precursors*, Sami Kinnunen,* *K Arstila, M Lahtinen, T Sajavaara,* University of Jyväskylä, Finland

Al_2O_3 films were deposited (Beneq TFS 200 reactor) on silicon substrate using trimethylaluminium (TMA) as an aluminium source and H_2O or D_2O as an oxygen source. Deposition temperature was varied between 70 and 120 °C. Time of flight elastic recoil detection analysis (ToF-ERDA) was used to determine elemental composition of the films. ToF-ERDA can resolve isotopes with different masses and this was utilized to study hydrogen impurity sources in the as deposited films. In addition, FTIR and Raman spectroscopy were used to study film chemistry and XRR to determine film thickness and mass density. Surface morphology was studied by means of helium ion microscopy.

Replacing water with D_2O might not be as straightforward as previously thought [1] when studying reaction mechanisms. Aluminium oxide films deposited with D_2O have roughly 30 % lower growth per cycle and total hydrogen content in the films differs from the films deposited with H_2O. Growth temperature plays an important role on source of hydrogen impurity and process chemistry. Moreover hydrogen and deuterium do not distribute evenly in the films (Figure 1) when deposition temperature is 80 °C or higher.

Therefore rare isotope based reaction mechanism studies might not be fully applicable for conventional ALD processes and great care must be taken when drawing conclusions from the isotope studies.

[1] M. Juppo, A. Rahtu,M. Ritala, and, and M. Leskelä. *In Situ Mass Spectrometry Study on Surface Reactions in Atomic Layer Deposition of Al_2O_3 Thin Films from Trimethylaluminum* and Water. Langmuir 2000 *16* (8), 4034-4039

AF-MoP-31 Density Functional Theory Calculation on the Reaction Between Different Nitriding Agents and Chlorine-terminated Silicon Nitride Surface*, Luchana Yusup,* *T Mayangsari, J Park,* Sejong University, Republic of Korea*; Y Kwon,* Kyung Hee University, Republic of Korea*; W Lee,* Sejong University, Republic of Korea

Major applications of silicon nitride in semiconductor manufacturing include the sidewall spacer of CMOS devices and the charge trap layer in three-dimensional NAND flash devices. The atomic layer deposition (ALD) is the most promising method for depositing silicon nitride with high conformality. Plasma enhanced ALD (PEALD) process are gaining attention due to lower deposition temperature and lower saturation dose as compared with thermal ALD. Experimental and theoretical studies on the PEALD of silicon nitride using aminosilane precursors showed that N_2 plasma give the highest growth rate, and the reaction was inhibited by H-containing plasma, such as NH_3 and N_2/H_2 [1]. Theoretical study investigating the effect of nitriding agent in thermal ALD or PEALD of silicon nitride processes is rare to date. In the present study, we investigated the reactivity of nitriding agent during the second half-reaction using density functional theory (DFT) calculations. The reactions of different nitriding agents, including NH_3, NH_2, N_2, and N, with chlorine-terminated silicon nitride surface were modeled in order to mimic the reaction in the thermal ALD and PEALD processes. The total energies of the geometry-optimized structures for physisorption, chemisorption, and transition state were calculated for each nitriding agent. The reaction of NH_3 with the chlorine-terminated surface was energetically favorable, while there was no observed reaction for N_2 with the surface. The single NH_2 ion reacts with the surface to form NH_2Cl, and two NH_2 ions also prefer to produce two NH_2Cl molecules. Contrarily, the single N ion reacts with the surface to form NCl, however, two N ions prefer to react with each other to form the N_2 molecule without the removal of chlorine atoms from the surface. Expectations from DFT calculation are in a good agreement with related experimental results.

[1] L. Huang et al., Phys. Chem. Chem. Phys. 16 (2014) 18501.

AF-MoP-32 Edge-On MoS_2 Thin Films by Direct Atomic Layer Deposition for Hydrogen Evolution Reaction*, Changdeuck Bae,* *T Ho, H Shin,* Sungkyunkwan University

The edge sites of molybdenum disulfide (MoS_2) have been shown to be efficient electrocatalysts for the hydrogen evolution reaction (HER). To utilize these structures, two main strategies have been proposed. The first strategy is to use amorphous structures, which should be beneficial in maximizing the area of the edge-site moieties of MoS_2. However, these structures experience structural instability during HER. The other strategy is nanostructuring, in which, to enhance the resulting HER performance, the exposed surfaces of MoS_2 cannot be inert basal planes. Therefore, MoS_2 may need critical nanocrystallinity to produce the desired facets. Here, we first describe that when atomic layer deposition (ALD) is applied to layered materials such as MoS_2, MoS_2 exhibits the non-ideal mode of ALD growth on planar surfaces. As a model system, the ALD of $MoCl_5$ and H_2S was studied. This non-ideality does not allow for the conventional linear relationship between the growth thickness and the number of cycles. Instead, it provides the ability to control the relative ratios of the edge-sites and basal planes of MoS_2 to the exposed surfaces. The number of edge sites produced was carefully characterized in terms of the geometric surface area and effective work function and was correlated to the HER performance, including Tafel slopes and exchange current densities. We also discussed how, as a result of the low growth temperature, the incorporation of chlorine impurities affected the electron doping and formation of mixed 2H and 1T phases. Remarkably, the resulting 1T phase was stable even upon thermal annealing at 400 ºC. With the simple, planar MoS_2 films, we monitored the resulting catalytic performance, finding current densities up to 20 mA cm^{-2} at -0.3 V versus the reversible hydrogen electrode (RHE), a Tafel slope of 50 to 60 mV/decade, and an onset potential of 143 mV versus RHE.

AF-MoP-33 Role of Initial Precursor Chemisorption on Incubation Delay for Molybdenum Oxide Atomic Layer Deposition*, Charith Nanayakkara,* EMD Performance Materials*; A Vega,* University of Texas at Dallas*; G Liu, C Dezelah, R Kanjolia,* EMD Performance Materials*; Y Chabal,* University of Texas at Dallas

Atomic layer deposition (ALD) is an attractive technique for thin film deposition due to its sequential and self-limiting surface reactions leading to conformal and controlled film growth. The nucleation of the precursor molecule to the substrate is extremely important to get an ideal ALD process. Any nucleation delay may initially lead to non-uniform island growth, requiring several cycles to obtain continuous and more homogeneous films. Therefore, effective nucleation by chemical reaction of the precursor molecule with the substrate is critical to obtain uniform ALD grown films, particularly ultrathin films

Molybdenum oxide thin films are important for a number of electrical, catalytic, and optical applications. Several Mo precursor-oxidant combinations have been used. For instance, molybdenum hexacarbonyl and ozone (ALD window of 152 - 172 °C),[1] and bis(tert-butylimido)bis(dimethylamido) molybdenum and ozone. (ALD window of 250 - 300 °C)[2]

Here, we introduce a new molybdenum precursor, $Si(CH_3)_3CpMo(CO)_2(\eta^3\text{-2-methylallyl}))$ (MOTSMA), which has a good thermal stability (>200 °C), higher volatility with increased vapor pressure (3s exposure results 0.6 Torr gas phase pressure with bubbler at 90 °C), and increased deposition rates. As is often observed in atomic layer deposition (ALD) processes, the deposition of molybdenum trioxide displays an incubation period (∼ 15 cycles at 250 °C). In situ FTIR spectroscopy reveals that ligand exchange reactions can be activated at 300 °C, leading to a shorter incubation periods (e.g., ∼ 9 cycles). Specifically, the reaction of MOTSMA with OH-terminated silicon oxide surfaces appears to be the rate limiting step, requiring a higher temperature activation (350 °C) than the subsequent ALD process itself, for which 250 °C is adequate. Therefore, in order to overcome the nucleation delay, the MOTSMA precursor is initially grafted at 350 °C, with spectroscopic evidence of surface reaction, and the substrate temperature then lowered to 250 or 300 °C for the rest of the ALD process. After this initial activation, a standard ligand exchange is observed with formation of surface $Si(CH_3)_3CpMo(\eta^3\text{-2-methylallyl})$ after precursor and its removal after ozone exposures, resulting in $Mo({=}O)_2$ formation. Under these conditions, the ALD process proceeds with no nucleation delay at both temperatures. Postdeposition X-ray photoelectron spectroscopy spectra confirm that the film composition is MoO_3. This work highlights the critical role of precursor grafting to the substrate as essential to eliminate the nucleation delay for ultrathin ALD grown film deposition.

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AF-MoP-34 Precursor Screening for Low Temperature Atomic Layer Deposition of SiO_2 using Ozone*, Dingkai Guo,* *B Hendrix, T Baum,* Entegris Inc.

In this work, we compare the SiO_2 ALD deposition behavior of several silicon precursors with different types of Si bonding and molecular structures. The experiments were conducted on a cross-flow thermal ALD tool (Ultratech CNT S200) using deposition temperatures ranging from 50 to 300ºC and the co-reactants H_2O, O_2 and 30wt% O_3 in O_2. None of the precursors tested in this study had significant deposition rates with O_2 or H_2O co-reactants. Precursors dominated by Si-O bonds also exhibited low deposition rates using O_3 as the co-reactant. Several Si-N bonded precursors, however, exhibited good deposition rates: Tert-pentylaminosilylene (TAS), Diisopropylaminosilane (DiPAS), Hexakis(ethylamino)disilane (HEADS), Bis(diethylamino)silane (BDEAS) and Tetramethylbis(dimethylhydrazino)disilane (SiNCH). Films from these precursors were characterized for deposition rate, index of refraction, dilute HF etch rate (WER), FTIR analysis, and step coverage.

Most precursors exhibited a decreasing deposition rate as temperature dropped below 150°C. However, TAS shows a steady rate at about 0.3Å/cycle, and HEADS increases to over 1Å/cycle. At temperatures below 150°C, the deposition requires longer O_3 pulses to become saturated, to decrease the etch rate, and improve the overall etch resistance.

AF-MoP-35 Surface Treatments on Vertically Aligned Carbon Nanotube Forests for Atomic Layer Deposition*, David Kane,* *R Vanfleet, R Davis,* Brigham Young University

Carbon Nanotube Templated Microfabrication (CNT-M) is a fabrication approach that uses the unique geometries afforded by vertically aligned carbon nanotube forests and thin film deposition on these forest to create structures with application in MEMS, chromatography, sensors, energy storage, and other areas. Thin film deposition into the highly porous nanotube forest structures requires a careful balance of diffusion and reaction rate. While some chemical vapor deposition approaches can be tuned to give adequate results, ALD may be the optimal approach. With ALD, the diffusional transport and eventual depositing reaction can be uncoupled to allow uniform deposition deep into the extreme geometries of these forests.

ALD on CNT forests presents a difficult set of challenges. The spacing between nanotubes is on the order of 100 nm while the desired penetration depth can be millimeters. Simple models give diffusion times that depend on the square of the depth and the inverse of the spacing. Thus, cycle times must be long and would need to increase substantially as the pores become smaller due to deposition. During the ALD process, as nuclei of the deposited material form and grow, the number of precursor binding sites increases significantly. This increases diffusion times and dosing needs for full ALD saturation coverage.

To produce a smooth film on the nanotubes, the deposition thickness should be greater than the spacing between nucleation sites. Nucleation site density can be increased by priming the surface with various treatments, including carbon infiltration, ozone or oxygen plasma. Similar penetration and reaction issues are important here as is seen with CVD and ALD depositions.

We will present results on penetration of surface treatment processes (carbon, ozone, and oxygen plasma) into CNT forests, nucleation site densities on these surfaces, and ALD on these high aspect ratio CNT forests.

AF-MoP-36 Quantum Chemical Design for Kinetically Enhanced ALD Precursors*, Thomas Mustard,* Schrodinger, Inc.*; C Winter,* Wayne State University, USA*; M Halls,* Schrodinger, Inc.

First-principles simulation has become an important tool for the prediction of structures, chemical mechanisms, and reaction energetics for the fundamental steps in atomic layer deposition (ALD). Details of reaction energetics for competing surface reaction pathways can be elucidated to provide the fundamental understanding of observed precursor reactivity and selectivity. Such predictive capability raises the possibility for computational discovery and design of new ALD precursors with tailored properties. Interactive studies of the thermochemistry controlling reactive precursor performance can give insight into structure-property relationships, which informs development efforts. We present a mechanism for the reduction of $TiCl_4$ using 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (DHP) and 1,4-bis(trimethylsilyl)-2,5-cyclohexadiene (CHD). From the reaction coordinates the forces controlling kinetic reactivity can be used to redesign a new family of reducing agents. These new reducing agents, based on 1,4-bis(trimethylsilyl)-1,4-dihydropyridine (DH-p), combine the best of CHD and DHP to enhance kinetic reactivity.

AF-MoP-37 QDB: A Database of Plasma Process Data

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Plasma-assisted atomic layer deposition processes have become more and more popular and increasingly enable better control and achieve high precision[1] . Plasma processes are widely used in semiconductor manufacturing and are notoriously hard to control. One of the key factors in plasma chamber design and process optimisation becomes modelling of the plasma kinetics and understanding of plasma–surface interaction. This is also a key to understanding processes on the atomic scale where different laws of physics could apply and scaling becomes non-linear.

We have established a database[2] for plasma chemistry including surface interactions, QDB, which aims to become a basis for ALD modelling development for tool manufacturers and others interested in research in this area[3].

The web software provides a platform for users to upload, compare and validate such data and exposes an API for its automated retrieval in a range of formats suitable for use in modelling software. The service currently has both academic and commercial users and its development is overseen by an international Advisory Board comprised of active researchers in theoretical and experimental plasma science. Data is input from both experimental and theoretical sources by Quantemol staff and by our community of users.

In this presentation we will describe recent developments in QDB: the increased provision of data relating to (a) heavy-particle processes (chemical reactions) and (b) the interaction of particles with surfaces. This has required the expansion of the QDB data model to include a characterization of the surface (substrate) composition and structure as well as the description of the behaviour of individual adsorbed species (desorption energy, diffusion energy, etc.)

It is hoped that the database and its associated online web application software and API will prove useful to the Atomic Layer Deposition community, particularly in commercial and research areas related to plasma-enhanced processes: an illustrative example is given in our presentation.

QDB is available at [https://www.quantemoldb.com/]

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[2] J. Tennyson et al., *Plasma Sources Sci. Technol.* , (submitted)

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AF-MoP-38 Surface Functionalization of Few-layer MoS_2 for Atomic Layer Deposition using Gold Chloride Salts

***Jaron Kropp**, T Gougousi,* University of Maryland, Baltimore County

Transition metal dichalcogenides (TMDs) such as MoS_2 have attracted much interest in the field of nanoelectronics in recent years. These are layered materials with a hexagonal structure similar to graphene. Unlike graphene, however, TMDs are semiconducting materials. While the bulk materials have an indirect band gap, monolayers of MoS_2, WS_2, etc. possess a direct band gap[1]. As such, they have attracted interest for use as a channel material in field-effect transistors. An important feature of the modern field-effect transistor is the gate dielectric. Recently, the electronics industry has transitioned from using native silicon oxide as the gate dielectric to using high-k metal oxides deposited via atomic layer deposition (ALD). Thus, integration of metal oxides on TMDs is of great importance for the use of TMDs in field-effect devices. Unfortunately, TMD surfaces are hydrophobic and not conducive to ALD[2,3]. As such, the surfaces must be functionalized prior to deposition. Here, we report a novel wet chemistry method for functionalization of MoS_2 surfaces using gold chloride salts.

Exfoliated MoS_2 surfaces are treated by immersion in an aqueous $HAuCl_4$ solution for 5-30 seconds and are subsequently subject to atomic layer deposition of 3 nm of Al_2O_3 using trimethylaluminum (TMA) and water as precursors. We measure the effectiveness of the surface treatment by investigating the post-deposition surface topography using atomic force microscopy (AFM). Immersion of the MoS_2 flakes in the gold chloride solution leaves behind adsorbed gold chloride molecules which render the surface hydrophilic and amenable to the growth of aluminum oxide films. While untreated surfaces show island growth (Figure 1a), immersion for as little as 10 seconds results in smoother, more conformal films (Figure 1b). Film growth is confirmed using energy dispersive x-ray spectroscopy (EDX). The elemental maps for sulfur and aluminum are shown in Figures 1c and 1d, respectively.

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AF-MoP-39 Atomic layer deposition of ZrO_2 thin film using a novel linked cyclopentadienyl-amido Zr precursor

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The ZrO_2 film exhibits a high permittivity, a wide band gap (4.6 – 5.8 eV), a suitable band offset on Si (1.4 eV), a low leakage current level and good thermal stability. For these reasons, the ZrO_2 thin film finds applications in dynamic random access memory (DRAM) capacitors and metal oxide semiconductor field-effect transistors (MOSFET). In this study, we introduce a novel linked cyclopentadienyl-amido Zr precursor, namely CMENZ (**1**). Also we compare the properties of the ZrO_2 thin film of **1** to those of commonly used $CpZr(NMe_2)_3$ and $(CpCH_2CH_2NMe)Zr(NMe_2)_2$ (**2**) by atomic layer deposition (ALD).

The evaporation characteristics of **1**, $CpZr(NMe_2)_3$ and **2** were investigated by thermogravimetric analysis (TGA). The amount of residue was about <2.6% for **1**, which had a less residue compared to **2** (5%). For both precursors **1** and **2**, the characteristic self-limiting ALD growth mode was confirmed. However, the self-saturation time of **1** (3s) was shorter than **2** (7s). The growth rate of **1** was 0.95 Å/cycle with ozone as a reactant gas and showed a wide ALD window in a range of 280–340 °C. This ALD window of **1** was noteworthy compared to $CpZr(NMe_2)_3$ which did not show ALD behavior above 300 °C due to the thermal decomposition. In addition, the deposited film of **1** represented better uniformity compared to that of **2**. From this study, it is expected that the **1** could be served as a promising precursor for industrial use because of the fast self-saturation and wide ALD window.

AF-MoP-40 Surface Oxidation of Titanium Oxynitride Films Prepared by PEALD

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The oxygen content within titanium oxynitride (TiON) thin films is crucial for the choice of their application. Moreover, the exposure of the films to ambient air is known to cause surface oxidation [1].

In this work, we study the surface oxidation process of TiON deposited in SENTECH ALD system SI ALD LL. The TiON thin films were prepared by plasma-enhanced atomic layer deposition (PEALD) on silicon substrate using tetrakis(dimethylamino)titanium (TDMAT) and N_2 plasma. We carry out Ar^+ ion sputtering of the film surface in combination with X-ray photoelectron spectroscopy (XPS) (Fig. 1, Supporting Information) as well as angle-resolved XPS for this analysis. After the calibration of the sputter rate, the sputter-time is optimized in order to ensure a near-surface analysis. We find that the thickness of the surface oxidation layer is below 1 nm (Fig. 2, Supporting Information). This result combined with ARXPS data and previously conducted XPS studies using synchrotron excitation [2,3] delivers an entire picture of the complete film configuration (depth profiling) prepared by this PEALD process.

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AF-MoP-41 Characterization of SiN$_x$ Plasma Enhanced Atomic Layer Deposition Process*, **Sun Jung Kim**, S Yong, H Chae,* Sungkyunkwan University (SKKU), Republic of Korea

In the semiconductor structure, silicon nitride (SiN$_x$) performed various roles such as gate spacer, gate dielectrics, and charge trap layer [1]. Especially, the structure of non-volatile memory was developed from primary forms using floating gate to charge trap flash (CTF) in early 2000's using trap SiN$_x$ layer [2]. As the demand for high integration density increases, the structure of non-volatile memory was modified 3D vertical NAND (V-NAND) with a conventional CTF structure. In many processes the demand for low temperature processes are increasing and plasma-enhanced ALD (PEALD) process is being adopted more in many fabrication steps.[3]

In this work, PEALD processes with trisilylamine (TSA) and NH$_3$ plasma were investigated. The SiN$_x$ thin film was deposited in an inductively coupled plasma (ICP) type reactor. PEALD process generates reactive radicals and ions with which it can reduce reaction temperature. The effect of various process variables was investigated in the PEALD process such as plasma power, flowrate of reactant gas, and substrate temperature. The chemical composition and binding energy of SiN$_x$ films were investigated with X-ray photoelectron spectroscopy (XPS). Quadrupole mass spectroscopy (QMS) was directly connected PEALD chamber for in-situ analysis of reactant gases. Using a QMS analyzer, we confirmed injection of each gas during PEALD process. From mass spectrum data at NH$_3$ plasma step, we can characterize intensity of NH$_x$ radical by changing process variables.

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AF-MoP-42 Transient Response of ALD-QCM with Synchronized Back Pressure Control of Sensor Head*, S Tanaka,* Tohoku University, Japan*; K Hikichi,* Techofine Co., Japan*; **Masafumi Kumano**,* Tohoku University, Japan

In an ALD system with multi element sources, many precursor and reactant gas molecules are transported with individual lines to a reactor chamber, causing a difficulty of complete purge in short time during each ALD step. To clear this problem, dual purge method has been developed, where just after shutdown of precursor and reactant gas flow, a pulsed purge gas flow is super imposed from upstream on the continuous purge gas flow, then gas molecules in the transport lines should be pushed out quickly to the reactor chamber 2). During each ALD cycle, continuous purge gas flow of 1 to 3 sccm is set and pulsed purge gas volume of 10-20ml at 10-20torr is imposed just after the precursor or reactant gas flow valve shut off . This pulsed purge gas flow generate a relatively large repetitive pressure increase in the reactor , which push the continuous sensor back purge flow back to the holder and leads to an unwanted ALD coating inside the sensor crystal holder.

To avoid this problem, second pulse purge flow , synchronized to the first pulse purge is super imposed to the QCM continuous back purge . System has been constructed and applied to a commercially-available high temperature QCM head (Inficon, model 750-717-G3, Adjustable ALD sensor. QCM response with synchronous back purge shows instantaneous pressure difference between reactor chamber(QCM sensor front side) and QCM sensor back side (inside of the holder). First pulse purge (for the reactor) generates pressure wave (peak pressure is lower than purge gas storage pressure). During the reactor pulse purge , second pulse purge (QCM back purge) gas is kept on and the sensor backside pressure (in the holder) is higher than the reactor pressure . As a result, no back flow from the reactor to sensor holder occur during the ALD pulse purge period. After the reactor purge time is over, synchronized purge also shut down, the pressure difference disappear and QCM frequency drop off to a low frequency .

In conclusion, transient response of the synchronous back purge of the QCM head can be well controlled and effective to minimize the perturbation from purge gas flow around the sensor head..

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M.Kumano, K.Hikichi, S.Tanaka ,

16th International conference on Atomic Layer Deposition , Dublin Ireland p02-102

This work was supported by "Creation of Innovation Centers for Advanced Interdisciplinary Research Areas Program".

AF-MoP-43 Precise Thickness Controllable Al$_2$O$_3$ Thin Film Using Non-Pyrophoric Al Precursors and Atomic Layer Deposition*, **Donghak Jang**, S Yeo,* Hansol Chemical*; K Mun, J Park,* Hansol Chemical, Republic of Korea

As the minimum feature size of semiconductor shrinks, suppression of leakage current on high-κ dielectric layer has been more important factors. While ZrO$_2$/Al$_2$O$_3$/ZrO$_2$ (ZAZ) dielectric film was effectively suppressed the leakage current, tendency of miniature was required precise control of film thickness. One of common Al precursors, TMA, is pyrophoric and highly reactive, which leads to difficulties in handling and precise control of film thickness. Thus, we developed two non-pyrophoric Al precursors for ALD processes. Al$_2$O$_3$ thin films were deposited on SiO$_2$ by ALD using DMASBO or DMAON and ozone as the oxygen source. The newly proposed ALD system exhibited a typical ALD characteristic, self-limited film growth. In our ALD process, DMASBO showed an apparent ALD temperature window between 240 and 300 ^{o}C with a growth rate about 0.6 Å/cycle. The ALD temperature window of DMAON was obtained in the range of 200-300 ^{o}C. The growth rate was about 1.0 Å/cycle. The as-deposited Al$_2$O$_3$ films were studied via ellipsometer and X-ray photoelectron spectroscopy (XPS).

AF-MoP-44 Diagnostic ALD Reactor with Multiple Modes of FT-IR Spectroscopy*, B Sperling, **James Maslar**, B Kalanyan,* National Institute of Standards and Technology

In situ Fourier-transform infrared (FT-IR) spectroscopy frequently is used to characterize ALD reactions. Various configurations are employed for observing dynamics in surface species, thin films, and interfaces. These include powder transmission, Brewster-angle transmission, attenuated total reflection, and reflection absorption. In this poster, we demonstrate a flow reactor that is capable of measurements in each of these modes. This has allowed us to directly compare the merits and drawbacks of the more common methods by using the well-studied TMA/H$_2$O chemistry as the benchmark. Results are reviewed along with suggestions for choosing the most appropriate sampling method.

AF-MoP-45 Leveraging Atomistic Modeling for Insights into Nucleation of Cobalt Precursors on Various Substrates*, **Andrew Adamczyk**, A Cooper,* Versum Materials*; M Kim,* Versum Materials Korea, Republic of Korea*; S Ivanov,* Versum Materials

Copper encapsulation with thin cobalt films have been shown to greatly improve electromigration performance of Cu interconnects[1]. Further shrinkage of electronic devices brings new challenges for more selective deposition of Co films and more controlled atomic layer deposition (ALD) of thin Co films. Improvement of precursor nucleation on desired substrates is critical for deposition of thin metallic films. First-principles analysis of ALD mechanisms can significantly decrease experimental costs through initial virtual screening of both potential precursors and surface cleaning requirements. In this study, Density Functional Theory (DFT) at the BLYP/DNP level with periodic boundary conditions was employed to study adsorption and surface reactions of selected cobalt precursors on bulk Co, TaN and SiO$_2$ surfaces, as well as mixed surfaces representing partial Co island growth on TaN and SiO$_2$. The bulk surface structures were collected from X-ray crystallography experimental data and terminated with -OH or –NH$_x$ functionalities based upon relevant ALD surface pretreatment conditions. The partial Co island growth was represented by the most stable conformation of a Co$_4$ cluster on bulk TaN and SiO$_2$ surfaces. This approach allowed better understanding of cobalt nucleation on various substrates by direct comparison of precursor adsorption and dissociation energies on small cobalt clusters relative to the underlying substrate surface. Figure 1 shows tert-butylacetylene dicobalt hexacarbonyl (CCTBA) adsorption on a Co$_4$ cluster on SiO$_2$ and TaN surfaces. Modeling results suggest more favorable Co nucleation and formation of thin films on SiO$_2$ surfaces rather than TaN surfaces. Precursor adsorption and dissociation energies on a Co$_4$ cluster relative to TaN and SiO$_2$ surfaces will be presented. The study allows for a more systematic evaluation of new ALD Co precursors.

Emiko Nakazawa, *et al.,* "Development of selective Co CVD capping process for reliability improvement of advanced Cu interconnect" Advanced

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Figure 1: CCTBA adsorption to a four Co atom cluster on (a) SiO_2 and (b) TaN surfaces. Density Functional Theory (DFT) model periodicity not shown for clarity.

AF-MoP-46 Crystalline AlN Films on Si(100) with Sharp Interface and Good Uniformity at Low Temperature by Plasma Enhanced ALD*, **Xinhe Zheng**, S Liu, Y He, M Li, J Wang, C Hou,* University of Science and Technology Beijing, China

Crystalline aluminum nitride (AlN) films are deposited on Si (100) substrates by plasma-enhanced atomic layer deposition (PEALD). Optimal PEALD conditions for AlN deposition are investigated. Under saturated deposition conditions, the clearly-resolved fringes are observed from X-ray reflectivity (XRR) measurements, demonstrating a perfectly smooth interface between the AlN film and Si (100) substrate. It is consistent with high resolution image of no interfacial layer analyzed by transmission electron microscope (TEM). The highly uniform thickness throughout 2 inch-size AlN film with blue covered surface is determined by spectroscopic ellipsometry (SE) measurements. Grazing incident X-ray diffraction (GIXRD) characterization indicates that the AlN films are polycrystalline with wurtzite structure and have a tendency to form preferential crystallization of (002) orientation with increasing of the thickness. A possible mechanism behind the preferred orientation with thickness is discussed.

AF-MoP-47 Comparison between PEALD-TiN Films using $TiCl_4$ or TDMAT as Ti-precursor*, **Hans-Dieter Schnabel**,* Westsächsische Hochschule Zwickau, Germany*; T Junghans, U Reinhold, C Reinhold,* Westsächsische Hochschule Zwickau

For some years thin films of Titanium Nitride (TiN) have been interesting for applications in microelectronics due to its semiconductor properties. To produce films in the nanometer-range mostly atomic layer deposition (ALD)-technique is used. For the thermal TiN-ALD high temperature about 450°C are necessary. To deposit TiN at low temperature (<200°C) the plasma enhanced ALD technique has found application. Some groups used Titanium tetrachloride as Ti-precursor (as example see [1,2]), other groups ([3,4]) utilized Tetrakis-(dimethylamino)-titanium (TDMAT).

The poster compares PEALD-TiN films, produced under comparable conditions (180°C, plasma power 300W) with $TiCl_4$ or TDMAT as Ti-precursor and ammonia (NH_3) plasma as nitrogen-source.

Properties of the films like thickness, growth rate and density (determined by ellipsometry and XRR measurement), conductivity (by four point probe resistivity measurement and calculated from ellipsometry data) and chemical composition (XPS-measurement) will be compared. The results will be discussed. It becomes apparent that not only differences in expected chemical impurities between the films exist.

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AF-MoP-48 High-speed Spectroscopic Ellipsometry for ALD Applications*, **Gai Chin**,* ULVAC Inc., Japan

As a comprehensive manufacturer of metrology tools and deposition tools, ULVAC developed an innovative high-speed spectroscopic ellipsometer for atomic layer deposition applications.

This novel spectroscopic ellipsometry can measure the thickness and optical constants of thin films at a dramatically fast speed. Its data acquisition time is as short as 10 ms. It does not require any active components for polarization-control, such as a rotating compensator and an electro-optical modulator.

It opened great opportunities for new applications of the spectroscopic ellipsometry in which the compactness, the simplicity and the rapid response are extremely important. It can be integrated into the deposition tool and successfully measured thin films in-situ and ex-situ. Obviously, ALD is one of the promising applications for this novel spectroscopic ellipsometry.

This paper describes the principle, system configuration and innovative efforts on developing this compact high-speed spectroscopic ellipsometer for ALD applications.

Some of the ALD applications will be introduced, such as measurement data obtained on Al_2O_3, HfO_2, TiO_2, Ta_2O_5 and TiN thin films. By acquiring thickness data from spectroscopic ellipsometry, the layer by layer growth and material properties of the films can be studied in detail. The growth rate per cycle was determined directly, and an automatic process control can be realized by feedback and feed-forward approach on the ALD tools.

AF-MoP-49 UHV FT-IR Spectroscopy for Atomic Layer Deposition: An Instrumental Contribution*, X Stammer,* Bruker Optics, Ettlingen, Germany*; **Richard Merk**, S Shilov,* Bruker Optics

In atomic layer deposition (ALD) studies, there is a growing demand to adapt a large measurement cell, an ultra-high vacuum (UHV) chamber or particularly an ALD preparation chamber to FT-IR spectrometer optics. The combination of the FT-IR technique and an external preparation chamber enables in-situ monitoring of ALD processing from fundamentals to applications. Bruker provides multiple innovative adaptation solutions of customized chambers to FT-IR spectrometers.

AF-MoP-50 New Tungsten Precursors at Scale - Properties and ALD Application*, **Andreas Wilk**, A Rivas Nass, R Ramon-Müller, O Briel,* Umicore AG & Co. KG, Germany

Umicore has significant expertise in making new MOCVD and ALD precursors available at high manufacturing volumes. The necessary scale up skills include substantial supply chain involvement (quite a few metals used in electronics applications fall under the Dodd- Frank Act and are considered conflict minerals), solid chemical background, purification competence, trace metal analytical capabilities and significant packaging knowhow. Over the last few years Umicore has proven their abilities and successfully provided a range of Ruthenium and Cobalt precursors at scale, which are currently used in various industrial ALD applications. These precursors have been chosen because of the metal back integration based on our recycling operations. Our latest scale up activities focus on new precursor chemistries for group VI based compounds which have increasing interest in new memory and logic applications.

On our poster we will show a number of new solid and liquid tungsten precursors in various oxidation states and with different ligands, which are currently considered for high manufacturing volumes and we will report on their availability and the relevant physical and analytical properties for new ALD applications.

AF-MoP-51 The Effect of Precursor Ligands and Substitution Chemistry on the Nucleation and Structure of Layered Chalcogenides*, H Zhang, **Adam Hock**,* Illinois Institute of Technology

Layered transition metal dichalcogenides (TMDs) such as WS_2 are promising candidates for next-generation electronics. We have developed precursors to highly crystalline WS_2 and characterized it using SEM, TEM, and XRD. Understanding the mechanism of nucleation and growth is important to optimize WS_2 quality and controlled, horizontal growth of TMDs.

In this talk we discuss the results of our mechanistic studies conducted on the tungsten chalcogenides systems. In addition to organometallic synthesis, ligand exchange reactions, and conventional spectroscopy, we also employed synchrotron X-ray absorption spectroscopy (XAS) to understand the oxidation state changes and the ligand behavior during the nucleation of W precursors. The surface reaction of W precursors and half-reaction with S sources were also observed by XAS. The ligand exchange reactions were followed by extended X-ray absorption fine structure (EXAFS) and metal oxidation state changes followed by X-ray absorption near edge structure (XANES). Finally, the precursor design parameters and ligand substitution patterns elucidated from the WS_2 system was expanded to the Wse_2 and Wte_2 systems, which will be compared and contrasted as time permits.

ALD for Manufacturing
Room Plaza Exhibit - Session AM-MoP
ALD for Manufacturing Poster Session

AM-MoP-1 Anhydrous Hydrogen Peroxide Gas Delivery for Semiconductor Manufacturing: Optimal Delivery Conditions for ALD Processes*, D Alvarez, J Spiegelman, **Keisuke Andachi**, R Holmes, Z Shamsi,* RASIRC

Introduction

H_2O_2 gas is a novel oxidant for ALD that improves passivation and nucleation density at semiconductor interfaces, potentially leading to reduced interfacial defect density.[1,2] We have previously reported a new technology capable of generating and delivering stable anhydrous H_2O_2 gas.[3] The method utilizes a solvent based H_2O_2 solution, a carrier gas and membrane pervaporator in order to deliver anhydrous H_2O_2. Several studies have reported on the advantages of hydrogen peroxide as an ALD oxidant versus water and ozone.[4,5]

Heat and Materials Compatibility Challenges

In practice, ALD process limitations have been found due to Manufacturing tool configuration and the heating of delivery lines as well as other components. H_2O_2 is thermodynamically unstable and can decompose into H_2O and O_2 on metal and other material surfaces. The decomposition rate increases with temperature and/or concentration. Most ALD manufacturing tools incorporate long heated lines and/or incompatible materials, and thus are not readily suitable for H_2O_2 use.

Materials Decomposition Study

The decomposition rates of various tube materials have been examined at elevated temperature. These materials included: Pre-conditioned SS; [https://en.wikipedia.org/wiki/Fluorinated_ethylene_propylene] (FEP) - coated SS; and SS with a metal oxide coating. The electropolished SS316L tubing (1/2"x3m) was passivated with H_2O_2 gas at 140C for 8 hours. FEP and the metal oxide coating were applied on the inner wall of the SS tubing by solvent based methods. H_2O_2 concentration vs temperature was monitored by FT-IR. H_2O_2 decomposition rates are significant at T> 90C for the Preconditioned SS and FEP materials. In contrast, the metal oxide coating mitigates decomposition from 60–140C, thus can enhance process performance. Additional material surface results for Hasteloy and Aluminium oxide will be presented.

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AM-MoP-2 OpenALD - A Framework for an Open Source ALD Reactor,

Vivek Dwivedi, NASA

In general terms the equipment that is used for a fully functioning Atomic Layer Deposition reactor is constant from reactor to reactor with specialized preprocessing, post processing and in situ characterization tools such as RGA's, QCM's and ellipsometers. In all reactor builds the following are constants: precursors are pulsed into a chamber volume utilizing high speed pneumatically actuated valves, reactor pressure is monitored using a pressure transducer/manometer, purge gas flow rates and constant reactor baseline pressures are set via mass flow controllers and thermocouples are used to monitor chamber temperature. Specialized commercial software is typically used to preprogram a desired recipe and for *in situ* diagnostics. This specialized software can be cost prohibited, lack expansion functionality and be a deterrent to fully understanding the inner workings of the deposition tool. This talk will introduce an OpenALD framework for reactor control and monitoring that utilizes the open source software Python and it's extension libraries to control multiple ALD reactors while provide flexibility and cost savings measures that can be is easily implemented. Various algorithms, techniques and code examples will be discussed along with implementation success stories.

AM-MoP-3 Multilayer ALD Metal Oxide Films Deposited by Spatially Resolved ALD Processes for Moisture Barrier Films,

Sang Heon Yong, *S Kim, H Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Organic light emitting diodes (OLEDs) are considered as flexible future panel displays due to many advantages such as high color quality, thin thickness. Thin film encapsulation (TFE) is one of essential technologies required flexible display to protect OLEDs from moisture and oxygen.[1] Inorganic films deposited by atomic layer deposition (ALD) process have demonstrated high barrier performance. But, extremely low throughput of ALD process is a major weakness for commercialization. To overcome the low throughput of ALD, high throughput 'spatial ALD' processes have been studied.[2] To achieve high flexibility of barrier layers, multilayer structure has been studied with various inorganic and organic layers [3]. In the multilayer structure, the inorganic layers typically function for the permeation barrier and organic layer for stress relief with increased diffusion pathway of moisture and oxygen.

In this study, Al_2O_3 films were deposited by a spatial ALD process. We characterized various process conditions such as the flowrate of Al precursor and oxygen precursor, scanning speed. We also investigated carbon-rich Al_2O_3 films by controlling the deposition conditions and observed the improved flexibility of the carbon-rich Al_2O_3 films as carbon contents increases in the barrier films. This carbon-rich Al_2O_3 films potentially replace to organic layer without losing flexibility much as shown in Figure 1. Water vapor transmission rate (WVTR) was determined by a calcium resistance test and optical test, and less than 10^{-4} g/m^2 ·day was achieved. Samples were analyzed by x-ray photoelectron spectroscopy (XPS) and field emission scanning electron microscope (FE-SEM).

Acknowledgement : This work was supported by BASF.

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AM-MoP-4 A Green Precleaning Process in Wettability Improvement for Thinner and Uniform ALD Al_2O_3 Film Deposition on Layered MoS_2 Film,

Cheng-Ying Wang, National Taiwan Normal University, Taiwan*; Y Ho, Y Chu,* National Chiao Tung University, Republic of China*; H Hsu,* ITRI, Republic of China*; B Chen, P Chen,* Minghsin University of Science & Technology, Taiwan*; M Lee,* National Taiwan Normal University, Taiwan*; C Jong,* NARLabs, Republic of China

Layered-transition metal dichalcogenides (TMDCs) with tunable energy band gap is promising for many electrical or optical devices application. However, the progress for the device fabrication and characterization are limited because of some integration issues which have not been overcome yet. Up to date, better device data was obtained from the exfoliated film transferred onto a dielectric substrate and source/drain contact metal processed by lift-off process. Furthermore, most of the studied transistor is operated by back gate structure because of poor wettability for ALD HK gate dielectric deposition. It was reported that an oxygen plasma treatment[1], UV-O_3 atmosphere treatment[2] or bi-layer dielectric stacking structure[3] were studied to form a thinner and continuous dielectric layer on TMDCs. Even that, a continuous film thicker than 10 nm and a defective interface is expected.

In this study, we focus on the clean process development by dipping TMDCs film into an alkaline solution (patented by Chu Chi Industrial Co. Ltd) for surface energy tuning. The process was carried out at room temperature. The PH value of the solution is above 10. Previous works[4-5] shown that the alkaline solution could effectively create a hydrophilic surface on bare Si wafer at lower temperature and in shorter time than conventional SPM process (using H_2SO_4+H_2O_2 >120C for 10mins) in current Si ULSI process. The C-V electrical data shown a defect-free interface between HK and Si substrate. Herein, a PLD direct growth MoS_2 film on sapphire and a MoS_2 film on SiO_2/Si substrate formed through sulfidation of tiny sputtering MoO_x were studied. The film thickness were around 5-6 nm and confirmed by cross section TEM. The surface energy of TMDCs films were examined by contact angle observation. The contact angle reduced and then kept from 49 to 38 degree for the non-treated and 10 second treated sample. The high k dielectric layer Al_2O_3 film was deposited by atomic layer deposition after the solution precleaning process. The film thickness measured by ellipsometry and confirmed by TEM is 10 nm. A clean and uniform interface between the Al-$_2O_3$ film and the MoS_2 film was observed. The electrical properties of the dielectric layer will also be discussed. This work proposes a green and promising precleaning process for TMDCs before high k film deposition.

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AM-MoP-5 Highly Sensitive Ion Trap Mass Spectrometer for Inline Process Control

__Ruediger Reuter__, V Derpmann, G Fedosenko, A Laue, T Graber, M Aliman, H Chung, Carl Zeiss SMT GmbH, Germany

Real-time inline control of process gas compositions with high sensitivity has been of particular importance in recent years in the semiconductor industry and beyond. Most of the real-time process gas analysis was carried out with differentially pumped Residual Gas Analyzer (RGA) which are based on a linear quadrupole mass filtering technique. The sensitivity of this technology is limited by the dynamic range of the secondary electron multiplying detector and its strong mass discrimination with increasing m/z–ratio. To generate a complete mass spectrum, a RGA usually needs a few minutes which is often too slow for real-time inline process control. A new mass spectrometer, based on Fourier-Transform 3D-Quadrupole Ion Trap technology, is more appropriate for real-time process control and will be presented in this work.

The 3D-Quadrupole Ion Trap mass spectrometer (*iTrap*) by ZEISS is installed in a vacuum chamber (~120mm x 120mm x 120mm) with a fast sampling valve for pulsed gas injection (pulse duration ~ 20ms). An electron gun is used to ionize the gas. The Ion Trap achieves ion trapping and accumulation by means of a radio frequency voltage applied to the ring electrode of the trap. With the aid of advanced electronic amplifiers and selective ion excitation technique, a very small current, generated by the ion oscillations, is induced on the upper and lower electrodes of the ion trap and can be measured electrically without using any separate particle detector. A mass spectrum is finally obtained by a Fourier Transform of the recorded electrode current signal in less than one second.

Real-time measurements of the hydrogen plasma cleaning process of Sn contaminated samples were performed with the *iTrap* mass spectrometer. The working pressure of the plasma cleaning process was 0.5 mbar. Decreasing signal of SnH_4 and other contaminations from the samples which are directly correlated to the cleaning process were observed with *iTrap*. This result is extremely useful for the process control of plasma processes and inline real-time contaminations control for high-end applications.

Measurements were also performed on a deposition chamber monitoring the deposition process and the cleaning steps in between. Fast dynamic changes in process gas (C_2F_4, O_2, NF_3, H_2) and reaction gas composition could be detected with a repetition rate of ~1 Hz.

AM-MoP-6 STD-PEALD Equipment Design and Evaluation of Nano Thin-Film Characteristics

M Jeong, Korea Electronics Technology Institute, Republic of Korea*; T Ryu,* Sung Kyun Kwan University*; K Hong,* Korea Electronics Technology Institute, Republic of Korea*; J Choi,* Sung Kyun Kwan University*; C Song, M Koo,* LEED Corp.*; __Yekyung Kim__, S Chang,* Korea Electronics Technology Institute, Republic of Korea*; I Jeong,* LEED Corp.*; H Kim,* Korea Electronics Technology Institute, Republic of Korea

The spatial atomic layer deposition (ALD) technique has been developed to complement the drawbacks of the time-dependent conventional ALD technique. However, the spatial ALD technique still has some weaknesses of low productivity, large equipment size which results in high developing cost and so on. The plasma-enhanced ALD (PEALD) which is controlled by time and space in a device, named space and time divided PEALD (STD-PEALD), was developed, in this study. The fast reciprocating motion of substrate with short distance as much of an injector pitch in the proposed STD-PEALD enables to reduce the size of the equipment and to ensure high productivity compared with the spatial ALD constructed so far. Also, the sequential exposure of precursor and reactive gas decreases the dust problem, generally occurs in spatial ALD process. The detailed structure of the proposed STD-PEALD was designed based on the results of thermal-structural coupled field analysis considering both the effect of heat and load produced during operation. Thermal stress was examined by the existence of a heat source. Also, load stress and deformation of the equipment were analyzed to determine the optimum design of the moving parts for the substrate which were made of electromagnetic coils. Additional analysis of fatigue life for the developed equipment was performed regarding of operation parameters--time, speed, etc. Finally, the performance of the developed STD-PEALD was verified by deposition of Al_2O_3 on various films. The high deposition speed and quality of deposition layer of the STD-PEALD were confirmed in this study.

AM-MoP-7 Demonstration of a Correlation between Barrier Property and Defect Visualization of ALD(Al_2O_3)/Graphene Film

K Hong, M Jeong, D Lee, J Seo, S Lee, Korea Electronics Technology Institute, Republic of Korea*; J Choi,* Sung Kyun Kwan University*; I Jeong,* LEED Corp.*; S Chang, __Yekyung Kim__, H Kim,* Korea Electronics Technology Institute, Republic of Korea

Graphene, which shows excellence in mechanical and electrical properties, has been widely researched in various fields. Due to the increase of research areas and demand of usage, commercialization of graphene with its outstanding properties is required. Quality control of mass-produced graphene is a crucial factor for large-scale production. However, the defects which degrade mechanical and electrical properties of graphene occur during synthesis and transfer process. To examine the quality of graphene, we developed an inspection system which can visualize the graphene grain boundary and defects precisely and fast. The visualization system consists an optical microscope with long working distance, a heating stage and gas supply system. Moreover, in this study, the Al_2O_3 layer was deposited by atomic layer deposition (ALD) method on the graphene prepared by chemical vapor deposition (CVD) method. The Al_2O_3/graphene/Cu film was then applied to the developed visualization stage to evaluate the effect of the existence of Al_2O_3 layer by ALD. The visualization strategy is based on the oxidation behavior of graphene and substrate Cu under the temperature and atmosphere condition, especially humidity of the air. Defect visualization of various thicknesses of ALD layer on graphene/Cu were carried out together with the water vapor transmission rate (WVTR). The effect of barrier property of Al_2O_3/graphene film on defect visualization was researched in this study.

AM-MoP-8 Transport and Kinetics of a Remote DBD Plasma for ALD Processing of Metal Oxides

T Beekman, __Yves Creyghton__, J Emmelkamp, Solliance/TNO, Netherlands*; A Sobota,* Eindhoven University of Technology, Netherlands

Different types of dielectric barrier discharge (DBD) plasma sources are being used in ALD platforms at Solliance. Replacement of H_2O by O_2/N_2 plasma in the thermal TMA-H_2O process offers various benefits such as increased speed (shortening purge periods) and low temperature deposition of alumina (100-150^{o}C). Another example is improved composition control in mixed metal oxide ALD such as Indium zinc oxide. We use linear plasma sources with a thin plasma volume (~0.1 mm) ending short above the moving substrate (~0.2 mm). Flow velocities at the plasma slit nozzle are in the 1-20 m/s range. The DBD plasma is generated with alternating pulses with 5 kV amplitude, 50 kHz repetition frequency and 300 W/cm^3 energy density. In order to optimize the geometry and plasma operating conditions for high radical flux homogeneity at moderate gas flows, an integrated fluid dynamics and chemical kinetics model has been set-up using Comsol modelling software. The model assumes constant densities of atomic radicals (O, N) and excited states of N_2 derived from published experimental data. The chemical kinetic reaction rates are obtained from validated models of O_3 production in atmospheric air. The model includes temperature dependent diffusion of radical and molecular gas species, surface recombination of radicals on metals and dielectric source materials, as well as heat transfer by conduction and flow. Both radical and heat production are taken into account as a boundary condition on the dielectric barrier. The calculated oxygen radical flux towards the substrate is compared with the oxygen content in a monolayer of Al_2O_3, based on the measured growth per cycle of 0.16 nm. In order to further validate our model a series of dedicated experiments with the plasma source has been performed. Stationary etching of a 40 nm thick amorphous carbon layer provides detailed information on the spatial distribution of reactive nitrogen species arriving at the substrate. Both temperature measurements within the plasma source and in the process gas directly downstream the nozzle slit have been performed. Finally the influence of the O_2/N_2 ratio on measured O_3 has been determined. Since the model predicts a lower O radical flux from the gas towards the substrate than needed for saturated growth we assume that dissociative recombination of O_3 into O_2 and O at the CH terminated surface contributes to layer growth. In-depth understanding of the influence of the flow distribution and surface recombination of radicals on plasma source and substrate materials has been gained and used for optimization of process settings and geometry.

AM-MoP-9 Effects of Sealing Components on ALD Film Quality*, Fred* ***Pourmirzaie,*** Flodynamix

Atomic layer deposition (ALD) of high quality thin films has recently penetrated manufacturing lines of several major memory and logic manufacturers due to the promise of unprecedented control of thickness, uniformity, quality and material properties. ALD tools were designed around the anticipation that future ultrathin materials are likely to be binary, ternary or quaternary alloys or nanolaminate composites. A unique chemical delivery system enables synergy between traditional, production-proven low pressure chemical vapor deposition (LPCVD) technology and atomic layer deposition (ALD) controlled by sequential surface reactions. Source chemicals from gas, liquid or solid precursors are delivered to arrive on reactive surfaces where self-limiting surface reactions yield film growth with layer-by-layer control. Surfaces are made reactive by the self-limiting reactions, by surface species manipulation, or both. The substrate is exposed to one reactant at a time to suppress possible chemical vapor deposition (CVD) contribution to the film. Precisely controlled composite materials with multiple-component dielectric and metal–nitride films can be deposited by ALD techniques. The research community has demonstrated these capabilities during the past decade. Accordingly, ALD equipment for semiconductor processing is unanimously in high demand. Sealing parts like O-rings and lip-seals used to isolate chamber from outside world play a critical role, more so in ALD processes than any other Semiconductor manufacturing process. This is because any minute outgassing or permeation through O-ring polymer poses grave risk to quality of film deposited. Conventional Perfluoroelastomer (FFKM) O-rings with inherent porosity are not the ideal material of choice for ALD processes. In this article, we will demonstrate the effect of outgassing and permeation from sealing parts on ALD film uniformity, stoichiometry and overall thin film quality. Flodynamix LLC has developed a unique fluoropolymer called Kratos® ideal for ALD and PVD processes.

	Viton®	**Kratos®**	**FFKM**
Permeation of O_2	**1.8**	**1.3**	**7.4**
Permeation of He	**15.5**	**13.2**	**72.0**
Permeation of N_2	**0.06**	**0.05**	**9.5**

Unit in 10^{-8} sccm-cm/sec-cm^2-atm @ 25°C

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Area Selective ALD
Room Plaza Exhibit - Session AS-MoP
Area Selective ALD Poster Session

AS-MoP-1 Area-selective ALD using Vapor and Solution-Phase Synthesized Perfluorodecyltrichlorosilane (FDTS) SAMs as Growth Inhibition Layers*,* ***Ali Haider,*** Bilkent University, Turkey*; S Altuntas,* TOBB University of Economics & Technology, Turkey*; P Deminskyi, T Khan,* Bilkent University, Turkey*; F Buyukserin,* TOBB University of Economics & Technology, Turkey*; N Biyikli,* Utah State University

One of the main type of organic materials used for growth inhibition in area-deactivated selective atomic layer deposition (AS-ALD) is self-assembled monolayers (SAMs). SAMs are made up of long organic molecules consisting of three elements: the head group, chain as the backbone, and a tail group. The tail groups of SAM molecules transforms the surface from an OH-terminated hydrophilic surface into a chemically saturated C-H_3 or C-F_3 hydrophobic surface. When compared with the conventional C-H terminated SAM chemistries, an organic back bone chain made up of fluorine (CF_2) and CF_3 tail groups might provide an enhanced hydrophobic character and potentially may result in an improved film-growth inhibition performance with higher nucleation initiation threshold ALD-cycle numbers. Moreover, the vast majority of the reported SAM-based AS-ALD work in literature utilizes SAMs which are synthesized in wet-solution phase to modify the substrate surface. Such wet processing features low-compatibility with main-stream device fabrication technology and suffers from long processing times and unavoidable defect sites leading to imperfections in growth inhibition. Vapor phase grown SAMs for AS-ALD could provide additional advantages such as faster processing, eliminating wet processing, topographical selectivity, and facile integration with ALD reactors and other fabrication equipments.

In this work, we report an experimental study for AS-ALD using perfluorodecyltrichlorosilane (FDTS) SAM molecules, which are deposited on Si(100) substrates using both vapor-phase and solution-phase synthesis approaches. A comparison between vapor and solution-phase grown SAMs will be provided in terms of growth inhibition performance. FDTS monolayer terminated surfaces formed via vapor and solution phase synthesis methods demonstrated exhibit both high-degree of hydrophobicity (contact angle ~120°) owing to long CF_2 organic back bone chain and CF_3 tail groups. Contact angle, scanning electron microscope (SEM), spectroscopic ellipsometer, and X-ray photoelectron spectroscopy (XPS) measurements results will be presented to demonstrate the effectiveness of FDTS molecules against thin film growth blockage. Finally, we will present micro-scale patterning of thin films using a photolithography patterned SAMs substrate.

AS-MoP-2 Nanoscale Patterning of C_4F_8 Plasma Polymer Blocking Layers via Femtosecond Pulsed Laser Processing for Selective Deposition of Noble Metals*,* ***Petro Deminskyi****, I Pavlov, S Ilday, O Tokel,* Bilkent University, Turkey*; H Eren,* Delft University of Technology, Netherlands*; A Haider, F Ilday,* Bilkent University, Turkey*; N Biyikli,* Utah State University

Area-selective ALD (AS-ALD) is a promising technique for low-temperature self-aligned nanoscale device fabrication by reducing or eliminating lithography/etch process steps. Several methods have been reported for the patterning of ALD-grown films: (1) patterning based on lithography and lift-off; (2) AS-ALD by area-deactivation; (3) AS-ALD by area-activation; and (4) the ideal but highly challenging inherently selective AS-ALD. Though numerous of techniques of surface patterning for AS-ALD have been reported (optical/e-beam lithography), cost-effective alternative solutions are highly attractive.

In this study, we show that by using the pulsed-laser processing technique it is possible to achieve nanoscale patterned surfaces for AS-ALD of nobel metals. To develop this alternative methodology, we have used: an ultrafast Yb-fibre laser, operating at a central wavelength of 1,030 nm which has a 170-fs pulse duration, 1 MHz repetition rate with adjustable laser power levels. For Pt ALD growth, we used trimethyl (methylcyclopentadienyl) platinum (IV) and ozone as Pt and O_2 precursors, with N_2 as the carrier gas. Samples have been characterized using HR-SEM, contact angle measurements, EDX-analysis, and XPS for elemental composition analysis.

Our study consists of the following steps:

- C_4F_8 plasma polymerization on Si(100) substrate surface in an ICP etch reactor;
- Micro- and nanoscale patterning of C_4F_8 plasma polymer by femtosecond (fs) laser pulses;
- Si surface patterning by nonlinear laser lithography (NLL);
- AS-ALD of Pt thin films on patterned C_4F_8/Si interface;
- Plasma polymerization of C_4F_8 on Pt thin film;
- Hydrophobicity study of dielectric/metal/substrate stack.

We'll present our experimental results on surface patterning via *fs* laser pulses and NLL for Pt AS-ALD. Here we speculate about the transparency of C_4F_8 polymer to ~1 µm wavelength. In this regardsTherefore, due to substrate heating, polymer can be removed from specific areas. Patterned structures with diameters as small as 250 nm have been achieved.

This new capability could pave the way for cost-effective lithography-free patterning technique. For future work, (1) surface patterning with smallest possible features; (2) super-hydrophobic surfaces with metal contacts underneath are under development of which the latest results will be presented as well.

AS-MoP-3 Feasibility Study of Single and Multi-layered Graphene as Plasma-compatible Deactivation Layers for Selective Deposition of III-Nitride Materials*,* ***Petro Deminskyi****, E Kovalska, A Haider, C Kocabas,* Bilkent University, Turkey*; N Biyikli,* Utah State University

Plasma-assisted atomic layer deposition (PA-ALD) is a promising method for low-temperature growth of III-nitride materials. However, selective film deposition using PA-ALD is quite challenging mainly due to the plasma-incompatibility of conventional deactivation/blocking layers including SAMs and polymers. The main motivation of this work was to explore alternative growth inhibition materials which could withstand plasma environment.

Towards this goal, we investigated single-layer graphene (SLG) and multi-layered graphene (MLG) as an effective lift-off mask for AlN, GaN, and InN grown via low-temperature PA-ALD. We achieved crystalline III-nitride thin films on graphene blocking layer and Si substrate surface. As far as SLG and MLG possess relatively weak Van der Waals forces between (1) graphene/substrate and (2) graphene/graphene interfaces, here, we gauge the importance of those forces for selective deposition of III-nitride materials. This strategy could be mainly used as an alternative patterning approach based on the graphene-assisted lift-off technique.

To evaluate the selective deposition studies, GaN, AlN, InN, and graphene have been removed from Si surface and were characterized using SEM and XPS. Spectroscopic ellipsometry measurements were performed to measure the film thickness on Si substrate surface and graphene-masked area. An extensive comparative study has been carried out with some successful results for certain binary III-nitride alloys. Possible blocking, nucleation, and graphene-penetration mechanisms will be discussed in conjunction with possible future strategies to further develop selective deposition methods for plasma-assisted film growth recipes.

AS-MoP-4 Electroless Noble Metal Deposition - A New Approach for Highly Selective Surface Controlled Deposition Process*, **Stanko Brankovic**,* Universtiy of Houston*; D Solanki, D Wu,* University of Houston*; Y Dordi, A Joi,* Lam Research

The improved understanding of nucleation kinetics has led to various discoveries in which the thin film growth was manipulated to enhance the evolution of atomically flat epitaxial overlayers. Exploiting some of these results has led to invention of several new methods and protocols for electrodeposition where underpotentially deposited (UPD) monolayer (ML) is used as a mediator, surfactant or sacrificial template. The one successful example is so called "*Deposition via Surface Limited Redox Replacement (SLRR) of UPD ML*" which gained a lot of applications for synthesis of noble metal thin films with different functionalities. This protocol/method represents the combination between the potential controlled step – formation of UPD ML and electroless step – SLRR of UPD ML by more noble metal ions (galvanic displacement). However, our studies show that there is still a lot of room left for improvements and further simplifications. They should expand application of this deposition protocol in many areas where traditional ALD process has been used.

In this talk we present results demonstrating electroless (e-less) ALD process where deposited Pb monolayer is used as a reducing agent and sacrificial material in SLRR reaction with noble metal ions such as Pt, Pd, Ru etc…. The full deposition cycle involves sequential exposure of the substrate to the solution for Pb ML deposition and then to solution for SLRR reaction and noble metal deposition. This results in an overall deposition of controlled amount of noble metal which is the function of the areal density of deposited Pb monolayer and stoichiometry of the SLRR reaction. Therefore, the process mimics to great extend the standard ALD cycle where adsorption of the metal precursors and surface catalyzed reaction are replaced by e-less Pb monolayer deposition and SLRR reaction. If two-step SLRR cycle is repeated an arbitrary number of times a highly compact, smooth and conformal noble metal thin film is grown. The deposition process is highly selective to the metal substrates at which Pb forms an UPD monolayer providing an advantage when certain integration requirements are considered. The process is designed (but not limited) for aqueous solutions with fairly simple and stable chemistry that can be easily scaled up to any size and shape of the substrate surface. Results demonstrating details and underlying phenomena controlling this process will be discussed. In addition, an example of a high quality of Pt, Pd and Ru films grown on Cu substrate will be shown as well as the applications of this process for metallization of structures relevant to semiconductor device fabrication.

AS-MoP-5 Inherently Selective Plasma-assisted ALD: A Feasibility Study for III-Nitride Materials*, **Necmi Biyikli**,* Utah State University*; A Haider, P Deminskyi,* Bilkent University, Turkey

ALD processes featuring inherent selectivity without using any area deactivation/blocking layers or area-activation/patterned seed layers, is an almost unexplored field, but is a highly challenging method with enormous potential to revolutionize the nanoscale processing technology. As ALD processes strongly depend on the chemistry of substrate surfaces and precursor molecules, there is significant potential for the development of selective chemistries and reactions possessing large kinetic barriers. Selective atomic layer deposition/epitaxy of nitride materials has not yet been reported mainly due to the plasma-incompatibility of utilized blocking layers. Likewise, inherently selective atomic layer etching is still challenging with there being very limited success and no reports yet on nitrides.

In this work, we aim to develop inherently selective PA-ALD recipes for the nitride material family. To realize this objective, individual deposition reactions featuring selective chemistry with large kinetic barriers for III-nitride materials against major surfaces will be investigated. This unique bottom-up fabrication tool-box for nitride materials would enable the self-aligned fabrication of critical nanoscale structures minimizing the need for expensive and complex lithography-based top-down processing. Current state-of-the-art selective atomic layer processes include selective-area deposition of oxides and metals only, by using various blocking layers which need to be removed afterwards via additional process steps. Our strategic goal isto achieve the major breakthroughs necessary to enable not only selective ALD for III-nitrides, but also the making of this selectivity inherent, i.e., chemically favorable, to eliminate the use of blocking layers and extra processing steps. The highly-challenging task of developing inherently selective nitride-ALD will be embraced through a systematic study featuring extensive materials characterization efforts to gain a full understanding of the material growth dynamics on various surfaces and carefully monitoring the self-limiting surface reactions.

Our initial investigation on the influence of several critical parameters which might lead to the development of inherently selective plasma-assisted surface reactions show that the choice of substrate material and reactor pressure have a considerable impact on the properties of the deposited film. The key achievement sought in our studies is to obtain a certain nucleation delay between different surfaces including metallic (Pt, Cu), oxide (SiO_2, Al_2O_3), and conventional substrates (Si). We would like to share our critical experimental findings thorughout the presentation.

Emerging Materials
Room Plaza Exhibit - Session EM-MoP
Emerging Materials Poster Session

EM-MoP-1 ALD of Copper(I) Halide Direct Bandgap Semiconductors*, T Homola, R Krumpolec, **David Cameron**,* Masaryk University, Czech Republic*; R Zazpe, J Přikryl, J Macák,* University of Pardubice, Czech Republic*; P Maydannik,* Lappeenranta University of Technology, Finland*; G Natarajan,* Indira Gandhi Centre for Atomic Research, India

Zinc blende-structure copper(I) halide materials (CuHa) are direct gap semiconductors with band energies in the ultra-violet region. They have high exciton and bi-exciton binding energies which have the potential for laser action with very low lasing threshold. Thin films and nanocrystallites of CuHa have been deposited by evaporation, sputtering and molecular beam epitaxy. Recently, preliminary work has shown that ALD has the ability to deposit thin films and nanocrystallite arrays which exhibit the characteristic photoluminescence of zinc blende CuCl. This paper investigates the growth processes and crystal structure and shows that CuCl films can be grown within an ALD window which ranges from 50°C to 150°C using [bis(trimethylsilyl)acetylene] (hexafluoroacetylacetonato)-copper(I) and HCl in butanol as Cu and Cl precursors, respectively. Initial nucleation depends on the length of the post-Cl purge times with short purge time leading to faster nucleation. After nucleation the deposition rate is similar in both cases.

In addition, the results of film deposition of CuCl and CuBr using alternative halogen precursors will be presented. The use of *in-situ* deposition of capping layers to prevent degradation of the CuHa due to atmospheric moisture and their effect on the stability and structure of the films will be described.

EM-MoP-2 Atomic Layer Deposition of Topological Insulator Selenides and Tellurides*, **Tommi Tynell**, C Wiegand, A Thomas, K Nielsch,* Leibniz Institute for Solid State and Materials Research Dresden (IFW Dresden), Germany

Group V-VI chalcogenides based on the tellurides and selenides of Bi and Sb are well known for their thermoelectric properties, but they also display topological insulator behaviour, characterised by strong spin-orbit coupling and conducting surface states taking the shape of a Dirac cone. Topological insulators display a number of interesting properties, and the fact that carriers in the surface states have their spin orientation locked to their momentum can be particularly useful for applications in the field of spintronics. Developing a process for depositing high-quality thin films of these materials is a priority in their experimental study, because it would enable the observation of the topological surface states without too much influence from unwanted bulk carriers. Epitaxial growth of Bi_2Te_3 has been achieved using MBE [1] and PLD [2], and ALD processes have also been developed for the V-VI chalcogenides [3-5]. However, issues remain with the surface quality of some ALD-deposited chalcogenide films. Namely, flaking of the surface has been observed [4,5], making the proper investigation of surface states impossible. Thus, developing an ALD process where the surface issues can be avoided is imperative for investigating the topological insulator properties of chalcogenide thin films.

In this work, Sb_2Te_3, Sb_2Se_3 and Bi_2Se_3 films have been deposited using chloride precursors for Sb and Bi, and alkylsilyl precursors for Te and Se. A variety of substrates, including (100) Si, (111) Si and (0001) sapphire have been utilised, and the influence of the deposition temperature as well as the pulsing and purging times have been investigated. The film growth, structure and surface characteristics have been analysed using x-ray reflectivity, x-ray diffraction and scanning electron microscopy.

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EM-MoP-3 New precursor for low temperature deposition of SiO_2 layer using thermal and plasma enhanced ALD techniques*, A Korolev,* ***Hima Lingam****, V Chitturi, P Cobb,* Nova-Kem*; M Boleslawski, D Suh, C Choi, H Jeong,* Wonik Materials

A new precursor for deposition of SiO_2 layers at substrate temperatures below 200 °C (VLTO1) has been developed recently at Nova-Kem. It is a sufficiently volatile liquid having a vapor pressure of 1 torr @ 75°C and thermally stable up to 200 °C. In a series of thermal and plasma enhanced ALD experiments (using O_3 and O_2 as oxidizers respectively) it has demonstrated excellent growth rate of 1.0 – 1.7 Å/cycle in the Si substrate temperature range of 50 – 150 °C. The highly uniform blanket SiO_2 films deposited by both methods exhibit high chemical purity, good Si:O stoichiometry and density, acceptable leakage current parameters and *k* values ranging between 4.3 and 4.9. The presented results favor VLTO1 in comparison with the leading low temperature SiO_2 precursors. A comparison of theoretically calculated parameters for VLTO1 and other known SiO_2 precursors is also discussed.

EM-MoP-4 Modeling of the Reactions of Hexachlorodisilane on NH and NH_2 Functionalized Silicon Nitride Surface*, X Wang,* The Dow Chemcal Company*;* ***Xiaobing Zhou****, B Hwang,* The Dow Chemical Company*; B Ketola, B Rekken, T Sunderland, A Millward, M Telgenhoff, V Shamamian, C Lee, Y Ahn, W Chung,* The Dow Chemcal Company

Chloro(di)silanes deposit silicon nitride films with ammonia co-reactant in either a thermal or plasma enhanced atomic layer deposition (ALD) process. The film growth involves alternate silylation and ammonolysis reactions. We have studied the silylation reactions of hexachlorodisilane (HCDS) on an NH and NH_2 functionalized silicon nitride (SiN) surface with density functional theory (DFT). The modeling suggests that the cleavage of the Si-Cl bonds in HCDS by the surface NH_2 groups has a 44.4 kcal/mol energy barrier that is substantially lower than the energy barriers for the cleavage of the Si-Si bond by the surface NH_2 groups and the cleavage of either the Si-Cl or Si-Si bond by the surface NH groups.

EM-MoP-5 New Silicon precursor for Low Temperature SiN_x ALD Applications*, A Korolev, H Lingam,* ***Venkateswara Chitturi****,* Nova-Kem*; M Boleslawski, C Choi, H Jeong, D Suh,* Wonik Materials

Silicon precursors for deposition of atomically-thin SiN_x layers at temperatures below 200 °C are of high interest in the microelectronic industry. We have evaluated several silicon precursors for potential SiN_x ALD using Schrodinger software suite and identified a new precursor (VLTN-1) that has a low Si-X bond dissociation energy as well as low activation energy for the dissociative chemisorption step. These theoretical properties favor VLTN-1 in comparison with known SiN_x precursors such as hexachlorodisilane, octachlorotrisilane, and diisopropylaminosilane. The new precursor has been experimentally synthesized, and its thermal properties were evaluated using TGA methods. The results of VLTN-1 deposition experiments are also presented.

EM-MoP-6 Structure and Growth Behavior of MLD Films Using Cyclic Azasilanes, Maleic Anhydride, Trimethylaluminum and Water*,* ***Ling Ju****, N Strandwitz,* Lehigh University

Molecular layer deposition (MLD) is used to grow hybrid organic-inorganic films. We reported a four-step MLD ABCD sequence using N-(2-aminoethyl)-2,2,4-trimethyl-1-aza-2-silacyclopentane (AZ), maleic anhydride (MA), trimethylaluminum (TMA), and H_2O and a three-step ABC sequence consisting of AZ, MA and H_2O.[1] The growth rate of the ABC sequence increased to 90 Å/cycle after approximately 50 cycles, indicating precursor diffusion into the films during deposition. Based on these results, additional quartz crystal microbalance (QCM) data have been acquired during individual reactions, and provide detailed information of precursor diffusion behavior, such as diffusion coefficient and diffusion depth of different precursors. Ellipsometric porosimetry and X-ray reflectivity (XRR) measurements estimate the density and porosity of the as-deposited films, as well as their structural evolution during annealing process. Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) suggest the differences in functionalities and chemical composition between the ABC and ABCD films, providing evidence for the reaction mechanisms and diffusion behavior. These studies provide better understanding of the structures and growth behavior of the MLD films, and avenues for basic studies of the effects of specific chemical functionalities on growth.

1 L. Ju, B. Bao, S. W. King and N. C. Strandwitz, J. Vac. Sci. Technol. A **35,** (2017).

EM-MoP-7 Divalent Group IV Precursors for Atomic Layer Deposition Features*, M Nim,* ***Hyunkee Kim****, K Mun, J Park, J Park,* Hansol Chemical, Republic of Korea

Recently, interest of group IV precursors with wide ALD window has increased for their application of semiconductor industry and flexible display. Especially, formation of encapsulation layer for gas barrier and transparent conducting oxide for electrode in flexible display application require Si and Sn precursors with low deposition temperature. In this work, we report divalent Group IV precursors with liquid phase at ambient temperature. Three new precursors were characterized by NMR and viscometer. Their vaporization characteristics and thermal stabilities were also investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). All the precursors showed to be effective precursors for thermal ALD of oxide thin films with O_3 as an oxidant gas and demonstrated wide ALD window in the range of 100 ℃ to 320 ℃.

EM-MoP-8 Plasma Enhanced Atomic Layer Deposition of Aluminium Sulphide*,* ***Jakob Kuhs****, Z Hens, C Detavernier,* Ghent University, Belgium

Recently, there has been much interest in metal sulphides due to their relevance for energy, photonics and micro electronics applications. Since many of the targeted devices like e.g. field effect transistors, solar cells and transparent conducting films require uniform coatings with precise thickness control, Atomic Layer Deposition (ALD) is an ideal deposition technique.

Aluminum sulphide has a number of promising applications. It can be implemented as an interface layer between high-k dielectric and a III-V semiconductor surface in field effect transistors. It can also be used as a lithium ion conductor for solid state batteries. Furthermore a thorough understanding of the ALD process of Al_2S_3 is crucial in order to realise ALD of Al doped zinc sulphide (ZnS:Al) which may have application as an n-type transparent conducting film. Until now this is done mostly by Electron-Beam Deposition, solution growth methods or CVD.

While thermal ALD of Al_2S_3 from trimethylaluminium (TMA) and hydrogen sulfide (H_2S) were already reported, to the best of our knowledge, no plasma enhanced ALD processes of Al_2S_3 were reported until now.

Here we report on a plasma enhanced ALD process for Al_2S_3. Thin films were deposited in a home-built pump-type ALD reactor by using TMA in combination with argon diluted H_2S-plasma as reactants. The substrates were Si(100) wafers covered with native SiO_2. Argon diluted H_2S-Plasma was used instead of a pure H_2S-Plasma in order to minimize the exposure of the ALD reactor to the highly reactive sulphur radicals. The plasma was generated remotely from the substrate by RF inductive coupling at 200 Watt. The substrate temperature was varied from 100°C to 500°C. Thin film growth rate was monitored in-situ by spectroscopic ellipsometry while the structural properties and composition were characterised ex-situ using X-ray diffraction, X-ray fluorescence, X-ray reflectivity, X-ray photoelectron spectroscopy and energy-dispersive X-ray spectroscopy.

Despite existing reports on thermal ALD using TMA and H_2S, no growth could be achieved with this process in our reactor. However, using a H_2S/Ar-plasma instead of the H_2S gas resulted in a linear growth after a short nucleation time (Fig. 1). The growth per cycle (GPC) of the plasma enhanced ALD process was 1.1 Å/cycle at a deposition temperature of 100°C and decreased down to 0.1 Å/cycle at a deposition temperature of 500°C (Fig. 2). Saturation of the ALD process was observed for TMA and H_2S/Ar-plasma pulse times both longer than 4s (Fig. 3). The obtained Al_2S_3 thin films were amorphous as deposited. From EDX analysis a ratio of approximately 2:3 between aluminium and sulphur was confirmed.

EM-MoP-9 The Film Property of Super-cycled Al_2O_3/SnO_x Atomic Layer Deposition and the Associated Thin Film Transistor Performance, ***Seung-Hwan Lee**, S Choi,* Hanyang University, Korea; *J Park,* Hanyang University, Republic of Korea

Crystalized SnO_2 is known as superior transparent conducting oxide (TCO) which could be used in application such as displays, solar cells and sensors. It can be achieved to attain higher TCO performance by doping other groups and one of them is aluminum dopant. By controlling Al contents in SnO_x matrix, the physical and optical properties was easily manipulated in atomic layer deposited aluminum tin oxide (ATO) layers, which were used with tetrakis(dimethylamino)tin (TDMAT) as a Sn precursor, trimethylaluminum (TMA) as an Al precursor and hydrogen peroxide (H_2O_2 30%) as a reactant. As Al_2O_3 and SnO_x cycles are mixed with various super-cycles (Al_2O_3:SnO_x=n:m), the film properties were systematically changed in terms of the crystallinity, growth rate, and refractive index. The growth rate and refractive index were varied from 1.9 Å/cycle/2.05 to 1.1 Å/cycle/1.63, respectively. Interestingly, it suggested that the inserted TMA molecule or deposited Al2O3 layer affected to suppress initial growth significantly. The film crystallinity was changed from tetragonal SnOx to amorphous like ATO as the Al contents increased in SnOx matrix. Also, as modulating the syper-cycled Al2O3/SnOx layers, the electrical properties of ATO films can be controlled form conductor to semiconductor easily. Consequently, this presentation will show the suitable ATO semiconductor boundary and the associated thin film transistor performance.

EM-MoP-10 Optical Properties and XPS Analyses of $Ti_xSi_{(1-x)}O_2$ Films Prepared by ALD and Comparison to ab-initio Predictions, ***Marek Elias**,* CEITEC, Brno University of Technology, Czech Republic; *P Ondracka,* Masaryk University, Czech Republic; *D Necas,* CEITEC, Masaryk University, Czech Republic; *J Vida,* Masaryk University, Czech Republic; *E Kedronova, L Zajickova,* CEITEC, Masaryk University, Czech Republic

$Ti_xSi_{(1-x)}O_2$ films with varied Ti:Si ratio were prepared by atomic layer deposition (ALD) combining cycles with tetrakis(dimethylamido)titanium and tris(dimethylamino)silane for Ti and Si monolayers, respectively, with oxidizing step. The process was enhanced by plasma and the substrate temperature was 250 ^{o}C. The films were characterized by optical spectroscopic methods (either reflectometry or ellipsometry) in wide spectral range from 0.56 to 10.3 eV and all the experimental data were fitted by dispersion model based on the parametrization of the joint density of states for valence-to-conduction interband transitions. The chemical composition and bonds were investigated by X-ray photoelectron spectroscopy. The results on the optical properties and chemical structure were compared to the films prepared by plasma enhanced CVD obtained also with varied Ti:Si ratio. Density functional theory was used to predict optical properties and binding energies of core electrons sensitive to chemical environment in $Ti_xSi_{(1-x)}O_2$ amorphous materials.

EM-MoP-11 Atomic Layer Deposition of MoO_x:N films: Electrical and Electrochemical Properties, ***Arpan Dhara**, D Saha, S Sarkar,* Indian Institute of Technology Bombay, India

Oxynitrides or nitrogen incorporated oxides of transition metals are rapidly gaining attention in materials research because of their tunable electrical and optical properties. They offer usage in variety of applications like photocatalysis, phosphors, electrochemical energy storage, magnetic materials etc. Primary changes in the material properties after incorporation of nitrogen occur due to the difference in electronegativity, electronic charge and polarizability between oxygen and nitrogen atoms. However, effective and homogeneous doping in the host material is a major practical issue till date. Constructive ways to increase the conductivity without significantly altering the material's chemical properties after doping are still a challenge. Usually nitrogen doping is carried out by annealing oxides under NH_3 or N_2/H_2 gas environment. In such circumstances the metal ions are sensitive to reduction which results in the formation of undesirable phases in the doped materials. Also the possibility of dopant inhomogeneity is a major drawback towards obtaining good quality doped materials.

Here we report, amorphous nitrogen-doped molybdenum oxide (MoO_x:N) thin films synthesized by atomic layer deposition (ALD) at relatively lower temperature of 170^0C. One ALD cycle of molybdenum nitride (MoN_x) is sandwiched for nitrogen incorporation between two MoO_x layers. The concentration of nitrogen is controlled by varying the ratio of MoO_x/MoN_x layers. Quartz crystal microbalance (QCM) measurement is carried out to study the mass change after every single precursor dosed into the reactor. Secondary Ion Mass Spectra **(**SIMS) shows the presence of nitrogen throughout the deposited films. Hence uniform doping is adequately achieved at the reaction temperature. It is observed that conductivity of MoO_x films increase with increase in nitrogen doping concentration. Room temperature and low temperature electrical properties of different films are also studied in detail to understand the transport mechanism with and without nitrogen incorporation.

Both doped and undoped MoO_x are deposited on high surface area MWCNTs and applied as anode material in lithium ion batteries. As expected, doped electrodes show improved performance because of the better ionic and electronic conductivity.

EM-MoP-12 *In Situ* Characterization of Thin Film Molybdenum Carbide using Spectroscopic Ellipsometry, ***Adam Bertuch**,* Ultratech; *J Hoglund,* SemiLab; *L Makai,* Semilab; *J Byrnes,* SemiLab; *J McBee, G Sundaram,* Ultratech

Molybdenum carbide (MoC_x) is an extremely hard transition metal carbide with demonstrated super conductive behavior. Thin film, two-dimensional (2D) molybdenum carbide in a synthesized state with a surface termination group called MXenes has been shown to exhibit either conducting or semiconducting properties and has been identified as a potential thermoelectric material. Synthesis and de-lamination techniques have been demonstrated for 2D Mo_2C by Hamlin *et al*.[1]

In this work we characterize the growth mechanism for depositing the first few cycles of plasma enhanced atomic layer deposition (PE-ALD) MoC_x film with the goal of achieving atomically thin continuous MoC_x. PE-ALD grown MoC_x has been demonstrated using $({}^tBuN)_2(NMe_2)_2Mo$ with H_2 plasma at 150 °C.[2] This deposition technique will be explored in greater detail using real time *in situ* spectroscopic ellipsometry (SE) with a wavelength range from 245 to 990 nm. The nucleation and initial film growth rates can be measured through each PE-ALD half cycle reaction to determine and evaluate the mechanism of growth occurring at the film to substrate interface.

References

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EM-MoP-13 Molecular Layer Deposition of Boron Carbide from Carboranes, ***Michelle Paquette**, L Dorsett, S Malik, A Caruso,* University of Missouri-Kansas City; *J Bielefeld, S King,* Intel Corporation

Atomic layer deposition (ALD) research has exploded in this era of electronic miniaturization, smart materials, and nanomanufacturing. To live up to its potential, however, ALD must be adaptable to many types of materials growth. To extend the reach of this layer-by-layer deposition framework, researchers have begun to explore molecular based processes. Still relatively rare, existing molecular layer deposition (MLD) processes are typically based on the condensation of "linear" 2D or "brush-type" organic polymer chains. To move toward a 3D MLD growth model, precursors with multiple reaction sites would be desirable. To this end, icosahedral carborane ($C_2B_{10}H_{12}$) molecules provide an interesting target. Carboranes have been used in the plasma-enhanced chemical vapor deposition of boron carbide films for low-*k* interlayer dielectrics, neutron detection, and a variety of protective coatings. These are symmetric twelve-vertex molecules, wherein the terminal H atoms at each vertex are known to be labile in the presence of plasma, heat, or a number of chemical reagents. The carborane molecule is very stable and can be derivatized with a range of functional groups; dozens of these derivatives are available commercially, many of which have relatively high vapor pressures. As such, the carborane molecule is particularly intriguing as a novel MLD precursor for 3D growth, possessing unique symmetry, chemical reactivity, and volatility properties not commonly encountered in traditional organic molecules. In this contribution, we describe early work in our group toward developing a novel MLD process for the growth of boron carbide films using a number of different carborane precursors and substrates.

EM-MoP-14 Sub-10 nm Scalable Hybrid Dielectric Engineering on MoS_2 for 2D Materials Based Devices, ***Lanxia Cheng**, J Lee, H Zhu, A Ravichandran, Q Wang, A Lucero, M Kim, R Wallace,* University of Texas at Dallas; *L Colombo,* Texas Instruments, USA; *J Kim,* University of Texas at Dallas

Successful realization of high-performance 2D-based devices requires integration of high quality dielectric film as surface passivation and current barrier. Using atomic layer deposition combined with surface pre-treatments, several studies have demonstrated the downscaling of high-k dielectrics to a few nanometers with promising properties. However, besides inorganic dielectrics, integration of organic-inorganic hybrid dielectric films on MoS_2 using MALD has been rarely investigated, which provides an alternative way of engineering dielectrics with excellent scalability, tunable film compositions, and controllable chemical and electronic properties.

In this work, we explored the deposition of low-k organic-inorganic OTS-Al_2O_3 or OTS-TiO_2 hybrid dielectric films on MoS_2 by molecular atomic layer deposition (MALD). With the assistance of reactive ozone species, our hybrid films demonstrated a controllable thickness scalability at a growth rate of 0.55 nm/cycle with excellent uniformity as verified by the AFM and HR-TEM images. The interfacial chemical composition and lattice structure characterization using XPS and Raman also show undetectable interfacial oxidation states and structural disordering on the MoS_2 surface, owing to its better chemical stability towards ozone exposure. Additionally, our XPS valence band and loss features analysis suggest a tunable band alignments of the MALD hybrid films by replacing the inorganic Al-O component with Ti-O, which also increase the film dielectric constant from 4.5 to ~7.8. Electrical results of top gated MoS_2 devices suggest that these MALD films have promising electrical properties, such as low leakage current (~10^{-5} A/cm^2), minimal doping and small hysteresis of ~40 mV at zero back-gate voltage. Our experimental findings have provided a low cost and reproducible way of fabricating scalable hybrid films on TMDs as gate tunneling dielectrics promising for 2D devices and flexible electronic applications.

We acknowledge partial financial support from the Southwest Academy on Nanoelectronics (SWAN) by the Nanoelectronic Research Initiative and NIST; and the NRF (No. 2015M3D1A1068061) in Korea, and TMEIC for providing the ozone generator.

EM-MoP-15 Critical Layer Thickness Determination for GaN Thin Films Grown on Sapphire Substrate via Hollow-Cathode Plasma-assisted Atomic Layer Deposition*, **Mustafa Alevli**, N Gungor,* Marmara University*; N Biyikli,* Utah State University

Device quality epitaxial GaN films require substrate temperatures typically higher than 600°C. However, with recent efforts using plasma-assisted atomic layer deposition, crystalline GaN films with preferred crystal orientation were obtained at substrate temperatures as low as 200°C. In this study, we report on the optical and structural properties of highly oriented (002) GaN with different thicknesses, ranging from 5 nm to 100 nm deposited via hollow-cathode plasma-assisted ALD (HCPA-ALD) on c-plane sapphire substrates. Although the compressive stress is a result of lattice mismatch between GaN films and substrate, it has been reported that the average strain in GaN thin films strongly correlates with the film thickness and usually changes from compressive to tensile as thickness increases. In the present research, the evolution of the average strain, phonon positions, Bragg reflection positions, and optical band gap energy in HCPA-ALD-grown GaN films have been analyzed. The XRD scans of all GaN samples revealed that the films are crystalline with hexagonal wurtzite structure. The films have been characterized from the mid-infrared to the ultraviolet spectral range by using spectroscopic ellipsometry in order to obtain the critical optical parameters including optical band edge and refractive index which helped us to understand the influence of film thickness on the aforementioned parameters. The measurements indicate that the increasing trend of the refractive index (n) reverses around ~60 nm. However, we have not observed a clear correlation between optical band gap and film thickness. The lowest optical band edge values obtained from ellipsometry is ~3.56 eV. Phonon modes in GaN films were studied by employing both Raman and infrared spectroscopic ellipsometry.

The E_1(TO), E_1(LO), A_1(TO), A_1(LO) and E_2(high) phonon modes were identified for all four samples. All the phonon peaks related to GaN are considerably blue shifted with respect to their bulk values. This particular behavior is similar to the ones observed in GaN quantum dots. The E_1(TO) and A_1(LO) phonon modes are following comparable trend where the phonon peak positions shift towards lower wavenumbers for increasing thickness up to ~60 nm, while the phonon peak positions move towards the bulk value for 100 nm film. E_2(high), E_1(TO), and A_1(TO) vibrational Raman peaks ranging from 500-600 cm^{-1} are difficult to separate, while the trending Raman peaks appear to evolve very strongly with thickness which is an indication of improving crystalline quality. The overall results suggested that GaN films with thicknesses above 60 nm feature different behavior compared to thinner GaN films.

EM-MoP-16 Digital Doping of ALD VO_2 for Thermochromic Applications*, **Alexander Kozen**, M Currie,* U.S. Naval Research Laboratory*; K Jungjohann,* Sandia National Laboratory*; B Downey,* U.S. Naval Research Laboratory, usa*; C Eddy, Jr., V Wheeler,* U.S. Naval Research Laboratory

Vanadium Dioxide (VO_2) is an interesting thermochromic material that undergoes a first order crystalline phase transition at a critical temperature (T_c) of 68˚C. This structural phase transition is accompanied by major changes in electrical and optical properties, particularly in the infrared. As such, VO_2 is suitable for many applications including microbolometers, adaptive thermal coatings, and passive spacecraft thermal shielding.

While the T_c of VO_2 is convenient for many applications, it is desirable to modify the T_c to other values for either new applications or improved performance in the previously stated applications. The T_c of VO_2 is known to be strain-mediated.[1] Strain in VO_2 has been induced via deposition of thin films onto lattice mismatched epitaxial substrates, as well as by doping with other transition metal elements besides V.[2], [3]

For the first time, we are investigating doping of ALD VO_2 using other elements such as Al, Ti, Nb, and W by incorporation of their oxides into the binary ALD VO_2 process (TEMAV + O_3). We will discuss the fundamentals and limitations of doped ALD VO_2 growth and basic materials characterization, and will demonstrate the impact of dopant concentration and identity on the phase transition properties (both optical and electrical) of the resulting films.

Generally, inclusion of dopants such as Ti and Al into the ALD VO_2 process in amounts between 1% and 10% results in surfactant-like film growth behavior, with increasing dopant concentrations reducing RMS roughness of the ALD films from ~2 nm to ~0.2 nm. Higher concentrations of dopants also interfere with film crystallization, inhibiting the magnitude of the metal-insulator transition. Smaller concentrations of dopants can modify the T_c of the VO_2 films either up or down, depending on dopant identity and concentration.

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EM-MoP-17 Characterization and Comparison of ALD Laminate Structures with HfO_2 + SiO_2 as MIM Capacitor Dielectric for GaAs HBT Device*, **Yao-Ting Shao**, C Hua,* WIN Semiconductors Corp., Republic of China

One well known application of ALD method is to deposit a high-k film as a capacitor dielectric. Single film, HfO_2 and Al_2O_3, as MIM capacitor deposited at 300C with 600A of thickness was evaluated first. 900A of PECVD Si_3N_4 film was deposited at 300C for comparison. The capacitance density and breakdown field are listed in table 1. The capacitance density of HfO_2 was high as expected, but breakdown field was too low to pass Time Dependent Dielectric Breakdown (TDDB) lifetime of 20 years at 20V that is a typical reliability requirement for the GaAs HBT device.

In order to pass the TDDB requirement four different laminate structures as capacitor dielectrics were designed with HfO_2 and SiO_2 deposited by ALD at 300C. The film thickness of HfO_2 (630Å) and SiO_2 (144Å) were fixed for the four different structures listed in table 2. HfO_2 are the first and last layers of those structures to ensure that the interface effect between dielectric and metal will be the same. Theoretically, the capacitors of four different dielectric structures should have the same capacitance density. But figure 1 shows that they exhibited significantly different capacitance densities and breakdown voltages at room temperature.

TDDB lifetime was tested afterwards shown in Figure 2. Extrapolation was applied to calculate lifetime at 20V after higher voltage stress at 125C. We found that L17 capacitor at 20 volts had the shortest lifetime than that of sample L9 and L3 capacitors. However,the breakdown voltage of L17 at room temperature was the highest. These reliability results were unexpected. The capacitance behavior of L3 and L17 at high temperature was investigated as well. The capacitance of L17 increased ~1.6% higher than that of L3, ~1.1% increase as temperature changed from 25^{o}C to 150^{o}C.

The capacitance density of L3 is a bit lower, but it exhibits high TDDB lifetime and less capacitance variation as the temperature is increased. This indicates that simple laminate L3 is much more attractive than complicated laminate L17 for GaAs HBT device. More related data will be presented in the conference.

**EM-MoP-18 Atomic Layer Deposition of Mo-doped VO_2 Thin Films by Nanolamination of VO_2/MoO_3 Alternating Layers*, Xinrui Lv,* *Y Yu, Y Cao,* Chinese Academy of Sciences, China

Mo-doped VO_2 thin films were fabricated by nanolaminated packing of VO_2/MoO_3 alternating layers using atomic layer deposition (ALD). In the deposition process, tetrakis-dimethyl-amino vanadium (IV) (TDMAV) and molybdenum hexacarbonyl [$Mo(CO)_6$] were used as vanadium precursor and molybdenum precursor, respectively. The deposition temperature was studied to satisfy the requirement of ALD temperature window for both metal precursors, which was testified as around 165 °C. Studies showed that the doping concentration of Mo in VO_2 depends on the ratio of ALD cycle number of molybdenum precursor to that of vanadium precursor. Additionally, effect of doping concentration on the semiconductor-to-metal transition (SMT) characters of VO_2 was also studied, and a considerable reduction of phase transition temperature (T_c) was observed in Mo-doped VO_2 thin films.

EM-MoP-19 Trace Metal Analysis on SiC Wafers using ICP-MS*, Jaya Chowdhury,* ChemTrace

High level power electronic devices such as SiC-MOS, SiC SiC-IGBT's are used in power electronic devices. High purity semi-insulating Silicon carbide (HPSI-SiC) wafers are widely used as the substrate replacing silicon in this case. Naturally, the defect free SiC substrate is necessary for a stable and high performing product. Understanding surface metal contamination distribution on SiC wafers is becoming a necessity with the use of these substrates in MOSFET's.

In this paper we will demonstrate a technique that has been developed for revealing high levels of trace metal impurities with high accuracy and sensitivity on the surface of the silicon carbide wafer materials. We will present data from several batches to validate necessity of quantifying the presence of high levels of TM contaminant present in un-acceptable amounts.

EM-MoP-23 Atomic Layer Deposited Single Crystal High-k Y-doped Cubic HfO_2 on GaAs(001) Utilizing HfO_2/Y_2O_3 Super-cycles*, Lawrence Boyu Young, C Cheng, Y Lin, K Lin,* National Taiwan University, Republic of China*; C Hsu,* National Synchrotron Radiation Research Center, Republic of China*; J Kwo,* National Tsing Hua University, Republic of China*; M Hong,* National Taiwan University, Republic of China

Si-based complementary metal-oxide-semiconductor (CMOS) technology has reached its physical limit as the scaling-down process is no longer available since the 22-16 nm node. To overcome this challenge, diverse solutions have been proposed in the past few decades. One of the most promising solutions is to replace the Si channel and SiO_2 gate dielectrics by high mobility III-V compound semiconductor and high-k gate dielectrics. Among the III-V compound semiconductors, GaAs with (001) orientation is a promising candidate to be integrated with the conventional Si(001) platform because of the relatively smaller lattice mismatch to Si than those of most of other III-V semiconductors. As the CMOS technology keeps scaling down in its dimensions, we urgently need materials with higher dielectric constant > 30 to push sub 7-nm CMOS technology. There are three well-known phases for HfO_2, monoclinic, cubic, and tetragonal phase, with the dielectric constants of 20, 30, and 70 (by calculation); the cubic and tetragonal phases are unstable at room temperature. In our previous work, we have successfully grown single crystal cubic HfO_2 on GaAs(001) by using MBE through 19% Y-doping1. In order to explore the potential of cubic HfO_2, it is necessary to demonstrate single crystal growth of cubic HfO_2 by utilizing ALD. In this work, we have epitaxially grown single-crystal cubic Y-doped HfO_2 (YDH) on GaAs(001) substrate using ALD HfO_2/Y_2O_3 super-cycles. The reflection high energy electron diffraction (RHEED) patterns revealed that the surface of the deposited YDH exhibited four-fold symmetry (Fig. 1). We have performed synchrotron radiation x-ray diffraction (SR-XRD) study to further study the crystal structure of the films. From the radial scan along the substrate normal, the two strong and sharp peaks located at 31.618° and 66.043° are attributed from the substrate GaAs(002) and GaAs(004). The only other two peaks observed at 34.88° and 73.66° are corresponding to the d-spacing of 0.257 nm and 0.128 nm, from which a lattice constant of 0.5136 nm was calculated, which is close to our previous result of MBE grown single crystal YDH. The off-normal ϕ-cone scan across the YDH{111} was performed to confirm the symmetry of the structure. The peaks were spaced by a 90° equal spacing, indicating that the structure exhibits a four-fold symmetry (Fig. 2). Furthermore, from the positions of GaAs{111} and YDH{111}, we have determined the epitaxial relationship between YDH and GaAs to be YDH(001)[010]//GaAs(001)[010].

#LBY, CKC, and YHL have contributed equally to this work.

*CHH, JK, and MH are the corresponding authors.

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ALD Applications
Room Plaza F - Session AA+AF-TuM

Displays and Flexible Applications (8:00-10:00 am)/ALD Fundamentals: In-Situ Monitoring and Analysis (10:45 am-12:00 pm)

Moderators: Hyungjun Kim, Yonsei University, Korea, Jin-Seong Park, Hanyang University, Han-Jin Lim, Samsung Electronics, Tom Knisley, Applied Materials

8:00am **AA+AF-TuM-1 Functional Materials using Atomic Layer Deposition for Emerging Display Applications*, Jin-Seong Park,*** Hanyang University, Republic of Korea **INVITED**

Atomic Layer Deposition (ALD) has remarkably developed in semiconductor and nano-structure applications since early 1990. The unique properties, including controlling atomic-level-thickness, manipulating atomic-level-composition control, and depositing impurity-free films uniformly, may accelerate ALD related industries and applications in functional thin film markets. One of big commercial industries, display market, just starts to look at the potential to adopt various functional inorganic/organic/hybrid films based on ALD/molecular layer deposition (MLD) techniques in emerging applications, such as transparent, flexible, and wearable electronics.

In this talk, I will take the brief emerging display market trend and forecast to understand what they are looking for. In fact, the AMOLED (active matrix organic light emitting diode) Television markets are just starting at early 2013. There are a few possibilities and needs to be developing for AMOLED, flexible and transparent Display markets. Then, firstly, the functional oxide conductor/semiconductor films deposited by ALD will be discussed for applying transparent conductor and thin film transistor as an active layer even on flexible substrates, including InOx, SnOx, ZnSnO, and InZnOx. Secondly, functional oxide and organic thin films, deposited by ALD/MLD have been demonstrated in emerging applications (flexible, transparent, and wearable things). In particular gas diffusion barrier property such as water and oxygen water vapor is important for passivation and encapsulation applications.

8:30am **AA+AF-TuM-3 Flexible Platinum Nanoparticle-based Piezoresistive Transducers Elaborated by Atomic Layer Deposition*, Etienne Puyoo*,** *C Malhaire, D Thomas, R Rafaël,* Institut des Nanotechnologies de Lyon, France*; M R'Mili, A Malchère, L Roiban, S Koneti, M Bugnet,* MATEIS, France*; A Sabac, M Le Berre,* Institut des Nanotechnologies de Lyon, France

For the last ten years, the research on piezoresistive transducers has mainly been focused on the use of nanomaterials to optimize sensitivity, power consumption and sensor miniaturization. For instance, strain gauges based on Si nanowires, carbon nanotubes, graphene, MoS_2, Ag nanowires and metallic nanoparticle (NP) assemblies[1-4], have been developed at the laboratory scale to achieve very large gauge factors (GF) that compete with those of the state-of-the-art bulk Si gauges. Although the use of nanomaterials has attracted a lot of attention in literature these past few years, many technological obstacles (manipulation of individual nanostructures, complexity of the process, sensor reproducibility etc.) have yet to be overcome to make nanomaterials the preferred material for strain sensors. Consequently, alternative reliable technologies for the fabrication of nanostructured strain gauges with high GF are still sought-after by the industry.

In this work, platinum NP-based strain sensors are elaborated by means of Atomic Layer Deposition (ALD) on flexible polyimide substrates (Fig. 1). Pt NPs are grown by Plasma Enhanced ALD from ($MeCpPtMe_3$) precursor and O_2 plasma on thermal ALD alumina in subsequent process steps at 200°C in an Ultratech FIDJI F200 reactor. As presented in Fig. 1, several Pt NPs layers and Al_2O_3 tunnel oxide layers are stacked on polyimide in order to fabricate the flexible strain sensors. Their electro-mechanical response is tested under mechanical bending in both buckling and conformational contact configurations. A maximum gauge factor of 70 is reached at a strain level of 0.5% (fig.2). Although the exponential dependence of the gauge resistance on strain can be attributed to tunneling effect, it is shown that the majority of the junctions between adjacent Pt nanoparticles are in short circuit state. Finally, we demonstrate the feasibility of an all-plastic pressure sensor integrating Pt nanoparticle-based strain gauges in a Wheatstone quarter-bridge configuration (fig. 3).

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8:45am **AA+AF-TuM-4 Color Coating of Electronic Textiles via Control of Refractive Index by Atomic Layer Deposition*, Hyun Gu Kim,*** *W Kwon, H Lee,* Incheon National University, Republic of Korea

Attempts to integrate various electronic systems and sensors into textiles have been made for future wearable electronics. Conducting textile which is a key component for these wearable electronics is called by electronic textiles (e-textiles). Since most of conventional textiles are electrically insulator, metallic materials should be added to textiles during or after synthesis processes of textile. In the aesthetic point of view, however, the addition of metal for fabrication of e-textiles has a big disadvantage that is grey and black color of textile from the reflection and scattering of metal components. In addition, the conventional dying technology could not be applied to the e-textile systems after addition of metals. In our recent paper, we reported that conventional cotton textiles were successfully changed to e-textiles by Pt coating by atomic layer deposition (ALD). In this work, we report a novel approach to change the color of e-textile by using TiO_2/Al_2O_3 multilayer structures prepared by ALD. The various color combinations of the TiO_2/Al_2O_3 multilayer were simulated on planar Pt surface by computer simulation software that is based on change of refractive index. In the computational work, the film structures of TiO_2/Al_2O_3 multilayers and thickness of each layers were controlled to obtain desire colors. The simulation results were applied to experiments on planar structure as well as textile structures. The mechanical durability and optical properties of the TiO_2/Al_2O_3-multilayer-coated e-textiles were characterized. This approach for color coating of e-textiles presented here could provide more opportunities for the application of ALD-based e-textiles to other wearable electronics.

9:00am **AA+AF-TuM-5 Comprehensive Studies of Atomic Layer Deposited InGaO Thin Films using InCA-1, TMGa and H_2O_2 for Oxide Semiconductor Thin Film Transistor Applications*, Jiazhen Sheng,*** Hanyang University, Republic of Korea*; B Shong,* Chungnam National University, Republic of Korea*; J Park,* Hanyang University, Republic of Korea

Oxide semiconductor thin film transistors (TFTs) have been extensively researched as a backplane technology in display industry, and among the well-known TFT active layer materials, including IZO, IGZO and ITZO, indium gallium oxide (IGO) has been suggested as a promising one due to its attractive performance. IGO thin films were deposited by ALD with different sequences at 200°C using [1,1,1-trimethyl-N-(trimethylsilyl)silanaminato]indium (InCA-1) as the indium precursor, Trimethylgallium (TMGa) as the gallium precursor, and hydrogen peroxide (H_2O_2 30%) as the reactant, that reactant pulse was launched before and after sequential metal precursor pulse to get a clear understanding on ALD multicomponent growth for oxide semiconductor materials. The gallium oxide shows successful deposition at 200°C when accompany with InCA-1-H_2O_2 sequence (Ga% ~ 20.6 to 28.3%), while no growth appeared without indium oxide deposition. The potential energy of InCA-1 and TMGa precursors on the hydroxylated Si(100) surface and hydroxylated trivalent indium on Si(100) surface were calculated by DFT, that revealed TMGa cannot adsorb on hydroxylated Si while was able to adsorb on hydroxylated InO_x surface. The ALD IGO shows controllable atomic composition and electrical characteristics, such as carrier concentration and resistivity, by adjusting supercycle in certain sequence. Thus, IGO thin film by ALD was applied to the active layer of TFT and the performance was optimized by adjust the supercycle, with mobility $9.45 cm^2/Vs$, threshold voltage -1.57V and subthreshold slop 0.26 V/decade.

Table 1. The growth rate and atomic composition of ALD growth thin film with various sequences (Growth rate obtained by SE and atomic percentages with AES)

Sequence	Growth rate (Å/cycle)	at. %C	at. %Ga	at. %In	at. %O
GaO	-	-	-	-	-
InO	0.97	0.5	0	42.8	56.7
In-Ga	0.77	0.7	3.8	39.6	55.9
Ga-In	0.33	0.4	28.3	14.9	56.4

InO-GaO	0.42	0.6	20.6	22.7	56.2

9:30am **AA+AF-TuM-7 Highly Sensitive VOCs Sensor Based on Atomic Layer Deposition of TiO_2 on Carbon Nanotubes*, Michela Sainato,*** University of Illinois at Chicago*; R Divan, L Stan, Y Liu,* Argonne National Laboratory*; I Paprotny,* University of Illinois at Chicago

Volatile organic compounds (VOCs) are largely used in industries as reaction intermediates for the synthesis of chemicals and in research laboratories as solvents. The probability of over-exposure to such toxic agents is very high; therefore, the development of gas sensors for early detection of toxic VOCs is necessary. So far, attempts have been focused on the development of thin-film n-type semiconducting metal oxide-based gas sensors, such as SnO_2, ZnO, TiO_2.[1]

Our approach targets the fabrication of low-cost low-power chemi-resistor sensors based on multiwalled CNTs (MWCNTs) functionalized by ALD with metal-oxide(MOX). Specifically, we report the design and synthesis of high-surface-area TiO_2 functionalized MWCNT based sensors. Prior to ALD TiO_2 deposition on MWCNTs surface, we performed site-specific O_2-plasma activation on the MWCNTs surface. The creation of physical active sites is an effective way to enhance and spatially control the growth of TiO_2NCs (not limited to ZnO, SnO_2). By varying the deposition temperature during the ALD process, the morphology and crystallinity of the TiO_2 varies. At 175°C, a continuous amorphous TiO_2 layer on the MWCNT is observed (Figure 1a).

The TiO_2 /MWCNT heterostructure chemi-resistive sensor arrays for the selective detection of low concentrations of different VOCs at room-temperature (RT) have been tested. The resulting TiO_2 (at 200°C)/MWCNT sensors operate at RT and show fast and reliable responses to benzene (C_6H_6) and to toluene (C_6H_5-CH_3) (Figure 1b) while TiO_2 (at 175°C)/MWCNT sensors show no response (Figure 1c).

In this talk we will discuss the role of the TiO_2 deposition temperature on the morphology and crystallinity of the TiO_2 and its influence on the VOCs sensing.

Our aim is to elucidate the mechanism by which the ALD coating increases sensitivity to the final composite materials, thus paving a way toward the integration of chemi-resistor sensors with improved selectivity, lifetime, and reliability toward specific VOCs, as well as improved environmental sustainability.

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10:45am **AA+AF-TuM-12 *In-situ* Real-time and *in-vacuo* Study of the Temperature Impact on the Al_2O_3 ALD Nucleation upon Pristine Monolayer Graphene*, Marcel Junige,*** Technische Universität Dresden, Germany*; J Kitzmann, C Chavarin,* IHP GmbH, Leibniz-Institut für Innovative Mikroelektronik*; M Geidel, J Reif, M Albert,* Technische Universität Dresden, Germany*; G Lupina, C Wenger,* IHP GmbH, Leibniz-Institut für Innovative Mikroelektronik, Germany*; J Bartha,* Technische Universität Dresden, Germany

Graphene (G) has attracted attention for THz switching capabilities in novel electronic device concepts: in a G-Base Transistor, a voltage at a sandwiched G-Base has been devised to control vertical electron tunneling through an emitter-base dielectric below, and hot electron tunneling through a base-collector dielectric above a G monolayer, respectively. This study strives for achieving these ultra-thin, demanding dielectrics by TMA–H_2O/–O_3 ALD.

Dielectric ALD has been applied to various types of G: either as-grown over the SiC/metal-catalyst substrate or transferred to another support substrate. Very distinct nucleation has been observed, largely depending on the G|substrate interaction, which in turn determines the energetic landscape of the G surface, i.e. the probability for initial precursor adsorption. SiC or metal underneath monolayer G have significantly enhanced dielectric ALD nucleation upon such G surfaces. In contrast, conducting ALD upon G over a dielectric or graphitic underground, substrate-inhibited island growth has commonly been exhibited due to G's intrinsic lack of dangling bonds, i.e. missing nucleation sites. However, such dielectric underlay is the relevant case for electronic applications. Accordingly, G has been pre-treated, functionalized, or seeded, entailing some additional effort along with the risk of defect generation. A rather simple approach for directly growing continuous, pinhole-free, and smooth films upon monolayer G over SiO_2 has recently been achieved by TMA–H_2O ALD at 100°C without any other G modification. This low-temperature method has based on self-terminating surface reactions with physisorbed H_2O molecules. Building on this, we systematically investigate here Al_2O_3 ALD nucleation phenomena upon pristine monolayer G in dependence on the deposition temperature by *in-situ* real-time Spectroscopic Ellipsometry (cf.Fig.) and complementing *in-vacuo* techniques, namely photoelectron spectroscopy as well as scanning probe microscopy.

On the downside of reduced deposition temperatures, ALD films then have exhibited lower mass densities, higher hydrogen concentrations (at unaffected Al:O ratios, indicating Al hydroxide), and lower electrical breakdown fields. Hysteresis in our I-V measurements also indicated charges at the interface or within the coating, pointing out insufficient electrical film quality for desired application as tunnel barrier. Therefore, we split the ALD process into two steps, switching from initially 100°C for better nucleation to subsequently higher temperatures for improved electrical properties. Likewise, we tested switching from initial H_2O to following O_3, as well as post-deposition anneals.

11:00am **AA+AF-TuM-13 Investigation of the Influence of Plasma Parameters During Aluminum Nitride Atomic Layer Epitaxy using Grazing Incidence Small Angle X-ray Scattering*, Virginia Anderson,*** *N Nepal, S Johnson, D Boris, S Walton,* U.S. Naval Research Laboratory*; Z Robinson,* SUNY College at Brockport*; A Kozen,* U.S. Naval Research Laboratory*; A Nath,* George Mason University*; S Rosenberg,* U.S. Naval Research Laboratory*; C Wagenbach,* Boston University*; J Hite,* U.S. Naval Research Laboratory*; K Ludwig,* Boston University*; C Eddy, Jr.,* U.S. Naval Research Laboratory

III-nitride semiconductors are tunable band gap materials, already in use in LEDs, and have additional uses in electronic switches and photovoltaics. Molecular beam epitaxy and metalorganic chemical vapor deposition (MOCVD) are performed at high temperatures, with AlN MOCVD growth requiring well over 1000°C. Early research investigating low-temperature plasma assisted atomic layer epitaxy (ALEp) to see if it could be added to the techniques able to produce high quality nitride semiconductor films is underway. Compared to conventional growth methods, ALEp offers elimination of miscibility gaps in ternaries and reduced thermal coefficient of expansion mismatch in heterostructures. Already published work shows that ALEp of AlN with high crystalline quality can be achieved at lower temperatures than those required for MOCVD[1], but more study is necessary to lower percentages of impurities and improve mechanistic understanding. Grazing incidence small angle X-ray scattering (GISAXS) can be carried out at ALEp process pressures in real time, and is sensitive to changes in surface morphology during nucleation, thus providing insight into the growth mode.

At the Cornell High Energy Synchrotron Source (CHESS) GISAXS probing of AlN ALEp on sapphire was performed. The AlN precursors were trimethylaluminum and either nitrogen/argon or hydrogen/nitrogen/argon plasma. Examination of the surface features during AlN growths at various growth temperatures and plasma conditions took place. The kinetics of the plasma were altered by changing the ratio of nitrogen-to-argon in the plasma feed gas, leading to differences in the relative production of nitrogen species. The GISAXS offers information about the surface feature evolution over the course of the film growth, and avoids *ex situ* surface oxidation of AlN, while atomic force microscope (AFM) measurements offer a final look at the surface once the samples are removed from the reactor.

Growths below 450°C were shown with *ex situ*, post-growth X-ray photoelectron spectroscopy to have higher impurities than samples grown at 480°C, and GISAXS shows an increase in short correlation lengths at the lower temperatures. Changing the plasma nitrogen/argon ratios also changed the impurity levels in the final films.

1. N. Nepal et al., *Appl. Phys. Lett.***103**, 082110 (2013)

11:15am **AA+AF-TuM-14 Studies of Surface Structure and Surface Chemistry During Plasma-Assisted Atomic Layer Epitaxial Growth of InN Semiconductor Thin Films on GaN Substrates**, ***Samantha Rosenberg,*** U.S. Naval Research Laboratory; *D Pennachio,* UCSB; *V Anderson, N Nepal,* U.S. Naval Research Laboratory; *C Wagenbach,* Boston University, USA; *A Kozen,* U.S. Naval Research Laboratory; *Z Robinson,* SUNY College at Brockport; *J Logan, S Choi,* UCSB; *J Hite,* U.S. Naval Research Laboratory; *K Ludwig,* Boston University; *C Palmstrøm,* UCSB; *C Eddy, Jr.,* U.S. Naval Research Laboratory

III-N semiconductors such as GaN, AlN, and InN are the basis for creating compound ternary and quaternary semiconductor materials well suited for applications in several important technological areas including high current, normally-off power switches.[1-3] However, the full range of ternary and quaternary III-N semiconductors cannot be achieved with conventional growth methods due to the high temperatures required. While atomic layer deposition (ALD) is a versatile low temperature growth technique and has gained wide use, it does not offer the required level of crystallinity and purity needed for high-performance III-N semiconductor devices. Therefore, we have developed a technique adapted from ALD, called plasma-assisted atomic layer epitaxy (ALEp).[2] Using surface science techniques we are working to develop a fundamental understanding of the ALEp growth process to further enable the method as a powerful new growth technique for semiconductor materials.

Here we employ *in-situ* and *in-vacuo* surface studies of GaN substrate preparation and InN ALEp heteroepitaxial growth to advance our fundamental understanding of the ALEp process. We conduct *in-situ* grazing incidence small angle x-ray scattering (GISAXS) experiments at the Cornell High Energy Synchrotron Source, utilizing morphological evolution monitoring to investigate the growth surface during sample preparation and film deposition. GISAXS results have shown that bulk GaN surfaces develop a correlated surface feature at finite q_y during the ALEp-based emulated Ga flash-off cleaning, while ALEp-based H_2 cleaning introduces additional short range order features. Neither of these features are found on Epi GaN surfaces suggesting they are associated with polish damage in the substrates. For both surfaces, features from ALEp-based preparations dominate the GISAXS scattering during subsequent ALEp InN growth and are quite different from ALEp InN growth on sapphire. GISAXS information is complemented with *in-vacuo* x-ray photoelectron spectroscopy and reflection high-energy electron diffraction studies conducted at the Palmstrøm Lab at UCSB. Initial results have shown a partial surface reconstruction after exposure to TEG and atomic H_2 commensurate with a reduction in carbon and oxygen from the surface. Further studies will consider traditional molecular beam gallium flash-off and further atomic hydrogen etching as ways to produce the most suitable GaN surface for our ALEp-based approach.

1. N. Nepal, et al., Appl. Phys. Lett. 103, 082110 (2013)
2. C. R. Eddy, Jr, et al., J. Vac. Sci. Technol. A 31(5), 058501 (2013).
3. R. S. Pengelly, et al., IEEE Trans. Microwave Theory Tech. 60, 1764 (2012).

11:30am **AA+AF-TuM-15 Plasma Gas Chemistry Influence on Growth of InN Films by Atomic Layer Epitaxy**, ***Neeraj Nepal,*** *V Anderson, S Johnson, S Rosenberg, A Kozen,* U.S. Naval Research Laboratory, USA; *C Hoskin,* Boston University; *D Meyer, B Downey, J Hite, V Wheeler,* U.S. Naval Research Laboratory, USA; *R Zachary,* SUNY College at Brockport; *D Boris, S Walton,* U.S. Naval Research Laboratory, USA; *K Ludwig,* Boston University, USA; *C Eddy, Jr.,* U.S. Naval Research Laboratory, USA

III-N semiconductors have been used in a variety of technologies such as high power transistors, emitters, detectors, and solar-cells. The relatively high growth temperature of III-N semiconductor synthesis techniques has impeded further development and application of the materials due to challenges with miscibility gaps for ternaries and strain related to thermal expansion mismatch with non-native substrates. To address these challenges, plasma-assisted atomic layer epitaxy (ALEp) offers a new approach with growth temperature less than half of those needed for conventional growth methods. Since growth using this technique is far from thermodynamic equilibrium, understanding the effects of ALEp growth parameter space on growth kinetics is essential to further improving the method and the resulting electronic materials.

In this paper, we report on the effect of plasma gas chemistry on growth of crystalline InN semiconductor films by ALEp on a-plane sapphire substrates at temperatures below 250 °C. First, the optimal ALEp growth windows and growth parameter space is identified. These studies involve variations in substrate surface preparation for epitaxy, plasma gas chemistry, growth temperature, precursor pulse/purge time. The effect of these parameters is assessed using different *ex situ* characterization methods such as atomic force microscopy, x-ray photoelectron spectroscopy, x-ray diffraction and four-point free carrier transport measurements. To further understand/develop plasma gas chemistry these optimal conditions are then applied to film growth monitored by real-time grazing incidence small angle x-ray scattering (GISAXS) measurements revealing changes in the growth mode through morphological evolution of the surface. It will be shown that the nature of GISAXS evolution directly relates to the material quality. Both *ex situ* and *in situ* growth studies show that the starting surface, N_2/Ar flow ratio, plasma time/pressure and H_2 content of the plasma significantly affects the surface chemistry, nucleation and growth of InN. For example, decreasing Ar flow through plasma source from 200 sccm to 25 sccm for constant N_2 flow of 75 sccm and adding H_2 at the last fraction of the plasma pulse in the ALEp cycle reduces impurities and increases the saturated growth rate. Based on various *ex situ* characterization methods, the quality of the ALEp grown semiconducting InN films is found to be similar or better than the material grown by conventional growth methods, such as molecular beam epitaxy, at much higher temperatures.

11:45am **AA+AF-TuM-16 Spectroscopic Ellipsometry of WO_3 Thin Films from ALD: *In-situ* Layer-by-Layer Growth Monitoring and *ex-situ* Optical Characterization**, ***Ufuk Kilic,*** *D Sekora, A Mock, M Schubert,* University of Nebraska Lincoln

Within the last two decades, tungsten tri-oxide (WO_3) ultra-thin films have been the subject of research for photovoltaic, gas sensing, and electrochromic applications due to its large band gap (3.4 eV) and photocatalytic properties [1,2]. In this study, we fabricated WO_3 ultra-thin films on silicon substrates by means of atomic layer deposition (ALD). Precise and accurate control of deposition conditions throughout the growth process is a critical challenge surmountable by integration of spectroscopic ellipsometry (SE). By utilizing in-situ SE monitoring of WO_3 depositions, we obtain thickness, film roughness, and substrate temperature throughout the layer-by-layer growth.

By implementing pressurized precursor control, WO_3 was deposited by subsequent exposures of $(tBuN)_2(Me_2N)_2W$, nanopure H_2O, and oxygen plasma to the substrate surface while under continuous SE observation. Due to lack of detailed reports on broad range optical properties of WO_3 thin films, a multi-sample analysis is necessary for accurate thickness and optical constant determination from SE [3]. Thus, two films are deposited for 75 and 150 cycles under the same conditions and ex-situ SE data is collected in the spectral range from 0.7-8.5 eV. The as-grown WO_3 dielectric function is determined along with the respective film thicknesses. Roughness was considered and verified by atomic force microscopy. With this information, the in-situ SE data is retroactively analyzed to attain inherent layer-by-layer deposition parameters.

We report the dielectric function of as-grown WO_3, accurate film thicknesses and growth rate. Further implementation of this method allows for precise control and real-time optimization of deposition parameters ultimately providing us with the ability to develop ALD recipes in-situ.

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[2] Liu, Rui, et al., Angewandte Chemie, 123.2: 519-522, (2011).

[3] Jarrendahl, K., and H. Arwin, Thin Solid Films, 313: 114-118, (1998).

ALD Applications
Room Plaza ABC - Session AA-TuM

Batteries I (8:00-10:00 am)/Emerging Apps II (10:45 am-12:00 pm)

Moderators: Christophe Detavernier, Ghent University, Belgium, Christophe Vallee, LETI-LTM, France, Gary Rubloff, University of Maryland, Tero Pilvi, Picosun Oy

8:00am **AA-TuM-1 Designing of Surface and Interface of Electrodes for Highly-stable Li Ion Batteries, Li-S Batteries and Metal-Air Batteries**, ***Xueliang Sun,*** University of Western Ontario, Canada **INVITED**

The poor cell lifetimes of Li/Na batteries are rooted mainly in side reactions occurring at the electrode-electrolyte interface. The use of surface coatings to control of the electrode-electrolyte interface is an important strategy to design new electrodes. This talk will include two parts:

In the first part, we will report our work on the applications of atomic layer deposition (ALD) in Li ion batteries [1] including synthesis of coating materials such as Al_2O_3, ZrO_2, TiO_2, $AlPO_4$and LiTaO3 [2,3,4] as well as the ALD coating materials to modify the anode ($Li_4Ti_5O_{12}$, SnO_2) [5] and the cathode (commercial $LiCoO_2$, NMC) [6].

In the second part, we will discuss MLD coating on Li-S batteries operating at 55C [7].

In the third part, we will discuss our recent results on ALD Al_2O_3 coating on Na metal for Na ion batteries and Na-Air batteries [8].

Reference:

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[3] J. Liu, Y. Tang, B. Xiao, T.K. Sham, R. Li, X. Sun. ***RSC Adv***. 2013, 3, 4492-4495.

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[8]Y. Zhao, L. Goncharova, A. Lushington, Q. Sun, H. Yadegari, B. Wang, W. Xiao, R. Li, X. Sun., **Adv. Mater.,** (2017) In press

8:30am **AA-TuM-3 ALD Vanadium Oxides for 3D Thin-film Lithium Ion Batteries***,* ***Felix Mattelaer,*** Ghent University, Belgium*; K Geryl,* Ghent University*; T Dobbelaere,* Ghent University, Belgium*; G Rampelberg,* Ghent University*; J Dendooven, C Detavernier,* Ghent University, Belgium

Several pathways are investigated to obtain high power and high energy density thin-film lithium ion batteries. The high power aspect can be obtained by scaling down the film thickness, which unfortunately decreases the films actual capacity. By coating thin-film electrodes onto 3D-structured substrates, the high power inherent of thin-film electrodes can be achieved while the energy density per footprint area can be increased.

In addition to 3D structuring, materials selection is of key importance for achieving high power and high energy density in thin-film lithium ion batteries. Traditional electrode materials such as $LiCoO_2$ are limited to a reversible range of lithium insertion, which leads to capacities of 550-700mAh/cm^3 for commercialized electrode materials. Traditionally, battery research mainly focuses on crystalline electrodes. Indications exist that higher energy density and higher power density can be achieved using amorphous materials. ALD is uniquely suited to deposit amorphous materials at low temperatures in a conformal way onto 3D structured substrates, validating the investigation of this class of materials.

In this work, crystalline and amorphous ALD vanadium oxides are deposited and examined as electrode materials. We demonstrate the deposition of amorphous V_2O_5 and two 'flavors' of VO_2 (water-based ALD and ozone-based ALD). By careful tuning of the post-ALD annealing conditions, the influence of initial ALD process, atmosphere, temperature and substrate on the crystallization and oxidation of the VO_2 films is revealed. Using this knowledge, the whole range of vanadium oxides can be obtained (VO_2–V_6O_{13}–V_4O_9–V_3O_7–V_2O_5), which are all displaying storage capacity with very high energy densities (e.g. 1380mAh/cm^3 for V_4O_9). The amorphous initial states (amorphous VO_2 and V_2O_5) on the other hand also display very high capacities, and much better kinetics than their crystalline counterparts. Moving from crystalline to amorphous vanadium oxides more than doubles the storage capacity for a given film thickness. Finally, the conformal deposition is demonstrated on silicon micropillar arrays, which demonstrates the transfer of the thin-film kinetics to a higher energy density per footprint area electrode.

In conclusion, a wide range of ALD vanadium oxides was demonstrated as potential thin-film cathode. In particular, amorphous vanadium oxides, and VO_2 (B) show promise thanks to their high energy density and good kinetics, enabling a much higher storage capacity than the stable range of V_2O_5.

8:45am **AA-TuM-4 PE-ALD of Transition Metal Phosphates as Lithium-Ion Battery Electrode Materials***, T Dobbelaere, F Mattelaer, J Dendooven,* Ghent University, Belgium*; P Vereecken,* Imec, Belgium*;* ***Christophe Detavernier,*** Ghent University, Belgium

In today's power-hungry society, lithium-ion batteries are the current state of the art of electrochemical energy storage. Their usage ranges from applications on large scales (e.g. off-grid storage) to medium (e.g. electric vehicles) and small ones (e.g. smartphones). For certain applications, e.g. chip-scale integration, the goal is to make them also on the microscopic scale. Although thin-film batteries have been demonstrated, mostly using planar, sputter-deposited films, their capacity is necessarily low because of the small amounts of active material. By using 3D microstructured substrates rather than planar ones, the capacity can be drastically increased. However, coating these substrates requires a conformal deposition method, leading to ALD as a promising technique.

Using a trimethyl phosphate (TMP) plasma as the phosphorus source, we are able to deposit three well-performing electrode materials: iron phosphate[1], titanium phosphate[2], and vanadium phosphate[3]. The process sequences are similar, with each one consisting of three steps: TMP plasma exposure, followed by O_2 plasma exposure, followed by a metal precursor exposure. The metal precursor is either tert-Butylferrocene (for iron phosphate), titanium isopropoxide (for titanium phosphate), or tetrakisethylmethylamido vanadium (for vanadium phosphate).

Each of the three processes shows ALD-type growth at a substrate temperature of 300 °C, with properties including linearity and (slow) saturation. They all have high growth rates, resp. 1.1, 0.7, and 0.8 nm/cycle, as shown in Fig. 1 (a,c,e). This is attractive for depositing thicker films in a time-efficient manner. They have low impurity levels, with ERD-measured stoichiometries of resp. $FeP_{1.5}O_{4.7}$, $TiP_{1.7}O_{5.6}$, and $V_{1.1}PO_{4.3}$.

Although each material can be crystallized by post-deposition annealing, this is not necessary (nor beneficial) because the as-deposited amorphous forms can be directly electrochemically lithiated and subsequently cycled. They yield capacities of resp. 0.7 μAh/cm^2 between 2.3-4.3V, 1.0 μAh/cm^2 between 2.3-3.2V, and 2.2 μAh/cm^2 between 1.4-3.6V, as shown in Fig. 1 (b,d,f). They can be used as practical electrodes, given that their coulombic efficiencies are close to 100% and that they show good capacity retention upon extended cycling.

[1] Dobbelaere et al., Chem. Mater. 2016, 28, 3435-3445

[2] Dobbelaere et al., J. Mater. Chem. A 2017, 5, 330-338

[3] Dobbelaere et al., In preparation

9:00am **AA-TuM-5 Comparing Temporal and Spatial Atomic Layer Deposition for Enhanced Performance of Li Ion Battery Electrodes***,* ***Alexander Yersak,*** *A Dameron,* University of Colorado - Boulder*; X Li, Y Yang,* Colorado School of Mines*; K Hurst, R Tenet,* National Renewable Energy Laboratory*; S George,* University of Colorado - Boulder

Ultrathin atomic layer deposition (ALD) coatings on Li Ion battery (LIB) electrodes can improve the capacity stability for both anodes and cathodes. The remaining challenge is to scale-up the ALD on LIB electrodes for commercialization. This work focused on comparing temporal and spatial ALD methods for coating the LIB electrodes. If the temporal and spatial ALD methods deliver comparable LIB performance, then the next step will be to extend the spatial ALD to roll-to-roll (R2R) spatial ALD.

The experiments utilized our spatial ALD rotating cylinder reactor [1]. Using this reactor, we have already demonstrated uniform ALD coatings in nanoporous anodic aluminum oxide (AAO) membranes with aspect ratios of 250 at an equivalent web speed of 10 m/min [2]. Porous battery electrodes have an estimated aspect ratio of ~50. Based on Monte Carlo simulations of ALD in the nanoporous AAO membranes, uniform ALD coatings should be possible in the porous battery electrodes at an equivalent web speed of 100 m/min.

We first examined the capacity stability for $LiCoO_2$ (LCO) cathode electrodes that were uncoated or coated with 4 Al_2O_3 ALD cycles using either temporal ALD or spatial ALD. The temporal ALD coatings were deposited using trimethylaluminum (TMA) and water at 120^{o}C. The spatial ALD coatings were deposited using TMA and ozone at 60^{o}C and a rotation speed equivalent to a web speed of 10 m/min. The cathode electrodes were taped to the inner drum of the rotating cylinder reactor for the ALD coating. For electrochemical testing, the LCO electrodes were cycled at 3.3-4.5V and charge/discharge rates of 1C and C/3.

The electrochemical testing results are shown in the supplemental figures. For the uncoated LCO electrodes, a significant capacity fade was observed after 10 and 94 charge/discharge cycles for rates of 1C and C/3, respectively. The ALD-coated electrodes show much better capacity stability especially for the 1C rates. The performance of temporal ALD and spatial ALD coated LCO electrodes is also comparable. We are now extending our rotating cylinder spatial ALD reactor to full R2R operation. We hope to have results from this R2R spatial ALD reactor by the ALD2017 conference.

[1] K. Sharma et al., *J. Vac. Sci. Technol. A* **33**, 01A132 (2015).

[2] K. Sharma et al., *J. Vac. Sci. Technol. A***34**, 01A146 (2016).

9:15am **AA-TuM-6 All-Solid-State Thin-Film Battery with a Novel Organic Cathode Material by Atomic/Molecular Layer Deposition***, **Mikko Nisula**, M Karppinen,* Aalto University, Finland

The miniaturization of electronic devices creates demand for energy storage systems of the same length scale. As the downsizing of conventional liquid electrolyte cells is difficult, the current focus is on all-solid-state thin-film batteries. In order to increase the energy density while preserving the power density of the cells, various 3D architectures have been proposed to enhance the effective surface area. Such an approach places an apparent need for a thin-film deposition method capable of manufacturing the electrode and electrolyte materials on high-aspect-ratio substrates. A strong candidate for the task is the atomic layer deposition (ALD) technique and the recent years have seen the emergence of a number of ALD processes for both electrode and electrolyte materials.

An interesting choice for the electrodes is the group of organic electrode materials such as quinones and conjugated carboxylates. While impractical for conventional batteries due to conductivity and dissolution issues, these downsides can be circumvented by applying the organic electrode material in all-solid-state thin film batteries. Recently, we demonstrated that these materials are attainable using the combined atomic/molecular layer deposition (ALD/MLD) by depositing the lithium terephthalate anode material.[1] Compared to the more conventional inorganic materials, the ALD/MLD approach yields a number of advantages such as simple binary deposition processes, low processing temperatures (<200 °C) and no need for a post-deposition anneal. Moreover, given their environmentally benign constituents, organic electrode materials would be well suited for the emerging *transient electronics* technology.[2]

In this contribution, we present an all-solid-state thin-film battery based on a novel lithium-bearing organic cathode material by ALD/MLD combined with ALD-made LiPON[3] as the solid electrolyte. As well as investigating the electrochemical performance of the solid-state battery by cyclic voltammetry and galvanostatic charging/discharging, we discuss the aspects of device fabrication such as the effect of electrode and electrolyte layer thicknesses on the device performance as well as the role of the interfaces and methods for controlling them.

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2. K. K. Fu, Z. Wang, J. Dai, M. Carter, L. Hu, *Chem. Mater.***28** 2016 3527 – 3539

3. M. Nisula, Y. Shindo, H. Koga, M. Karppinen, *Chem. Mater.***27** 2015 6987 – 6993

9:30am **AA-TuM-7 Atomic Layer Deposition of Hierarchical CNTs@FePO$_4$ Architecture as a 3D Electrode for Lithium-Ion and Sodium-Ion Batteries***, **Jian Liu,*** The University of British Columbia, Canada*; B Wang, Q Sun, R Li, T Sham, X Sun,* University of Western Ontario, Canada

Three-dimensional (3D) microbatteries hold great promise as on-board energy supply systems for microelectronic devices [1]. The construction of 3D microbatteries relies on the development of film deposition techniques that can enable coatings of uniform electrode and electrolyte materials in high-aspect-ratio substrates [2]. Herein, a 3D FePO$_4$ on carbon nanotubes (CNTs@FePO$_4$) structure is fabricated by coating FePO$_4$ on CNTs/carbon paper substrate using atomic layer deposition (ALD) [3]. Compared to FePO$_4$ on a planar substrate, the 3D CNTs@FePO$_4$ electrode exhibits significantly increased areal capacity and excellent rate capability for lithium-ion and sodium-ion storage. The 3D CNTs@FePO$_4$ maintained areal capacities of 64 μAh cm^{-2} and 33 μAh cm^{-2} after 180 cycles for LIBs and SIBs, which are 16 and 33 times higher than those of planar FePO$_4$ electrode, respectively (Figure 1). Moreover, hybrid 3D CNTs@FePO$_4$@Li$_3$PO$_4$ structure is fabricated by coating Li$_3$PO$_4$ solid-state electrolyte on 3D CNTs@FePO$_4$. The CNTs@FePO$_4$@Li$_3$PO$_4$ electrode shows stable cycling performance in lithium-ion batteries. Hard X-ray Photoemission Spectroscopy analysis discloses that Li$_3$PO$_4$ coating prevents the formation of undesirable LiF in the solid-electrolyte interphase layer, which is believed to be responsible for the performance degradation in CNTs@FePO$_4$ (Figure 2). It is expected that this work will pave the way to building reliable 3D nanostructured electrode and electrolyte architecture for high areal capacity microbatteries.

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[2] J. Liu, X. Sun, Nanotechnology, 2015, 26, 024001.

[3] J. Liu, B. Wang, Q. Sun, R. Li, T.-K. Sham, X. Sun, Adv. Mater. Interfaces 2016, 1600468.

9:45am **AA-TuM-8 Unravelling The Role of ALD Al$_2$O$_3$ and TiO$_2$ Protective Coatings on Lithium-Ion Battery Electrodes.***, **Felix Mattelaer,*** Ghent University, Belgium*; M Kurttepeli,* University of Antwerp*; S Deng,* Ghent University, Belgium*; D Cott, P Vereeceken,* IMEC, Belgium*; J Dendooven,* Ghent University, Belgium*; S Bals,* University of Antwerp*; C Detavernier,* Ghent University, Belgium

Nanoscaling of lithium-ion battery electrodes enhances the kinetics and footprint capacity, but also sensitively increases the electrode-electrolyte interfacial area. While this is beneficial for fast lithium-ion diffusion, most capacity fading mechanisms are also related to interface phenomena, such as solvent decomposition and metal dissolution. Interface stabilization by ALD coatings has been heavily investigated since 2010. Partially thanks to the ease of deposition, the main part of research has been devoted to ALD of Al$_2$O$_3$ as protective coatings. However, it is a poor lithium-ion conductor, and other ALD films can both provide enhanced cycle life while maintaining the excellent thin-film battery kinetics.

In this work, we use two thin-film lithium-ion battery electrodes as model systems to benchmark ALD Al$_2$O$_3$ and ALD TiO$_2$ as interfacial modifiers for lithium-ion batteries. On a near-ideal electrode (lithiated thin-film TiO$_2$), the lithium-blocking nature of ALD Al$_2$O$_3$ is revealed. Al$_2$O$_3$ films beyond 3nm are completely blocking, while thinner coatings impose an impedance of >10^{12} Ωcm. ALD TiO$_2$ does not pose a kinetic bottleneck and is never blocking. On a less-than ideal model system (overcharged thin-film LiMn$_2$O$_4$), it is shown that 5nm ALD TiO$_2$ can prevent solvent decomposition, which more than 10 better capacity retention at 100C.

Finally, ALD is used to decorate a CNT forest with both a V$_2$O$_5$ film as a lithium-ion battery cathode, and an amorphous TiO$_2$ coating as a protective coating to extend cycle life. The dual-layer conformality is confirmed using EDX-STEM tomography. The electrode is cycled with two lithium-ions per V$_2$O$_5$ unit cell. A high areal capacity and excellent kinetics are found for the V$_2$O$_5$-coated CNTs, but a fast capacity degradation is observed and associated to vanadium dissolution during cycling. Coating the V$_2$O$_5$/CNTs with 5 or 25 cycles of ALD TiO$_2$ retained the excellent kinetics, but almost completely alleviated the vanadium dissolution issue, improving the cycle life dramatically. Furthermore, the coating was found to aid in the cycling-driven amorphisation of the V$_2$O$_5$.

In conclusion, ALD Al$_2$O$_3$ was identified as a very resistive coating towards lithium, using thin-film electrodes as model systems. ALD thin-film V$_2$O$_5$ on CNTs was demonstrated a high-power lithium-ion cathode. The deterioration mechanism of deep charging of the V$_2$O$_5$/CNTs is shown to be related to vanadium dissolution. ALD TiO$_2$ coatings improved the cycling performance by alleviating this dissolution issue, while maintaining the excellent thin-film battery kinetics.

10:45am **AA-TuM-12 ALD Layer Opportunties for Reversible Bonding of Ultrathin Glass Substrates***, **Messaoud Bedjaoui**, S Poulet,* LETI, France

Over the past few years, we are witnessing to a rapid development of flexible electronics leading to a number of promising devices in the area of energy sources and advancing displays (e.g microbatteries, organic state lighting, liquid crystals displays…) especially with the emergence of ultrathin and flexible glass substrates (<100µm). However, handling of ultrathin substrates is a great challenge for front-end and back-end processes. On the other hand, wafer bonding techniques are being increasingly used to achieve innovative stacking structures. In order to bond ultrathin substrates containing temperature-sensitive devices, a bonding process that yields high bond strengths operating at a moderate temperature (<600°C) is needed.

The purpose of this work is to present a new cost reduction concept of handling for ultrathin glass substrates covering both bonding and debonding processes. In order to elaborate flexible thin film components using this kind of ultrathin substrates, their bonding based on intermediate atomic layer deposition (ALD) as well as debonding from thick carrier has to be studied. First of all, we investigate the bonding behavior of glass/Al$_2$O$_3$, glass/TiO_2 and glass/Al_2O_3-TiO_2 layer structures submitted to room temperature up to 600°C annealing. Surface and bonding energies are measured in an anhydrous atmosphere and bonding defectivity is analysed using scanning acoustic microscope (SAM). Layers deposited by ALD onto glass carrier are suited for direct bonding.

This work is also focused on the debonding process by demounting the interface layer fabricated using atomic layer deposition in humid atmosphere conditions (>80%RH and T°>90°C). Spontaneous debonding phenomena occurred solely for low temperature (80°C to 150°C) Al_2O_3 layers on thick glass carrier even after annealing treatment. This debonding, unobservable for TiO_2 and Al_2O_3-TiO_2 bilayer bonding structures, may be explained by chemical or structural modification such as internal stress, pinholes formation or stoichiometry instability. The intermediate bonding layers have been also characterized using infrared spectroscopy, scanning electron microscopy (SEM) and complementary analysis (spectroscopic ellipsometry, X-ray photoelectron spectroscopy) before and after exposition to humid atmosphere (Figure 1, Figure 2, Figure 3 in supplemental document). Based on these results, an Al_2O_3 debonding mechanism is proposed. These studies demonstrated that the approach of this work provides a method to fabricate temperature-sensitive devices on bonded ultrathin glass and to achieve a low cost solution of debonding from glass carrier which can be repeatedly reused after simple cleaning.

11:00am **AA-TuM-13 Atomic Layer Deposition and Precursor Development for Chemoresistive Gas Sensing Materials***, **Rachel Wilson**, C Blackman, C Carmalt,* University College London, UK

Chemoresistive gas sensors are simple to use, have low cost, small size and high sensitivity. The performance of such sensors is defined by the composition, morphology and structure of the sensing materials. This work demonstrates the use of Atomic Layer Deposition (ALD) to engineer *n*- and *p*-type metal oxide films for gas sensor applications.

A major drawback of using *n*-type materials for gas sensing is their sensitivity to moisture and humidity. *P*-type gas sensing materials however, are believed to be less moisture sensitive, making them attractive materials within the semiconductor industry. However, *p*-type metal oxides have received relatively little attention compared to their *n*-type congeners, which may be ascribed to their apparently low sensitivities, limiting their potential applications. ALD provides atomic level control of film growth, allowing fabrication of materials with defined thickness, making it an ideal tool for exploring the fundamental sensing properties of these materials.[1] The long term goal is to identify the most promising new materials and provide key information regarding the optimization of the materials synthesis to obtain gas sensing materials with maximum sensitivity and selectivity.

Metal oxide thin films have been deposited using a flow-type ALD reactor which was built in house. TiO_2 films have been deposited using titanium isopropoxide and water precursors. Nickel and copper complexes have been synthesized for use as potential ALD precursors for the deposition of nickel (II) oxide (NiO), and copper (I) oxide (Cu_2O) using water as the co-reactant. These include but are not limited to; alkoxides, guanidinates and amides. NiO has been deposited via ALD and CVD methods.

Metal oxide films have been deposited onto alumina sensors, which have been exposed to different concentrations of gases. By measurement of the films electrical resistance the gas sensitivity can be determined and hence we can define the thickness which gives the maximum sensor response (and see if this is comparable with the Debye length). Although the use of TiO_2 as a gas sensor material is widely known, we have manged to obtain responses at very high resistance values with excellent kinetics of response. We have shown that the pattern responses of the electrical resistance towards certain gases indicate typical *n*-type semiconducting behavior. The TiO_2 film thickness plays a dominant role within the conduction mechanism. Gas sensitivity testing of *p*-type NiO films is currently underway.

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11:15am **AA-TuM-14 Physics with and Physics of Atomic Layer Deposited Nanofilms***, **Neal Sullivan**,* Arradiance*; A Lehmann,* Universitat Erlangen-Numberg*; A Brandt,* University of Texas at Arlington

In high energy physics (HEP), the need for precise timing (pico-seconds), was established by the inability to extract all measurable information (i.e. 4-vectors) from multi-TeV particle collisions at the Fermilab Tevatron in 2003[1] Psec-resolution requires a detector that is small enough that variations in the fastest transit times of the photons or electrons correspond to a time jitter smaller than the resolution. Microchannel plates (MCP) possess this requisite timing dimension, but MCP-based photodetectors, were not considered for these applications due to the high-cost / area, and poor lifetime – typically less than one month under use conditions. While photomultiplier tubes (PMTs) are the workhorse devices for photo detection, microchannel plate-based PMTs (MCP-PMT) significantly advance the state-of-the-art achieving more than 100-fold improvements in spatial and temporal resolution. This work presents the development of ALD-functionalized MCPs that have improved MCP-PMT performance and extended lifetimes by more than 40x.

ALD process development for both secondary emissive and conductive layers as well as the integration of these ALD nanofilms with the MCP device at Arradiance will be discussed in detail. The tradeoffs required and the overall device performance is compared to the standard reduced silicate lead glass (RSLG) MCP. Application lifetime and MCP-PMT performance results, collected by Dr. Lehmann at the PANDA experiment over the last 5 years and at Professor Brandt's lab at University of Texas Arlington, will be presented and the implications for high energy physics will be examined. Analytical studies, assessing the role of each of the functional ALD films in lifetime improvement will be presented, with an eye towards understanding the underlying physics of the nanofilm in the MCP-PMT

High speed photodetectors with micron space resolution and temporal resolution less than 10 picoseconds (psec) represent a disruptive technology across the physics frontiers of energy, intensity, and cosmic with the capability to support experiments addressing the origin of mass, neutrino physics and proton decay, and the nature of dark matter and energy. Additional technology and commercial areas such as: homeland security, astronomy, space instrumentation, remote night time sensing, TOF mass spectrometry, and medical imaging (PET scanning) all stand to benefit from this technology.

[1] Henry J. Frisch, et. al., A Brief Technical History of the Large-Area Picosecond Photodetector (LAPPD) Collaboration, http://arxiv.org/abs/1603.01843 March 2016

11:30am **AA-TuM-15 Highly Resistive ALD Coatings for Microchannel Plates Operating at Cryogenic Temperatures***, **Till Cremer**, B Adams, M Aviles, J Bond, C Craven, M Foley, A Lyashenko, M Minot, M Popecki, M Stochaj, W Worstell,* Incom Inc.*; J Elam, A Mane,* Argonne National Laboratory*; O Siegmund, C Ertley,* University of California, Berkeley

We report on the structure-property relationships of highly resistive nanocomposite films synthesized by atomic layer deposition (ALD). These nanocomposites are composed of metal nanoparticles dispersed in a dielectric matrix, resulting in an amorphous material with semiconductor-like electrical properties characterized by a negative thermal coefficient of resistance (TCR) . The material's (thermo-) electrical properties depend on film thickness, composition, nanostructure, and the chemical nature of the dielectric and metal components. We show how the structure-property relationships developed in this work can be used to design coatings with improved thermo-electrical properties.

Atomic layer deposition (ALD) has enabled the development of a new technology for fabricating microchannel plates (MCPs) with improved performance performance that offer transformative benefits to a wide variety of applications. Incom uses a "hollow-core" process for fabricating glass capillary array (GCA) plates consisting of millions of micrometer-sized glass microchannels fused together in a regular pattern. The resistive and secondary electron emissive (SEE) functions necessary for electron amplification are applied to the GCA microchannels by ALD, which – in contrast to conventional MCP manufacturing– enables independent tuning of both resistance and SEE to maximize and customize MCP performance.

Incom is currently developing MCPs that operate at cryogenic temperatures and across wide temperature ranges. All MCPs exhibit a negative TCR: when the MCP is cooled, the resistance increases, and when heated, the resistance drops. Consequently, the resistance of each MCP must be tailored for the intended operating temperature. This sensitivity to small temperature changes presents a challenge for many terrestrial and space based applications including for detectors capable of operation either at room temperature or at cryogenic temperatures. Our results demonstrate how the structural and compositional changes (dielectric-to-metal ratio and elemental composition) affect the resistivity and, specifically, the TCR of the nanocomposite. Developing structure-property relationships for the resistive material enables us to develop highly resistive materials with a) improved TCR characteristics, and b) fabricate MCPs optimized to operate at cryogenic temperatures.

11:45am **AA-TuM-16 Reactions on ALD TiO_2, ZnO, and Al_2O_3 Metal Oxides during Nucleation of UiO-66-NH_2 MOF Thin Films as Hydrolysis Catalysts for Chemical Warfare Agent Simulants.**, ***Dennis Lee**, J Zhao, C Oldham,* North Carolina State University*; G Peterson,* Edgewood Chemical Biological Center*; G Parsons,* North Carolina State University

Highly toxic compounds such as chemical warfare agents (CWAs) (e.g., sarin (GB), soman (GD), VX), ammonia or chlorine gas, or NO_x-based pollutants can pose a severe chemical threat. Recently, highly crystalline, stable, and microporous metal-organic frameworks (MOFs), in particular UiO-66-NH_2 MOF, have become active materials to effectively degrade deleterious chemicals. These MOFs are readily formed as powders, but for effective application, new means are needed to create controllable and conformal MOF thin films, especially on high aspect ratio textiles and fibrous substrates. We recently reported that ALD metal oxides act as suitable nucleation agents for UiO-66-NH_2 thin films, but nucleation mechanisms and how they are driven by ALD oxide composition were not well understood.

Here, we describe surface reaction mechanisms on ALD Al_2O_3, TiO_2, and ZnO during nucleation of UiO-66-NH_2 MOF. The MOFs are excellent quality, with high crystallinity and net surface area exceeding 1000 m^2/g_{MOF}. We find that ALD Al_2O_3 and TiO_2 layers are fairly stable under solvothermal MOF growth condition. On the other hand, crystalline ALD ZnO surface partially dissolves in the synthetic environment. The chemical instability of ZnO promotes MOF nucleation in the liquid phase, likely via reaction on Zn^{2+} ions, creating a significant amount of MOF crystals, up to 145 $m^2/g_{fiber+MOF}$, but limiting MOF thin film growth. The stability of ALD Al_2O_3 and TiO_2 enables good MOF coatings, but the density of nucleation sites is markedly larger on TiO_2 vs Al_2O_3, resulting in 65 $m^2/g_{fiber+MOF}$ on TiO_2 vs 34 $m^2/g_{fiber+MOF}$ on Al_2O_3. Accordingly, we find the MOF-fabric formed with TiO_2 performs better than those with Al_2O_3 for hydrolysis of dimethyl 4-nitrophenyl phosphate (DMNP), a chemical warfare agent simulant, allowing the half-life for degradation to be in the range of 10 minutes versus several days measured for control metal oxide samples without the conformal MOF thin film.

We will discuss how ALD surfaces with different composition can impact on the MOF mass loading, which correlates with DMNP destruction performance, and how functionalized textiles can be also utilized for removing hazardous gases, such as ammonia, chlorine, and hydrogen sulfide.

ALD Fundamentals
Room Plaza D - Session AF1-TuM

ALD Fundamentals: Precursors and Process Development (8:00-10:00 am)/Precursors and Mechanism (10:45am-12:00 pm)

Moderators: Sean Barry, Carleton University, Canada, Simon Rushworth, EpiValence, UK, Markku Leskela, University of Helsinki, Finland, Ravindra Kanjolia, EMD Performance Materials

8:00am **AF1-TuM-1 Photo-assisted ALD of Oxides and Metals***, **Ville Miikkulainen**, K Väyrynen,* University of Helsinki, Finland*; V Kilpi,* Picosun Oy, Finland*; K Mizohata, J Räisänen, M Ritala,* University of Helsinki, Finland **INVITED**

Photo-assisted ALD, i.e. activation of ALD chemistry by UV and visible-range photons provides many potential advantages, such as lower deposition temperature, novel growth chemistries, selective area deposition, and elimination of film defects. However, there are only a few reports available on the topic, materials deposited being e.g. ZnO, Al_2O_3 and Ta_2O_5.[1-3] The main challenges are the reactor design and the complexity of the heterogeneous photochemistry. The reactor must ensure intensive light on the substrate while avoiding film growth on the optical components.

Our research group at University of Helsinki has been developing photo-assisted ALD processes for oxide and metal films. Customized Picosun™ R-200 ALD reactor with two alternative UV sources is employed. Pulsed Xenon lamp and VUV deuterium lamp allow a wide range of wavelengths. Nitrogen curtain flow is used to protect the optical window from film deposition.

A single-source approach with metal alkoxides has proved itself an effective method for depositing metal oxides. We have deposited oxides of Ti, Zr, Hf, Nb, and Ta from the corresponding alkoxides with the sequence alkoxide–purge–illumination.[4] In this presentation, results on process characteristics and film properties will be discussed. Area-selectivity of the photo-assisted Ta_2O_5 ALD was demonstrated by depositing a University of Helsinki emblem with two aluminum shadow masks. Resolution does not allow device level patterning but can be exploited to protect contact areas, for example.

Regarding photo-assisted ALD of metals, supplementary parameters must be considered. The deposited material is optically absorbing and electrically conductive, and typically reduction of the metal is required upon an ALD cycle. In this presentation, experimental results on photo-assisted ALD of Ru and Cu will be discussed.

Semiconductor Research Corporation (SRC) and Finnish Centre of Excellence in Atomic Layer Deposition (ALDCoE) are acknowledged for funding. Picosun provided the customized reactor for the project.

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8:30am **AF1-TuM-3 Oxidation State Discrimination in the Atomic Layer Deposition of Vanadium Oxides***, **Matthew Weimer**, I Kim, P Guo,* Argonne National Laboratory*; R Schaller,* Argonne National Laboratory, Northwestern University*; A Martinson, A Hock,* Argonne National Laboratory

Tunable control over the oxidation state of transition metal oxides (or sulfides) remains a significant challenge in ALD. Traditionally, the oxidation state of the metal precursor or strength of oxidant dictates the final oxidation state of the metal, and stoichiometry of elements, in the resulting film. In this work, a single vanadium 3^+ precursor performs self-limiting growth of thin films that span common oxidation states of vanadium, 3^+, 4^+, and 5^+. ALD of V_2O_3, VO_2, and V_2O_5 are realized via *four* distinct reaction mechanisms accessed at the same temperature by judicious choice of oxygen sources and co-reactants. Saturation behavior in all cases, the O_3, H_2O_2, H_2O/O_2, and H_2O_2/H_2 processes, is observed by *in situ* quartz crystal microbalance (QCM) and surface chemistry is studied with quadrupole mass spectrometry. As expected O_3 oxidizes vanadium fully to the 5^+ state to grow crystalline V_2O_5. Growth with O_2 has not observed and self-termination with H_2O occurs after less than 250 cycles corresponding to film growth of ~ 5 nm as measured by spectroscopic ellipsometry. When H_2O and O_2 are introduced in sequence, synergistic growth of amorphous V_2O_5 occurs. In this synergistic process, a clear distinction between non-oxidative protic ligand exchange, the H_2O reaction, and metal oxidation, the O_2 reaction, is demonstrated in either reaction order. In addition, it is apparent from these results that this vanadium precursor requires an oxidation mechanism in sustained ALD film growth.

In an extension of this approach, we can produce films with the intermediate vanadium 4^+ oxidation state, VO_2, through reducing equivalents – H_2 gas. In traditional A/B-type ALD, H_2O_2 produces an amorphous mixed $4^+/5^+$ oxide that is easily reduced to vanadium 3^+ oxide, V_2O_3, or oxidized to vanadium 5^+ oxide, V_2O_5, by varying the atmosphere of a low temperature anneal. Phase pure VO_2 is not readily accessible. When H_2 is dosed after H_2O_2 during growth, amorphous films of VO_2 are grown that can be crystallized with a low temperature, 350 °C, anneal. These VO_2 films show the characteristic temperature dependent Raman spectroscopy response in the expected temperature range, Figure 1, of the well-known insulator to metal transition (IMT) for VO_2. Conformal films of VO_2 were grown on indium-tin oxide (ITO) nanorods in this method, Figure1, in order to modify the phonon response of the ITO nanorods. A distinct blue-shift of the wavelength of all absorption spectral features above the IMT transition temperature is observed and can be modulated through VO_2 film thickness.

8:45am **AF1-TuM-4 Controlled B Doping in ZnO Atomic Layer Deposition using Boric Acid in Methanol as the B Source*, Yan Zhang,*** *A Mane,* Argonne National Laboratory*; J Liu, O Farha,* Northwestern University*; K Kovi,* Argonne National Laboratory*; J Hupp,* Northwestern University*; J Elam,* Argonne National Laboratory

ZnO is a well-known transparent conducting oxide with applications in numerous fields including microelectronics, solar cells, sensors, and light emitting diodes. There is fundamental scientific interest as well as commercial incentive to engineer ZnO and improve the electrical and optical properties. Towards this end, research efforts have been devoted to introducing trivalent Al or B atoms as dopants in ZnO thin films using various deposition methods. Atomic layer deposition (ALD) has the advantages of precise thickness control on the atomic scale, excellent conformity on high aspect ratio substrates, and relatively low deposition temperatures. These characteristics make ALD an attractive approach for fabricating ZnO-based devices. One of the major challenges in the ALD of ZnO:B is the lack of suitable boron-containing precursors. Ideally, the B precursor should have a high vapor pressure and reactivity, be safe to handle, and should yield a high B doping efficiency.

In this work, we have used for the first time a solution of boric acid in methanol (BA-MeOH) as the B precursor for ZnO:B ALD. Although BA has a room temperature vapor pressure of only ~10^{-5} Torr, in methanol the BA forms trimethyl borate (TMB), which has a much higher vapor pressure of ~100 Torr. Moreover, the reaction between DEZ and TMB is nearly as favorable as that between DEZ and H_2O. Encouraged by these properties, we proceeded to study the ALD of ZnO:B using in-situ quartz crystal microbalance measurements (Fig. 1a) and found that the BA-MeOH added mass and inhibited the subsequent ZnO ALD in a manner very similar to ZnO:Al ALD using trimethyl aluminum. Furthermore, the doping level was well controlled by varying the B deposition cycle percentage in each ALD supercycle between 1% and 8%. Next, the doping efficiency, electrical properties, and optical properties of ALD ZnO:B films were investigated. We achieved a high mobility of 18 $cm^2\ V^{-1}\ s^{-1}$ with a low carrier concentration of $4\times10^{19}\ cm^{-3}$ using a boron cycle percentage 1% (Fig. 1b). Future work will incorporate these ALD ZnO:B films into devices such as thin film transistors and diodes.

9:00am **AF1-TuM-5 Atomic Layer Deposition of Cobalt(II) Oxide/Hydroxide Thin Films*, Tomi Iivonen,*** *E Tirkkonen, K Mizohata, K Meinander, M Leskelä,* University of Helsinki, Finland

Cobalt(II) oxide (CoO) and cobalt(II) hydroxide [$Co(OH)_2$] have recently emerged as candidates for several applications related to energy storage, such as lithium ion batteries ($LiCoO_2$), supercapacitors ($NiCoO_x$) and (photo)electrochemical water splitting [CoO / $Co(OH)_2$]. As the basis of these applications is the redox chemistry of cobalt, it is important to be able to control the oxidation state of Co during the deposition process.

Currently, majority of the reported ALD processes for cobalt oxide are based on ligand combustion chemistry, using either oxygen plasma or ozone. However, while the use of oxygen plasma or ozone enables facile deposition of oxide films, in the case of cobalt, the control of its oxidation state is lost due to unavoidable formation of Co^{3+}.

Here we report a deposition process for CoO / $Co(OH)_2$ films based on the use of *bis*-trimethylsilylamido cobalt [$Co(BTSA)_2$] and water vapor. As $Co(BTSA)_2$ is reactive towards water, the films can be deposited without cobalt being oxidized during the surface reactions. The process can be used to deposit CoO / $Co(OH)_2$ in a temperature window of 75–250 °C. The growth per cycle –value (GPC) is strongly dependent on the deposition temperature, ranging from 1.2 Å to 0.25 Å (Figure 1A). The hydrogen content, and thus the amount of $Co(OH)_2$ present in the films varies with the applied deposition temperature, as evidenced by Time-of-Flight Elastic Recoil Detection Analysis study (Figure 1B). X-ray photoelectron spectroscopy confirms that the oxidation state of Co in the films is +II.

9:15am **AF1-TuM-6 High Purity Indium Oxide Films Prepared by Modified ALD using Liquid Ethylcyclopentadienyl Indium*, Fumikazu Mizutani,*** *S Higashi,* Kojundo Chemical Laboratory Co.,Ltd., Japan*; T Nabatame,* National Institute for Materials Science

Introduction

Among various precursors, cyclopentadienyl indium (CpIn) is one of the most promising precursors for atomic layer deposition (ALD) of high purity indium oxide films, because cyclopentadienyl group (Cp) in CpIn is very easily eliminated from indium by reacting with hydroxyl group during ALD process [1]. However, CpIn is solid at room temperature, while liquid precursor is demanded for use in commercial ALD instrument [2]. Therefore, we prepared liquid ethylcyclopentadienyl indium (EtCpIn), which is expected to have similar ALD characteristics, and investigated its ALD process for depositing high purity oxide films.

Experiments

EtCpIn was synthesized by using modified procedure for CpIn, and 1H-NMR spectra of the EtCpIn supported its estimated structure (Fig. 1).

Indium oxide films were deposited onto Si wafer at 150 °C. Argon was used as a carrier and a purging gas. EtCpIn, plasma oxygen, and water were employed as reactants. EtCpIn was held in a stainless steel cylinder heated to 120 °C. Oxidizing reactants in the ALD cycles were exposed in two ways: water followed by plasma oxygen (WpO), and only plasma oxygen (pO).

Thicknesses of the films were measured by spectroscopic ellipsometer. Purities of the films were investigated using radio frequency glow discharge optical emission spectrometry (Rf-GDOES).

Results and Discussion

Fig. 2 shows the relationship between film thickness and the number of ALD cycle for WpO and pO. Growth rates of the films (WpO, pO) were almost the same (0.03 – 0.04 nm/cycle), and quite small compared with the case of CpIn [1]. The difference is caused by the plasma, which was not used in CpIn case [1]. Since we used plasma oxygen to obtain high purity films, hydroxyl groups were completely oxidized and disappeared before EtCpIn exposure, and no Cp elimination was occurred during EtCpIn exposure.

Fig. 3 shows depth profiles of indium oxide films by WpO process and by pO process. Very small amount of carbon incorporation is seen in pO film, while no obvious incorporation is detected in WpO film. These results indicate that Cp were completely eliminated by reacting with hydroxyl group, though still non-negligible amounts is remain by plasma oxidation.

Summary

A novel liquid precursor, ethylcyclopentadienyl indium, for atomic layer deposition of indium oxide films was synthesized, and high purity indium oxide films were deposited using water and plasma oxygen as oxidizing reactants.

Reference

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9:30am **AF1-TuM-7 A New Scandium Precursor for the ALD of Scandium Oxide*, Jean-Sébastien Lehn,*** *C Dezelah, D Moser, R Kanjolia,* EMD Performance Materials

Scandium oxide is a high-κ dielectric material with potential application in microelectronic capacitor structures. Additionally, scandium-containing mixed oxides, such as $GdScO_3$, $DyScO_3$ or $Al_xSc_{(2-x)}O_3$ are also interesting high-κ dielectric materials. Scandium precursors containing acac, Cp, MeCp, or amidinate ligands have been used previously for the ALD of scandium-containing thin films.[1-5]

A new scandium precursor will be presented: bis(methylcyclopentadienyl)(3,5-dimethylpyrazolato)scandium(III). This precursor (hereafter called Sc-07) combines the advantages of a high vapor pressure (0.27 Torr at 100 °C) with a low melting point (< 40 °C), and a very good thermal stability. A low-melting precursor reduces the risk of clogging a line via condensation during use, and facilitates large-scale synthesis and purification via distillation to obtain ultra-high purity material.

Scandium oxide films were grown by ALD on a home-built system using Sc-07 and water, and the growth/cycle was high, at approximately 1.3 Å/cycle. The ALD window covers the range of 230-275 °C. Thanks to its high vapor pressure, ALD growth of Sc-07 could be obtained at a source temperature of 100 °C; film growth was observed even with the bubbler set at 80 °C. Vapor delivery compares well with other scandium precursors, such as the amidinate, $Sc(thd)_3$ and $ScCp_3$, which were delivered at 140 °C, 115-119 °C, and 105 °C, repectively.[1,2,5]

The films have refractive indices of 1.8-1.9, which is consistent with the bulk value. XPS showed that carbon in the films was below detection limit, and that the Sc/O ratio corresponds to the expected Sc_2O_3, as shown in the attached XPS depth profiles. Detailed XPS energy scans show no evidence of nitride nitrogen.

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9:45am **AF1-TuM-8 ALD Y_2O_3 Film Using Liquid Yttrium Precursor and Water***, **Akihiro Nishida**, A Yamashita, M Hatase, T Yoshino, M Enzu,* ADEKA Corporation, Japan

Yttrium oxide (Y_2O_3) is well-known as a stable compound having a wide band gap, high dielectric constant and high refractive index. It has been employed in several industrial applications as a ceramic, dielectric insulator, superconductor, optical film, protective film and buffer layer. However, almost all yttrium ALD precursors are solids at room temperature and thus undesirable for industrial use. Lowering the melting point is required in order to solve several problems such as a difficult purification process, clogging precursor delivery lines, and the generation of particles.

In this study, we carried out the investigation of several types of yttrium ALD precursors. As an example, we found that the yttrium precursor tris(sec-butylcyclopentadienyl)yttrium [$Y(sBuCp)_3$] is a liquid at room temperature. $Y(sBuCp)_3$ showed a very clean TG curve without decomposition and residue. Over 2 months', long term thermal stability of $Y(sBuCp)_3$ at 150℃ was observed by TG-DTA measurement. Additionally, we demonstrated ALD Y_2O_3 using $Y(sBuCp)_3$ and water as the coreactant. The deposition temperature was varied from 200 to 400℃. It was also found that carbon and nitrogen contamination in each Y_2O_3 film was not detected by XPS measurement when deposited at 200℃ (Fig. 1). Furthermore, we verified that smooth films were deposited by XSEM measurement (Fig. 2). Therefore, we conclude that $Y(sBuCp)_3$ is suited for manufacturing ALD processes compared to conventional solid precursors.

10:45am **AF1-TuM-12 Thermal ALD of Gold Thin Films***, M Mäkelä, T Hatanpää, K Mizohata, J Räisänen, M Leskelä, **Mikko Ritala**,* University of Helsinki, Finland

ALD gold thin films are desired for various applications including plasmonics and catalysis. In recent years a great amount of work has been invested into finding a suitable gold precursor for ALD. All the previously presented potential gold precursors are rather unstable thermally or have ligands that may complicate the film growth.[1,2] Until now there has not been a thermal ALD process of gold.

In this study a thorough analysis of a range of potential gold precursors was made and dimethyl(diethyldithiocarbamato)gold(III), $Me_2Au(S_2CNEt_2)$, was found to exhibit exceptional stability and nearly complete one-step evaporation in thermogravimetric analysis. The compound was synthesized in-house and used in thermal ALD together with ozone. Ozone is a general co-reactant in ALD oxide processes but the instability of gold oxide allows the deposition of metallic gold with ozone.

The evaporation temperature of $Me_2Au(S_2CNEt_2)$ was 99 °C and the films were deposited at 120 °C and above. Self-limiting film growth was confirmed at 180 °C. Thermal decomposition of $Me_2Au(S_2CNEt_2)$ was observed only at 250 °C which is a very high temperature for a volatile gold precursor. The Au thin films were uniform, polycrystalline, continuous and conductive. Typical resistivity values of 40 nm thick films were 4 – 16 µΩ·cm. Chemical composition of a film deposited at 180 °C was analyzed by time of flight elastic recoil detection analysis (TOF-ERDA) that showed the film to be pure and contain only 2.9 at.% oxygen, 0.85 at.% hydrogen, and 0.2 at.% of carbon and nitrogen each. This is the first thermal ALD process for gold and exhibits good growth characteristics and high film quality.

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11:00am **AF1-TuM-13 Nucleation Behavior of Ru on SiO_2 by Atomic Layer Deposition Using Cyclopentadienylethyl(dicarbonyl)Ruthenium and Oxygen***, **Guo Liu**,* EMD Performance Materials*; C Dezelah,* EMD Performance Materials, USA*; D Moser, R Kanjolia,* EMD Performance Materials

Ru has been widely investigated for potential applications in microelectronics as an electrode material as well as for catalysis and other applications. The thermal Ru ALD process with O_2 is known to have a nucleation delay for many Ru precursors. It is important to understand the nucleation behavior of a Ru precursor to achieve uniform growth with precise thickness control. Ru ALD of cyclopentadienylethyl(dicarbonyl)ruthenium, $Cp(Et)Ru(CO)_2$ or RUCCOE, has been reported to have high growth rates of 1.5-3 Å /cycle (1) or ~1. 0 Å/cycle with an 80-90 cycle nucleation delay. (2) In this work, correlations of the complex nucleation behavior of RUCCOE with the deposition temperature, precursor dose, and argon carrier/purge gas flow rate etc. have been investigated.

There is a considerable variation in the nucleation delay even at the same deposition temperature of 300°C . This variation can be described by the average growth rate per cycle (GPC) over a fixed number of cycles. For examples, an increase in Ru pulse time can cause a rapid drop of the average GPC, and a small change in the purge gas flow rate for RUCCOE under deposition conditions 2 and 3 can significantly vary the average GPC for the same 2s. RUCCOE pulse time as shown in Figure 1.

The nucleation delay of RUCCOE also depends on the substrate as well as the deposition temperature in the range of 275-350°C. The lower the deposition temperature, the slower the nucleation process. Equal growth rate on native and 100nm thermal SiO_2 and true linear growth were not achieved until about 350°C, at which temperature a nucleation delay of 40-50 cycles has been observed.

The cause of this variable nucleation delay behavior is believed to be a result of CO absorption on the substrate surface. CO is known to be capable of inhibiting Ru nucleation under certain deposition conditions. (3) RUCCOE loses CO at ~190°C but the partially decomposed precursor is thermally stable up to 350°C or possibly higher. CO evolved from RUCCOE can be partially absorbed on the substrate. An increase in the RUCCOE pulse time will increase the local CO concentration on the surface while a higher temperature can speed up CO desorption and thus change the Ru nucleation.

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11:15am **AF1-TuM-14 Mechanistic Aspects of Ru ALD Based on $Ru(DMBD)(CO)_3$ using Downstream Quadrupole Mass Spectrometry***, **Zhengning Gao**,* Washington University, St. Louis*; R Kanjolia,* EMD Performance Materials*; P Banerjee,* Washington University, St. Louis

The precursor 2, 3 - dimethyl butadiene Ruthenium tri-carbonyl ($Ru(DMBD)(CO)_3$), is a volatile molecule with favorable properties for the deposition of both Ru and RuO_2 films via ALD. The precursor can generate a vapor pressure of 1 Torr at 33 ºC and completely volatilizes at 140 ºC leaving no residue. Recently, the deposition of Ru and RuO_2 films have been demonstrated[1] using $Ru(DMBD)(CO)_3$. The films demonstrate a higher growth rate and lower deposition temperature window as compared to other Ru precursors. However, the exact reaction mechanism for $Ru(DMBD)(CO)_3$ during every half-cycle remains largely unexplored. Knowledge of $Ru(DMBD)(CO)_3$ half-reactions is critical to design processes with faster nucleation cycles. Such approaches are particularly attractive for applications such as, battery charge collecting electrodes and seed layers for the Cu damascene process which demand high conductivity from ultra-thin films.

In this talk, we will discuss the mechanism of ALD of $Ru(DMBD)(CO)_3$ and H_2O using *in situ* downstream quadrupole mass spectrometry (QMS). QMS provides a real-time analysis of reaction by-products produced due to incoming precursor interaction with functionalized surfaces. Using QMS, the by-product species can be identified and the amount quantified.

The QMS signal of the Ru(DMBD)(CO)$_3$ consists of three distinct species. First, the mass-to-charge ratio (m/e) of 67 corresponds to the DMBD ligand dissociating from the molecule. Second, a strong m/e = 16 is also observed as the DMBD further cracks into smaller fragments. Finally, m/e = 44 is observed and is related to CO_2 and HCOOH formation from the reaction of the tri-carbonyl groups with H_2O. The QMS signal of these three species will be discussed in the context of varying process parameters such as Ru(DMBD)(CO)$_3$ and H_2O pulse times and the temperature of the ALD process. Additionally, *ex situ* film characterization including atomic force microscopy and transmission electron microscopy will be presented to correlate the process signatures obtained via QMS to the film type and morphology.

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11:30am **AF1-TuM-15 Atomic Layer Deposition for Rhenium Based Materials***, **Jani Hämäläinen**, M Mattinen, M Vehkamäki, K Mizohata, K Meinander, J Räisänen, M Ritala, M Leskelä,* University of Helsinki, Finland

Many rhenium compounds are highly interesting for several applications. The last-stable-element-discovered rhenium metal is vital in superalloys for jet engines and in catalysis [1]. Re-Pt catalysts are, as an example, used in making lead-free, high-octane petrol [2]. Another potential use for the rhenium is for copper diffusion barrier layers in microelectronics [3]. The super-hard ReB_2 is tough enough to scratch diamond [4], whereas the "covalent metal" ReO_3 has an electrical conductivity comparable to silver [5]. In contrast, ReS_2 has recently emerged as a potential 2D material for various optoelectronic and electronic applications because of the unique and unusual behavior of the ReS_2 to retain a direct bandgap even in bulk form as the monolayers are effectively decoupled from each other [6].

Atomic layer deposition (ALD) is an established method in the semiconductor industry to prepare thin films in controllable and repeatable manner, even at monolayer level, on large and complex surfaces. Therefore, development of ALD processes for rhenium based materials could become highly beneficial for various applications. Here, recent progress in development of rhenium based materials by ALD at the University of Helsinki is presented. This includes the developed ALD processes for both Re metal and ReS_2 thin films using $ReCl_5$ with NH_3 and H_2S based ALD chemistries, respectively. Both of these materials have been deposited by ALD for the first time. The grown films have been analyzed with several methods, including FESEM/EDX, GIXRD, AFM, TEM, XPS, TOF-ERDA, and 4-point probe.

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11:45am **AF1-TuM-16 Plasma-enhanced Atomic Layer Deposition of Silver using the Ag(fod)(PEt$_3$)-precursor and NH$_3$-plasma***, **Matthias Minjauw**, E Solano,* Ghent University, Belgium*; S Sree,* KU Leuven, Belgium*; R Asapu,* University of Antwerp, Belgium*; M Van Daele, R Ramachandran,* Ghent University, Belgium*; S Verbruggen, S Lenaerts,* University of Antwerp, Belgium*; J Martens,* KU Leuven, Belgium*; C Detavernier, J Dendooven,* Ghent University, Belgium

Currently, there is a high interest in the fabrication of Ag nanostructures for applications in plasmonics, catalysis and nanophotonics. So far only a few Ag ALD processes have been reported in literature, due to the low thermal stability and insufficient volatility of Ag-precursors. The most promising Ag ALD process uses the Ag(fod)(PEt$_3$)-precursor in combination with H_2-plasma (H_2*), [1] and this resulted in the adoption of this process by several research groups in recent years. [2-5] In this abstract, we report a new process using the Ag(fod)(PEt$_3$)-precursor in combination with NH_3-plasma (NH_3*). This process offers a sixfold increase of the growth rate (0.24 nm/cycle) in the linear growth regime and an enhanced nucleation compared to the widely adopted H_2*-process (0.04 nm/cycle). The nucleation enhancement results in higher densities of smaller Ag nanoparticles, which is important for applications in catalysis and plasmonics.

The linearity and saturation behavior of the NH_3* and H_2*-process was confirmed on Au substrates. The conformality of the NH_3*-process was confirmed on complex 3D substrates. The nucleation and island growth mode of both processes was compared on SiO_2-substrates by combining ex situ grazing-incidence small-angle X-ray scattering (GISAXS) and scanning electron microscopy (SEM). It was found that for the same amount of Ag per surface area on the substrate, the particle areal density is 9 times larger for the NH_3*-process compared to the H_2*-process, and the particle sizes are much smaller. X-ray diffraction (XRD) showed that the deposited Ag films were polycrystalline fcc Ag. X-ray photoelectron spectroscopy (XPS) indicated low impurity levels in the bulk of films grown with both processes. At the surface of films grown using the NH_3*-process, the nitrogen atomic concentration was ~20%. From in situ Fourier transform infrared (FTIR) spectroscopy experiments, clues were found that these impurities derive from nitrogen containing surface species generated during the NH_3*-pulse which are interacting with the precursor molecules during the precursor pulse. We hypothesize that these surface groups lead to a more efficient removal of the precursor ligands, resulting in a higher precursor surface coverage compared to the process using H_2-plasma and hence explaining the enhanced nucleation and growth rate of the NH_3*-process.

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ALD Fundamentals
Room Plaza E - Session AF2-TuM

ALD Fundamentals: Theory & Mechanism (8:00-10: am)/Emerging Materials and Devices (10:45 am-12:00 pm)

Moderators: HyeongTag Jeon, Hanyang University, Korea, Harm Knoops, Oxford Instruments Plasma Technology, Iian Buchanan, Versum Materials, UK, Dustin Austin, Oregon State University

8:00am **AF2-TuM-1 Tuning Material Properties by Ion Energy Control during Remote Plasma-ALD on Planar and 3D Substrates***, **Tahsin Faraz**,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, UK*; M Verheijen, C van Helvoirt, S Karwal, A Sharma,* Eindhoven University of Technology, Netherlands*; D Hausmann, J Henri,* Lam Research*; A Bol, M Creatore, W Kessels,* Eindhoven University of Technology, Netherlands

Recently, it has been shown that the ion energy can play a significant role on the material properties of thin films prepared by plasma-enhanced atomic layer deposition (PEALD).[1] In this work, we demonstrate the impact of ion energy control during PEALD on planar and 3D substrate topographies using a commercial remote plasma ALD system (Oxford Instruments FlexAL) equipped with radio-frequency (RF) substrate biasing (13.56 MHz, up to 100 W power, -350 V resulting DC bias voltage). In such low pressure, remote inductively-coupled-plasma reactors, the ion energy can be controlled independently of the ion flux by applying an RF bias signal on the substrate table during the plasma exposure step.

Enhancing ion energies with substrate biasing during PEALD was observed to have pronounced effects on the material properties of several oxide and nitride films that serve important applications as dielectric materials. Energetic ion bombardment with substrate biasing increased the refractive index (*n*) and mass density (*ρ*) of TiO_2 ($n = 2.54\pm0.03$, $\rho = 4.2\pm0.2$ g/cm^3) at 300 °C and HfO_2 ($n = 2.10\pm0.03$, $\rho = 9.5\pm0.2$ g/cm^3) at 150 °C, and enabled their residual stress to be altered from tensile to compressive. PEALD of these oxides at 150 °C typically yields amorphous films, but applying a bias during the O_2 plasma exposure step enabled the formation of crystalline material (rutile TiO_2, monoclinic HfO_2) at low temperature. Biasing during PEALD on 3D trench nanostructures (aspect ratio ~ 4.5:1) effectively showed the role of directional ion bombardment by inducing differing film properties at different (planar and vertical) regions of the 3D substrate. For TiO_2 and HfO_2 at low temperature, biasing led to selective formation of crystalline material on planar surfaces and amorphous material on vertical sidewalls of the trenches. For SiN_x, biasing during N_2 plasma exposure led to selective degradation of film regions growing at planar surfaces of the trenches but not the regions forming at vertical sidewalls. This resulted in the material deposited at the sidewalls to have a higher etch-resistance and allowed those sidewall films to remain selectively after a 30 s wet-etch in dilute HF. These results demonstrate the potential of substrate biasing during PEALD in enabling routes for topographically selective[2] processing on 3D substrates. Furthermore, it will be discussed how substrate biasing enhances PEALD process capability by providing not one, but several additional knobs (magnitude, duration and duty-cycle of bias, etc.) for tuning a wide range of material properties.

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8:15am **AF2-TuM-2 Stress Control of Plasma ALD Films Deposited at Low Temperature by Application of Substrate Biasing***, **Thomas Miller,*** Oxford Instruments Plasma Technology, UK*; A Kurek, A O'Mahony,* Oxford Instruments Plasma Technology*; H Knoops,* Oxford Instruments Plasma Technology, UK*; O Thomas, R Gunn,* Oxford Instruments Plasma Technology

Stress in thin films can be important for a wide range of applications affecting mechanical properties of films but indirectly also other device and film properties. Due to the thinness of ALD films, stress is relatively unexplored, even though amorphous thermal ALD Al_2O_3 films have relatively high stress levels[1]. In this contribution, stress control of Ta_2O_5, MoO_3 and Al_2O_3 plasma ALD films deposited at relatively low temperature is demonstrated by the application of substrate biasing.

It has been shown that the addition of RF substrate biasing during the plasma half-cycle can used to control the stress of plasma ALD Al_2O_3 from compressive to tensile, depending on the DC bias that accumulates at the substrate.[2] RF substrate biasing can affect thin film formation in a number of ways, however, what is not fully understood is how this stress is introduced, how it depends on the ALD material and on the influence of table temperature.. This work uses the FlexAL tool offered by Oxford Instruments Plasma Technology, which utilises an Inductively Coupled Plasma (ICP) to create a remote plasma source. Generally remote plasma provides low ion energies to allow for low damage processing. Substrate biasing allows increase of this ion energy to also process in a higher ion energy regime.

Thin films were grown to 20nm, on 200mm Si (100) wafers, with substrate temperatures of 100°C to 150°C. Film stresses were determined using TOHO Technology FLX-2320 by measuring wafer curvature and using Stoney's equation. Ta_2O_5, MoO_3 and Al_2O_3 films grown by plasma ALD were characterised with respect to film stress at DC bias voltage between 0-250V.

Results point to the ability of controlling stress of materials grown by plasma ALD, by the addition of RF power to a biased electrode. Al_2O_3 films were shown to deliver compressive and tensile stress at a table temperature of 110°C depending on the applied bias voltage. MoO_3 was shown to be affected by the biased electrode by an increase in compressive stress; however at 140°C even without bias the films had compressive stress. Ta_2O_5 shows a trend that suggests it can be controlled from tensile to compressive films. In each case, the additional ion bombardment energy shifts the stress towards a more compressive (or less tensile) condition, similar to the behaviour of ion bombardment in the PECVD of silicon nitride films.[3]

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8:30am **AF2-TuM-3 Benefits of an O_2 Plasma in a Bi_2O_3 ALD Process***, **Matthias Müller**, K Komander, C Höhn, R van de Krol,* Helmholtz Zentrum Berlin, Germany*; A Bronneberg,* Dutch Institute for Fundamental Energy Research, Netherlands

Bismuth-based ternary oxides, e.g. $BiVO_4$ or $CuBi_2O_4$, are promising photoabsorber materials for solar-driven water splitting [1,2]. The main limitation of these Bi-based metal oxides is the short charge carrier diffusion length (LD=10-70 nm), compared to the light penetration depth (α=250-500 nm) [2]. Consequently thin films on nanostructured templates are needed for efficient solar water splitting. A conformal deposition can easily be achieved by ALD. It has been recently demonstrated that photoactive $BiVO_4$ can be deposited by ALD in a supercycle approach using $BiPh_3$, VTOP, and water as precursors [3]. In this work we focus on plasma-enhanced deposition of Bi_2O_3 as a first step towards the deposition of high-quality Bi-based ternary oxide films by ALD.

Until now $Bi(thd)_3$ has mainly been used to prepare Bi_2O_3 films using water as oxidant [4]. However, due to the low reactivity of water towards thd-ligands [5] the obtained deposition rates are relatively low. Furthermore, these films contain a high amount of C impurities (>8 at.%). Real-time spectroscopic ellipsometry (RTSE) indeed revealed that H_2O is a very inefficient oxidizer whereas an oxygen plasma readily removes the thd-ligands (Fig. 1). Consequently, the use of an O_2 plasma as oxidant reduces the C content to 2.4 %. Furthermore, we achieve a high uniformity, i.e. 94 % over a 4" Si wafer.

Typically when modeling the SE data, the growing film is approximated by a single layer. The present surface groups (after the precursor and oxidant half-cycle) form an additional surface layer, but due to the minimal thickness this cannot be unambiguously distinguished from the bulk. However, in this ALD process the rather large $Bi(thd)_3$ molecule (diameter > 10 Å [4]) creates an adsorbed $Bi(thd)_x$ monolayer which is distinguishable from the Bi_2O_3 bulk. An optical model including a $Bi(thd)_x$ surface layer (Fig. 2) reveals a surface layer thickness of about 4 Å. This agrees well with the precursor diameter. The adsorbate is fully removed during the plasma exposure step (Fig. 2a). During this step the Bi-O bond is formed (Fig. 2b).

We will explain in detail the data modeling and discuss how these results aid in understanding film growth when large molecules are used as ALD precursors. In addition, the photoactivity of plasma-enhanced ALD grown Bi_2O_3 for solar water splitting will be discussed.

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8:45am **AF2-TuM-4 High Quality Thin Films Produced by Innovative PEALD Equipment with Microwave ECR Plasma***, **Hiromichi Enami**, N Mise,* Hitachi High-Technologies Corp., Japan*; H Hamamura, T Usui,* Hitachi R&D Group*; J Kalliomaki, V Kilpi,* Picosun Oy, Finland*; T Malinen,* Picosun Oy

PEALD is expected to be utilized for many applications such as transistors, OLED, Solar-cells and MEMS, because it can generate various thin films at lower temperature than thermal ALD. But currently the conventional PEALD has a limited range of applications due to its poor-quality film deposited at low temperature.

In order to get a high-quality film at low temperature, it is indispensable to generate radical and ion species effectively during the plasma treatment step of PEALD and to use them efficiently for the film formation. Microwave ECR plasma technology which was established by Hitachi High-technologies can generate a large number of radicals and ions in an extremely-low-pressure condition and can supply them with low exhaustion. Fig.1 shows the process pressure dependency of the radical and ion emission intensity in N_2 plasma generated by microwave ECR. Peak intensities of both radicals and ions drastically increase as pressure decreases.

For establishing a brand new method for high-quality film generation at low temperature, this Microwave ECR plasma is combined with the leading ALD system from Picosun. This combined system is called "MECRALD" as one of PEALD systems.

In order to verify the effectiveness of this MECRALD combination, MECRALD was applied to generation of films such as SiN, SiO_2, AlN and AlO. High-quality films are realized with higher density, lower C & O contamination, and lower roughness on 300mm wafers compared with the conventional technologies. It is also confirmed that MECRALD generates films with wet etch rates and electric performances which are better than the conventional technologies and as good as LP-CVD at 700 to 800 degree C.

This innovative MECRALD can be one of the superior solutions for next-generation integrated devices and other novel devices which need high-quality films at low temperature.

9:00am **AF2-TuM-5 ALD of Aluminum Fluoride using $Al(CH_3)_3$ and SF_6 Plasma***, **Martijn Vos**,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, UK*; W Kessels, A Mackus,* Eindhoven University of Technology, Netherlands

In this work we explored the use of SF_6 plasma as a co-reactant for atomic layer deposition (ALD) of aluminum fluoride (AlF_3). By combining SF_6

plasma with trimethylaluminum (TMA, $Al(CH_3)_3$) AlF_3 films with good material properties were grown. Metal fluorides such as AlF_3, MgF_2 and CaF_2 generally have a wide bandgap (>10eV) and low refractive index (1.3-1.6). Due to these interesting properties they find use in many applications, including passivation layers in Li-ion batteries, electron transport layers in photovoltaics and protective coatings for optical devices. Previously, ALD of fluorides has been demonstrated using TiF_4 and TaF_5 as the fluorine source for the deposition of MgF_2, CaF_2 and LaF_3 and more recently using HF for AlF_3, ZrF_4, MnF_2, HfF_2, MgF_2 and ZnF_2.[1,2] The novel approach of using SF_6 plasma as a fluorine source is a promising alternative to HF, because of the ease of handling that SF_6 offers. Furthermore, SF_6 plasma allows for increased reactivity at lower temperatures and reduced purge times, similar to the use of O_2 plasma for metal oxide ALD.

AlF_3 films were prepared on Si samples over a temperature window of 50°C to 300°C. Since SF_6 plasma etches Si and SiO_2, a thin Al_2O_3 layer was deposited prior to AlF_3 growth. Using *in situ* spectroscopic ellipsometry (SE) the growth per cycle (GPC) was determined to decrease from 1.5Å at 50°C to 0.5Å at 300°C. Interestingly, no significant impurity levels of S and C were detected in the bulk of the AlF_3 films using X-ray photoelectron spectroscopy (XPS), even for low deposition temperatures. Furthermore, XPS measurements showed an O content of around 0.5-1at.% and a F/Al ratio of 3. The low impurity content and the stoichiometric F/Al ratio are in line with a refractive index of 1.35 at 633nm as determined by SE. The thickness non-uniformity on a 200mm wafer was determined to be 3.9% (standard deviation, 1 sigma), without additional optimization. Moreover, deposition on GaP nanowires showed good conformality of the AlF_3 film along the full length of the nanowires. In addition, the reaction mechanism of the ALD process will be addressed based on a combination of optical emission spectroscopy (OES) and quadrupole mass-spectrometry (QMS). These measurements suggest that CH_4 is released during the TMA dosing, and that HF and CF_x–species are formed during the plasma exposure. Overall this work shows that SF_6 plasma is a promising co-reactant and can be the basis for ALD of a wide range of metal fluorides.

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9:15am **AF2-TuM-6 Ferroelectricity in Undoped ZrO_2 Thin Films on Pt Electrode without Post-Annealing Treatment**, *M Chen, **Po-Hsien Cheng**,* National Taiwan University, Taiwan

Ferroelectricity in HfO_2-based thin films, including the $Hf_{0.5}Zr_{0.5}O_2$ and HfO_2 doped with Al, Gd, Si or Y, has attached considerable attention recently due to their high compatibility and scalability with the complementary metal-oxide-semiconductor (CMOS) transistors. However, it is necessary to have a post-annealing (600~1000◦C) to attain ferroelectric crystallization, which increases the difficulty of CMOS process integration. ZrO_2, which is similar to HfO_2 in material properties, is also a CMOS-compatible material. However, ferroelectricity in ZrO_2 has not been fully understood yet. Here we report significant ferroelectricity in ZrO_2 thin films for the first time. The ferroelectricity with a remnant polarization up to $12\mu C/cm^2$ was achieved in undoped ZrO_2 nanoscale thin films prepared by remote plasma atomic layer deposition (RP-ALD) on the Pt electrode. Significant ferroelectric hysteresis loop was observed in the as-deposited ZrO_2 thin films without treated with the post-annealing, which is highly beneficial to the device integration. The existence of the ferroelectric orthorhombic phase with noncentrosymmetric space group *Pbc21* in the as-deposited ZrO_2 thin films was confirmed by high-resolution transmission electron microscopy. In addition, all the paraelectric, field-driven antiferroelectric, and ferroelectric behaviors of ZrO_2 were observed by changing the film deposition temperature and by performing post-annealing treatment, indicating the tunability of ferroelectricity in undoped ZrO_2 thin films. The result reveals the great potential of the undoped ZrO_2 thin films prepared by the RP-ALD technique for the next-generation non-volatile memories and ultralow-power transistors.

9:30am **AF2-TuM-7 Improving the Conductivity ($<10^{-3}\ \Omega$ cm) of HfN_x by Ion Energy Control during Plasma-assisted ALD**, ***Saurabh Karwal**, B Karasulu, M Verheijen, J Niemelä, T Faraz, W Kessels, M Creatore,* Eindhoven University of Technology, Netherlands

Transition metal nitrides (TMNs) find applications as gate metal in FinFETs and heat mirrors due to their low resistivity ($\rho < 10^{-4}\ \Omega$cm) and high infrared reflectivity, respectively. They are also used as copper diffusion barriers in interconnect technology. Amongst TMNs, hafnium nitride (δ-HfN_x) is a material that exhibits a high IR reflectivity and low resistivity (14.2 $\mu\Omega$cm for single crystals).

In this work, we report on HfN_x thin films that were prepared *via* plasma-assisted atomic layer deposition (ALD) adopting tris(dimethylamino)cyclopentadienylhafnium [$CpHf(NMe_2)_3$] as Hf precursor and H_2 plasma or H_2-Ar plasma as co-reactant.[1] We demonstrate that the resistivity of HfN_x films depends on the substrate potential (ion energy control) developed upon application of a RF substrate bias. By controlling the ion energy, the chemical composition and microstructure of the films can be tuned. We found that HfN_x films deposited using H_2 plasma under no bias yields an electrical resistivity of $(9\pm0.2)\cdot10^{-1}\ \Omega$cm whereas a decrease of the film resistivity by more than two orders of magnitude to $(3.3\pm0.1)\cdot10^{-3}\ \Omega$cm was observed for films prepared at a substrate potential of -130V.

The high resistivity under no bias condition is attributed to the prominent grain boundary scattering, next to a low Hf(III) oxidation state fraction of 0.65±0.02.[3] The low Hf(III) fraction is partially due to the presence of 20.1±0.7 at.% O, which leads to a resistive Hf-O bond that converts Hf(III) to Hf(IV) and depauperates HfN from free conduction electrons.[3] Preliminary density functional theory (DFT) simulations suggest that the dissociative binding of H_2O (present in the background of ALD chamber) on a pristine HfN surface is highly favoured both kinetically and thermodynamically (E_a = 0.11 eV and ΔE = -2.05 eV). On the contrary, a higher Hf(III) fraction of 0.82±0.02 is obtained for the film prepared with a substrate potential of -130V. This improvement can in part be attributed to the steady decrease in O content (≤2 at.%) upon increasing the substrate potential. The increase in Hf(III) fraction was also found to correlate with the decrease in grain boundary scattering, resulting in a decrease of the film resistivity.

Moreover, HfN_x films prepared by Ar-H_2 plasma instead of H_2 plasma exhibits even a much lower electrical resistivity of $(4.1\pm0.1)\cdot10^{-4}\ \Omega$cm when applying a substrate potential of -167V. The decrease in grain boundary scattering stems from an increase in the grain size (according to SEM analysis), in parallel with an increase in Hf(III) fraction reaching a value of 0.86±0.02.

1 Karwal, S. *et al.*, *J. Vac. Sci. Technol. A Vac. Surf. Films***35** (2017)

9:45am **AF2-TuM-8 Plasma Technology for Spatial ALD of Conductive Layers***, **Yves Creyghton**, A Illiberi, F Roozeboom,* Solliance/TNO, Netherlands

The use of plasma in Spatial ALD at high pressures is challenging because plasmas tend to filamentary structures above pressures of several Torr. Atmospheric pressure 'glow discharge' can be generated in noble gases but this is no economic option. We have developed Dielectric Barrier Discharge (DBD) plasma sources for generating a thin layer of plasma (~ 0.1 mm) proximate to moving substrates. Remotely generated plasma species must be transported by high gas flow towards the substrate in order to reduce radical recombination losses. This is applicable for ALD of metal oxides in O_2/N_2 plasma where N radicals contribute to O-radical formation in the downstream section. We found that for remote plasma ALD of metals and nitrides (TiON) no saturated growth can be reached, probably because radical recombination is too fast. Therefore, we developed *direct* Surface DBD plasma sources. Creating the plasma layer partially remote results in homogeneous plasma in contact with the substrate. The structure changes only in a minor way even under strongly varying surface conductivity conditions, thus allowing for homogeneous and stable ALD growth of conductors on dielectric substrates or vice-versa. An additional challenge is imposed by substrates without grounded potential. Since in gas bearing based spatial ALD no mechanical contact exists between the top surface layer and the ALD injector head, electrically floating layers are common practice. We found that the direct SDBD plasma sources cause positive charging of non-grounded substrates which is often resulting in the formation of micro-arcs intermixed with a homogeneous plasma layer. Micro-arcs have a detrimental effect on layer properties. In depth study of the micro-arcs via transparent conductive substrates, has resulted in modified plasma source electrode geometries and electrical operation conditions avoiding any micro-arc formation. The innovative plasma sources have been applied for ALD of titanium oxynitride using TDMAT as precursor and H_2/N_2 plasma in a temperature range from 50 to 250 ºC. A full material analysis was carried out which clearly showed the TiN structure. The layer resistivity was found to be strongly dependent on deposition temperature and could be decreased from 0.1 down to 10^{-3} Ω.cm upon increasing temperature from 150 to 250 ºC. XPS analysis shows a correlation between temperature and carbon content in the layer which decreased from 14 to 3% while the oxygen content was still high (~18 %). The conference presentation will emphasize the role of plasma conditions (source-to-substrate distance, power, H_2/N_2, gas flow) and the scalability of the direct plasma SALD process for industrial use.

10:45am **AF2-TuM-12 Atomic Layer Deposition of Lithium Titanate on Planar and 3D-Structured 200 mm Silicon Substrates***, **Sascha Bönhardt**, S Zybell, W Weinreich,* Fraunhofer IPMS, Germany*; C Hoßbach, V Neumann,* Technische Universität Dresden, Germany

Thin film battery technology delivers high added value for autonomous microsystems e.g. wireless sensor networks, Internet of Things (IoT) applications and medical implants. The transition to solid state electrolytes means significant improvement for battery safety and even opens possibilities for integration into silicon technology.

The 3D micro battery concept, including the deposition of functional layers on structured surfaces with high aspect ratio, has been shown to improve both, capacity and rate performance of all-solid-state lithium ion batteries (LIB)[1]. Our aim is the development and characterization of functional stacks allowing direct integration into 3D microsystems. For CMOS compatible design and production, we manufacture functional electrode and electrolyte layers on 200 mm wafer using industrial thin film deposition equipment.

In this work, we investigate atomic layer deposition of lithium titanate (LTO) for use as anode material in LIBs. Although it's comparatively low capacity, spinel lithium titanate has superior rate performance and stands out due to its zero-strain characteristics and the three dimensionality of ion transport [2]. With these properties LTO is a very promising anode material for 3D micro batteries.

In this work we present the successful deposition of lithium titanium oxide by ALD and subsequent formation of the desired spinel lithium titanate by rapid thermal anneal. It can be shown that LTO formation could also be achieved with an additional capping layer applied. That behavior is mandatory for forming multi-layer stacks w/o vacuum break or air exposure. Deposition took place on planar and 3D structured Si-substrates showing linear growth behavior and excellent step coverage as well. The applied ALD technique of preparing lithium titanium oxide is using lithium-tert-butoxide (LTB), tetrakis(dimethylamino)titan (TDMAT) and water as precursors. Films were analyzed by X-Ray diffraction (XRD), scanning electron microscopy (SEM), X-Ray photon spectroscopy (XPS) and Ellipsometry (EL). Electrical data is provided by electrochemical impedance spectroscopy (EIS) and cyclovoltametry (CV).

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11:00am **AF2-TuM-13 Nano-ceramic Composite Separator Modified by ALD for Lithium Ion Batteries of Improved Safety and Reliability***, **Erik Østreng**,* Picosun Oy*; R Ritasalo, S Ek,* Picosun Oy, Finland*; R Dominko,* National Institute of Chemistry

Li-ion battery represents a gigantic market as one of the energy and storage solutions for a wide range of cleantech applications [1,2]. Safety and reliability are the main technology issues that hinder applications of Li-ion batteries. Among these a membrane (e.g. separator) between active components of two electrodes plays the most critical role [1]. After multiple charge and discharge -cycles, the polymer membrane can undergo severe deformation and softening or even melting if the temperature reaches the polymer's softening point. As a consequence, large area short circuit can take place between the anode and the cathode and cause severe safety issues. Deposition of inorganic nano-ceramic thin film on conventional polymer (membrane) can effectively solve deformation and melting issues. Atomic Layer Deposition (ALD) is a gas-phase deposition technique for high-quality and pin-hole free thin films with precisely controlled layer thickness [1,2] thus providing a unique solution for improvement of the properties of the separator.

The objective of this study is to improve the performance of the Li-ion batteries by ALD-coated membranes to meet the large-scale application of power and energy storage for Li-ion batteries. The inorganic nano-ceramic thin film layers consisting of nanoscale thicknesses of Al_2O_3, ZnO and TiO_2 are deposited onto organic microporous polypropylene (PP) membrane by ALD. The thermal shrinkage and wettability of the separators and electrochemical performance of the cell are studied.

The thermal stability and wettability of the separators were clearly improved by the ALD coating, the effect being more notable with thicker ALD films (e.g. Fig. 1). The best electrochemical performances were shown by the cell assembled with the separator having a 15 nm Al_2O_3 layer. The results presented in Fig. 2a show relatively good cycling stability after a few cycles at 500mAh/g with excellent Faradaic efficiency (FE) that was stabilized at 97.5% after 20 cycles while the separator with a 0.5nm Al_2O_3 layer in Fig. 2b shows severe capacity fading which goes along with increase of polarisation during the discharge and charge process. We have demonstrated that controlled deposition of nano-ceramic ALD layers plays a crucial role both in the properties of the separator and the cell performances. Up-scaled ALD tools capable of handling large volumes of separators could make this technique affordable for the use in advanced energy storage technologies.

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Acknowledgements: The research has received funding from TEKES and HELIS in H2020 program.

11:15am **AF2-TuM-14 Physical and Electrical Characteristics of ALD Tin Disulfide Multilayer***, **Juhyun Lee**, G Ham, S Shin, H Kim, S Lee, H Choi, H Jeon,* Hanyang University, Republic of Korea

Many research groups have exhibited extensive research activities in two-dimensional (2D) materials, such as graphene, layered metal dichalcogenides, due to their unique properties in comparison with conventional thin film and layer structure materials. Layered metal dichalcogenides have attracted significant attention due to their interesting physical properties and possibility of application to flexible electronic device. Among these 2D materials, graphene is the extensively studied because of its high carrier mobility and transmittances. However, it has a zero bandgap in pristine form without functionalization or structural modification like a ribbon shape, resulting in poor transistor performance. In order to solve these problems, layered metal dichalcogenides (LMDs), such as MoS_2 and WS_2 has been researched due to their suitable electrical and physical properties. Tin disulfide (SnS_2) is another layered material to compete with current 2D materials. The 2D SnS_2 has S-Sn-S tri-atomic planar molecular arrangements with weak van der Waals bonding among molecules. The properties of 2D SnS_2 with bandgap of 2.1eV can lead to good transistors performance with large I_{on}/I_{off} and high mobility. Tin in SnS_2 is one of earth-abundant elements, notably a group IV element (Sn) and low melting temperature metal. Therefore, we tried to deposit this material at very low temperatures and to improve a crystalline quality of SnS_2 by measuring the physical and electrical properties.

In this study, we focused on the transistor characteristics of multi-layered SnS_2 deposited at 100 °C and step annealed from 100°C to 350 °C. Firstly, we will demonstrate physical and electrical characteristics of ALD-grown multilayered SnS_2 field-effect transistors (FETs) at low temperatures. The properties of annealed and as-deposited SnS_2 will be analyzed by XRD, RAMAN, TEM, XPS. And the transistors using few layers of SnS_2 will be fabricated and their electrical properties will be investigated. Process temperatures we applied are the temperatures which are compatible with flexible device fabrication, and the process we used is the process which is currently applied device fabrication.

11:30am **AF2-TuM-15 PEALD Platinum Nano-island SET Fabrication and Electrical Characterization***, **Daniel Thomas**, E Puyoo, M Le Berre,* Institut des Nanotechnologies de Lyon, France*; L Militaru, S Koneti, A Malchère, L Roiban,* INSA de Lyon, France*; A Sabac,* Institut des Nanotechnologies de Lyon, France*; K Ayadi, C Chevalier, J Grégoire, F Calmon, B Gautier,* INSA de Lyon, France

Single electron transistors promise unrivaled efficiency, however the cost and difficulty associated with achieving stable operation have hindered their pathway to industry. Numerous novel techniques have been demonstrated for SET creation[1], however many of these techniques require specialized, non-scalable fabrication techniques such as SEM, FIB, and colloidal chemistry. Among the methods available for the nanoisland formation necessary for SET operation, ALD and PEALD growth methods present the advantages of a large-scale approach that yields well-controlled monolayer growth[2]. Moreover, this approach facilitates low-temperature in-situ growth of Pt nanoparticles.

PEALD grown Pt nanoparticles were embedded in an ALD grown Al_2O_{-3} dielectric matrix at 200°C. As a first investigation, Pt-island growth was observed via TEM plane views performed after 30, 45 and 60 PEALD growth cycles (Figure 1). The resulting nanoislands were well-dispersed, with average sizes increasing from 1.7 nm to 4.3 nm with the number of cycles. Next, the optimal 30 cycles were selected for building both mono-layer and multistack layers of dielectrically isolated Pt nanoislands. Through simple UV lithography and evaporation steps, nanogap transistor electrodes were built on top of these Pt nanoislands layers. The shadow edge evaporation technique[3] provides us with material flexibility and the ability to build nanogaps demonstrated down to 6nm, with high lateral widths (~100 microns). The combination of these processes result in a high yield, low requirement fabrication process for building single electron transistors.

The resulting transistors, fabricated with Drain and Source electrode widths between 2µm and 8µm, were analyzed using STEM and TEM cross-sections to confirm proper fabrication (Figure 2). Electrical measurements were performed at varying temperatures and coulomb oscillations were present across all electrode widths and were identifiable at up to 170K (Figure 3). Upon further investigation of the conduction mechanisms, it was determined that the majority conduction was through trap assisted hopping as modeled by Poole-Frenkel emission controlled by way of Coulomb blockade.

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11:45am **AF2-TuM-16 Thermal Annealing Effects on Electron Emission Properties of ALD MgO***, **Violeta Prodanovic**, H Chan,* Delft University of Technology, Netherlands*; A Mane, J Elam,* Argonne National Laboratory, USA*; L Sarro, H v.d. Graaf,* Delft University of Technology, Netherlands

An experiment is conducted to investigate the influence of thermal annealing on secondary electrons emission (SEE) by ALD grown MgO employed in a novel photodetector Timed Photon Counter (TiPC). This effect is studied for 25 nm MgO film deposited on Si substrate (reflective SEE), and MEMS fabricated membranes with thicknesses in range of 5 – 25 nm (transmission SEE). Furthermore, morphological and structural properties are determined by AFM, XPS and XRD analysis, together with a new procedure for in situ measurements of the specific resistivity of MgO.

An essential part of TiPC is the tynode (transmission dynode), an array of freestanding membranes with thicknesses in the order of a few nanometers. After the impact of an incoming electron on one side of the tynode, noise-free amplification is provided through secondary electrons emission on the opposite side of the membrane [1]. MgO is already known for its excellent reflective SEE properties, reported in the range of 3.3 – 24.3 [2], depending on the deposition and measurement method. For fabrication of tynodes ALD is employed as the most apt technique for growing ultra-thin films of good quality, with excellent control over thicknesses and extremely low surface roughness (Fig. 1). Moreover, mechanical properties of this material, mainly its low compressive residual stress of around 200 MPa, and chemical inertness to some common MEMS etchants (such as vapour HF) ensure suspension of strong membranes.

We report RSEE coefficient of 4.7 for 25 nm thin MgO deposited by thermal ALD at 200 °C using $Mg(Cp)_2$ and H_2O as precursors. It is observed that thermal post-annealing of this film at temperatures in range 250 – 400 °C for 3 – 4 hours improves the SEE. The optimal temperature of such treatment is found to be 300 °C, giving the maximum RSEE of around 6.25 (Fig. 2). Apart from enhanced yield, thermal bake out resulted in a shift of maximum RSEE towards higher energies of primary electrons of around 100 eV. Identical study carried out for 25 nm thin MgO membranes showed an increase in transmission SEE of approximately 20%. XRD analysis revealed that film remained amorphous in this temperature range, which suggests the increase of SEE yield is mainly driven by removal of surface contamination on samples. Conducting similar experiment at higher temperatures will provide useful information on how induced crystallinity affects SEE properties of ALD MgO.

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ALD Applications
Room Plaza ABC - Session AA1-TuA
Batteries II (1:30-3:30 pm)/Emerging Apps III (4:00-5:00 pm)

Moderators: Ganesh Sundaram, Ultratech, Andy Sun, University of Western Ontario, Canada, Erik Østreng, Picosun Oy, Nicholas Strandwitz, Lehigh University

1:30pm **AA1-TuA-1 Highly Improved Performance of High Voltage ALD Coated Cathodes Showing Minimal Capacity/Voltage Fade at 4.8V**, ***Lamuel David**, D Mohanty,* Oak Ridge National Laboratory; *K Dahlberg,* Xalt Energy LLC; *D King,* Forge Nano (a PneumatiCoat Company); *D Wood III,* Oak Ridge National Laboratory

Energy density of current lithium-ion batteries (LiBs) based on layered $LiMO_2$ cathodes (M=Ni, Mn, Co) needs to be improved significantly for widespread electric vehicle use in the automotive industry. In this work, we show that atomic layer deposition (ALD) of LiPON on Ni-rich NMC and Li-Mn-rich (LMR) NMC active particles substantially improves LIB performance even when cycled at increased upper cutoff voltage (UCV). Our results show that LiPON coatings prevented capacity degradation and decreased voltage fade when cycling at 1C-1C rate at UCV of 4.8 V. These samples also exhibited exceptional rate performance with 5x improvement (160 mAh/g) in capacity for NMC and 3x improvement (210 mAh/g) in capacity for LMR NMC when the particles were coated with LiPON. Electrochemical impedance spectroscopy (EIS) confirmed that LiPON-coated materials exhibited a significantly lower increase in the charge transfer component of impedance during cycling. The ability to mitigate surface related degradation mechanisms of these materials as demonstrated in this report provides insight into enhancing performance of high-voltage and high-energy LIBs.

1:45pm **AA1-TuA-2 Physical and Electrochemical Effects of Post-deposition Annealing on Atomic Layer Deposited Al_2O_3 Coatings on $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$**, ***David Jackson**, T Kuech,* University of Wisconsin-Madison

A systematic study investigating the effects of annealing on atomic layer deposited (ALD) Al_2O_3 coated Li-ion battery cathodes was performed. $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC) cathode powders were ALD coated at 100 °C, annealed from 300 to 700 °C, and then used to fabricate coin cells to investigate the electrochemical effects of the treatment. Analyses have shown that cell properties vary as a function of annealing temperature, and that the resulting electrochemical behavior and the cathodic solid-electrolyte interphase formed during cycling are significantly correlated.

Cells were characterized using charge-discharge cycling at 5C and C/5 rates, electrochemical impedance spectroscopy, charge endpoint slippage analysis, pre-assembly and postmortem X-ray photoelectron spectroscopy, and an elevated temperature storage test. It was observed that Al diffusion into the NMC bulk activates around 500 °C anneal temperature, where the Al atoms overcome a kinetic barrier allowing to them leave the surface Al_2O_3 layer. While efficiency of the cells during 5C rate cycling is higher in the unannealed samples, the starting capacity is also reduced, with Li likely being sequestered in the coating layer. At the highest temperature, 700 °C, the surface is similar to an Al “surface doped” NMC due to diffusion. This Al-doped surface leads to the highest self-discharge of all samples, though charge capacity retention in C/5 cycling is among the highest of all samples.

In samples annealed at 500 °C, an anomalous high charge slippage occurred between the first two cycles, indicating the presence of parasitic reactions. Postmortem XPS analysis of these samples show relatively high amounts of LiF formed in the SEI during cycling. Some connection between LiF formation and high charge slippage indicate the presence of uniquely active surface species formed during the initial stages of Al diffusion into the bulk.

These results demonstrate a new parameter that may be utilized to further control properties of ALD coated battery materials beyond that currently established with the well-studied Al_2O_3 coatings.

2:00pm **AA1-TuA-3 Novel Mechanism of Atomic Layer Deposition Al_2O_3 on $LiMn_2O_4$ for High Capacity Lithium-ion Batteries**, ***Lin Chen,*** Illinois Institute of Technology; Argonne National Laboratory; *R Warburton,* Purdue University; *K Chen,* Northwestern University; *J Libera,* Argonne National Laboratory; *M Hersam,* Northwestern University; *J Greeley,* Purdue University; *J Elam,* Argonne National Laboratory, USA

Previous studies demonstrated that Al_2O_3 coatings prepared by atomic layer deposition (ALD) improved the capacity of $LiMn_2O_4$ (LMO) cathodes for lithium ion batteries. This improvement was attributed to a reduction in surface area and diminished Mn dissolution. However, here we propose a different mechanism for ALD Al_2O_3 on LMO based on in-situ and ex-situ investigations coupled with density functional theory calculations. We discovered that Al_2O_3 not only coats the LMO, but also dopes the LMO surface with Al leading to changes in the Mn oxidation state as revealed by in-situ mass spectrometry and infrared spectroscopy as well as ex-situ X-ray photoelectron spectroscopy. Different thicknesses of Al_2O_3 were deposited on nonstoichiometric $LiMn_2O_4$ for electrochemical measurements. The LMO coated using one cycle of ALD Al_2O_3 (1 × Al_2O_3 LMO) yielded a high initial capacity, 16.4% larger than its uncoated LMO counterpart in full cells. The stability of 1 × Al_2O_3 LMO is also much better as a result of greatly stabilized structure with Al-doping. Furthermore, 4 × Al_2O_3 LMO demonstrates remarkable capacity retention, nearly reaching 100% at 0.5 C for 200 cycles while uncoated LMO only retains 78.2%. Stoichiometric $LiMn_2O_4$ was also evaluatedwith similar improved performance achieved. All superior results, accomplished by great stability and reduced Mn dissolution, is thanks to the synergetic effects of Al-doping and ALD Al_2O_3 coating. This new understanding offers a viable avenue to tune the performance of other Mn-containing, high capacity cathodes by employing $LiMn_2O_4$ as amodel system.

2:15pm **AA1-TuA-4 Atomic Layer Deposition of Superionic Solid-State Electrolytes for Lithium Batteries**, ***Xiangbo Meng,*** University of Arkansas; *J Connell, P Lopes, J Libera,* Argonne National Laboratory, USA; *K Zavadil,* Sandia National Laboratory; *J Zhang,* Pacific Northwestern National Laboratory; *J Elam,* Argonne National Laboratory, USA

Rechargeable lithium batteries are very promising energy storage devices for portable electronics, transportation, and smart grids. As an important component of lithium batteries, liquid electrolytes currently are widely utilized, serving as a lithium-ion conductor but an electrical insulator. The direct contact between the electrodes and the liquid electrolyte, however, causes undesirable electrochemical reactions the ubiquitous formation of solid electrolyte interphases (SEIs). SEIs differ in quality with the coupling selection of anodes, cathodes, and liquid electrolytes, but always adversely consume lithium and liquid electrolytes. On the other hand, the flammable nature of liquid electrolytes poses serious safety concerns in lithium batteries. Among various potential solutions, solid-state electrolytes are highly regarded.

Aimed at developing new superionic solid-state electrolytes, we recently explored two individual processes for binary Li-S and Al-S compounds, respectively, using atomic layer deposition (ALD). By combining the two ALD processes and tuning their cycle ratio, we then synthesized a series of ternary compounds of lithium aluminum sulfides, i.e., Li_xAl_yS. The subsequent impedance measurements verified that the resultants Li_xAl_yS films are promising solid-state electrolytes with tunable ionic conductivities up to over 10^{-4} S/cm, 1000 times higher than the LiPON counterparts reported previously. We further characterized the growth and properties of the ALD Li_xAl_yS films using *quartz crystal microbalance*, *inductively coupled plasmamass spectrometry*, and *X-ray photoelectron spectroscopy*. In addition, we also investigated the surface chemistry for the Li_xAl_yS ALD using in-situ *Fourier transform infrared spectroscopy*. Very interestingly, the resultant Li_xAl_yS films demonstrated an exceptional performance in inhibiting the growth of lithium dendrite structures in lithium batteries.

2:30pm **AA1-TuA-5 Cubic Garnet $Li_7La_3Zr_2O_{12}$ Solid Lithium Electrolyte by ALD**, ***Eric Kazyak**, K Wood, K Chen, A Bielinski, A Davis, T Thompson, J Sakamoto, N Dasgupta,* University of Michigan

Lithium-conducting solid-state electrolytes (SSEs) are a promising platform for achieving the high energy density, long-lasting, and safe rechargeable batteries needed for a wide range of applications. By eliminating the need for flammable and unstable liquid electrolytes, SSEs dramatically reduce the risk of fire while enabling high voltage and energy density chemistries including Li metal. In particular, the ceramic oxide material cubic garnet $Li_7La_3Zr_2O_{12}$ (LLZO) is a promising option due to its stability and high ionic conductivity. Two major challenges to commercialization are manufacturing of thin layers and creating stable, low-impedance, interfaces with both anode and cathode materials. Atomic Layer Deposition (ALD) has recently been demonstrated as a powerful method for depositing both solid electrolytes and interfacial layers to improve stability and performance at electrode-electrolyte interfaces in battery systems. The self-limiting reactions afford the ability to conformally coat arbitrary geometries for 3D batteries, powders, and porous cathodes, an important advantage over the current state-of-the-art LiPON solid electrolyte and previous approaches for thin-film LLZO.

In this study, we present the first reported ALD of the pentenary oxide Al-doped LLZO. Constituent binary processes are successfully combined in a thermal ALD process at 225°C to deposit high purity, dense amorphous LLZO films. The cycle-by-cycle growth of the multi-component film is quantified by in situ quartz crystal microbalance (QCM) measurements. We demonstrate the ability to tune composition within the amorphous as-deposited film, anneal to achieve the desired cubic garnet phase, and characterize the annealed films via *in situ* synchrotron XRD during annealing. The ability to conformally coat high aspect ratio structures of arbitrary composition with ultrathin layers of dense, amorphous LLZO is shown, demonstrating the potential for integration into 3D battery architectures, including porous electrode structures. Approaches to overcome Li loss and phase segregation during annealing are demonstrated and discussed.

The film exhibits preferential orientation when annealed on single crystal substrates, and the cubic-tetragonal phase transition was observed at ~500°C, significantly lower temperature than reported for bulk synthesis methods. By tuning the composition and annealing conditions, the resulting film can be tuned from pure-phase $La_2Zr_2O_7$ pyrochlore, a high temperature thermal barrier material with several commercial applications, to high purity tetragonal LLZO or high phase-purity cubic LLZO, the superionic solid electrolyte material.

2:45pm **AA1-TuA-6 Improving Interfacial Stability of Sulfide-Based Lithium-Ion-Conducting Solid Electrolytes with ALD***, **Jasmine Wallas**, A Heist, S Lee, S George,* University of Colorado - Boulder

Rechargeable solid state Li-ion batteries may revolutionize energy storage. Solid state Li-ion batteries also have the potential for better safety, cycling performance, SEI stability and energy density than liquid electrolyte Li-ion batteries. However, solid electrolytes generally suffer from low ionic conductivity and/or poor interfacial stability. In this work, we demonstrate that the interfacial stability of solid electrolytes can be improved with ALD coatings.

$Li_{10}GeP_2S_{12}$ is a sulfur-based ceramic electrolyte with extremely high ionic conductivity of ~10^{-2} S cm^{-1}. This ionic conductivity is comparable with liquid electrolytes at room temperature. However, $Li_{10}GeP_2S_{12}$ solid electrolyte suffers from interfacial instability with Li metal. Contact with Li metal leads to substantial electrolyte decomposition and the formation of a resistive interphase. However, Al_2O_3 ALD coatings can greatly increase the interfacial electrochemical stability.

In this work cells were composed of symmetric Li electrodes with $Li_{10}GeP_2S_{12}$ solid electrolyte (see supplemental Figure 1). The $Li_{10}GeP_2S_{12}$ solid electrolytes were coated with various numbers of Al_2O_3 ALD cycles. The Li metal was then pressed into the $Li_{10}GeP_2S_{12}$ solid electrolyte. The thickness of the Al_2O_3 ALD coating was varied to optimize interfacial stability. Internal cell resistance measurements were used to monitor the formation of the resistive interphase. The experiments were conducted at 60°C.

The uncoated $Li_{10}GeP_2S_{12}$ solid electrolyte developed extremely high internal resistance and reached the defined failure point (>1000 Ω) within the first 40 hours of the test (see supplemental Figure 2). The Al_2O_3 ALD coatings substantially increased interfacial stability and maintained lower internal resistance. The $Li_{10}GeP_2S_{12}$ solid electrolyte coated with 25 Al_2O_3 ALD cycles increased the chemical stability and extended the time to the failure point to 400 hours (see supplemental Figure 2). The lifetime of the Al_2O_3 ALD-coated $Li_{10}GeP_2S_{12}$ solid electrolyte is more than a factor of 10 longer than the uncoated $Li_{10}GeP_2S_{12}$ solid electrolyte.

3:00pm **AA1-TuA-7 Atomic Layer Deposition of Solid-State Electrolytes for All-Solid-State Lithium Ion Batteries***, **Biqiong Wang**, J Liu, Y Zhao, A Lushington, R Li, T Sham, X Sun,* University of Western Ontario, Canada

The development of batteries with higher energy density, longer cycle lives, and assured safety levels have been the pressing need to satisfy the stringent demands of portable electronic devices, electric vehicles and grid-energy storage systems. [1] Replacement of the conventional liquid electrolytes with solid-state electrolytes (SSEs) will not only eliminate the inherent safety issues but also provide more flexibility in battery design and management. [2] Atomic layer deposition (ALD) offers exclusive advantages of highly controllable thin film depositions especially on high-aspect ratio three-dimensional substrates. [3, 4] In our group, various SSEs have been developed by ALD including Li_3PO_4, lithium silicate, lithium silicophosphate, $LiTaO_3$, and $LiNbO_3$. [5-7] All of the as-deposited thin films presented acceptable ionic conductivity, among which Li_3PO_4 exhibited the best value of 3.3x 10^{-8} S/cm at room temperature (Figure S1). Nevertheless, the electrochemical properties of materials by ALD have shown deviations from those obtained by other methods. Synchrotron-based spectroscopy, including X-ray Photoemission Spectroscopy (XPS) and X-ray Absorption Spectroscopy (XAS), were performed to study their detailed electronic structures. Insightful information on both local chemical environment and structures can be extracted. Further analysis of the spectra can give semi-quantitative information. In Figure S2, Nb L-edge X-ray absorption near edge spectra (XANES) show that Nb in the Li_xNb_yO systems by ALD exists as Nb5+ in an octahedron structure with oxygen. While introducing more Li content by controlling the ALD subcycle number of Li, the higher degree of the splitting of the double feature due to the crystal field splitting indicates a probable more distorted local structure in the thin films. To summarize, developing SSE by ALD is indispensable to building reliable high-energy-density batteries. Fundamental studies of the ALD materials are crucial to revealing the growth mechanisms and the correlations between electronic structures and electrochemical properties, shedding lights on future designs of SSEs by ALD.

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3:15pm **AA1-TuA-8 Highly Stable WS_2 Thin Film Anode Grown by Plasma-enhanced Atomic Layer Deposition (PEA LD) for Na-ion Battery***, **Dip Nandi**,* Yeungnam University, Republic of Korea*; S Yeo,* Yonsei University, Republic of Korea*; M Ansari,* Yeungnam University, Republic of Korea*; H Kim,* Yonsei University, Republic of Korea*; T Song, S Kim,* Yeungnam University, Republic of Korea

Plasma-enhanced atomic layer deposited (PEALD) tungsten sulfide (WS_2) thin film was used as an anode in sodium-ion battery (NIB) without any carbon and binder. Thin films of WS_2 were directly grown using an alternate exposure of $W(CO)_6$ and H_2S plasma at a relatively low temperature of 350 ^{o}C using shower-head type ALD reactor without any post sulfurization process. The stoichiometric presence of W and S in the as-deposited films was observed from Rutherford backscattering spectroscopy (RBS) analysis. The films were crystalline in nature with (002) orientation as revealed by the transmission electron microscopy (TEM) analysis. For NIB application, the WS_2thinfilms were directly grown on stainless steel (SS) current collector and used as an electrode without any further modification. Coin cells were then fabricated and tested in a half-cell configuration against Na. The electrochemical reactions during cathodic as well as anodic sweep were studied using cyclic voltammetry (CV) measurements. Reversible conversion and intercalation reactions were evident from the CV which was repeatable in nature after 1st cycle. Improved electrochemical reactivity of the ALD grown thin film against Na^+ ion could be observed from this CV measurement. Films with five different thickness using different ALD cycles were used for charge-discharge cyclic measurements. Cells with ALD-WS_2 as an anode showed high electrochemical stability up to 200 charge-discharge cycles with more than 95% Coulombic efficiency. Different current rates were also used for cyclic measurements to show the suitability of these ALD grown thin film anodes for a wide range of portable electronic appliances.

4:00pm **AA1-TuA-11 ALD-Tin Oxide as Impermeable Electron Extraction Layers for Temperature Stable Roll-to-Roll-Compatible Perovskite Solar Cells***, **Lukas Hoffmann**,* University of Wuppertal, Germany*; K Brinkmann,* University of Wuppertal*; J Zhao, T Hu,* Nanchang University, China*; D Schlamm, J Malerczyk, T Becker, D Theirich,* University of Wuppertal*; S Olthof, K Meerholz,* University of Cologne*; H Gargouri,* Sentech Instruments, Germany*; B Cheng, Y Chen,* Nanchang University, China*; T Riedl,* University of Wuppertal

Organo-lead halide perovskite-based solar cells (PSCs) reached power conversion efficiencies (PCE) beyond 20% within the past years [1]. Nevertheless, the decomposition of the active material in the presence of water or elevated temperatures and follow-up corrosion of e.g. metal electrodes are showing to be one of the big issues to overcome before commercialization [2].

Here we demonstrate the use of tin oxide (SnO_x) grown by ALD, which is electrically conductivity and shows outstanding permeation barrier properties [3], as electron extraction layer (EEL) and concomitant permeation barrier against moisture and decomposition products of methylammonium lead iodide perovskites, perovskite solar cells with outstanding long-term stability can be achieved [4]. Specifically, the tin oxide layers in this study were fabricated by Tetrakis(dimethylamino)tin and different oxidants (water, ozone, O-plasma) at low temperatures (80°-100°C) in low and atmospheric pressure ALD. Strikingly, the solar cells based on SnO_x remain stable over 4500 hours at elevated temperatures as well as in ambient air, whereas devices based on other EELs, without sealing properties, degrade to roughly 50% of their initial efficiency within 100 h. Moreover, SnO_x enables the design of ITO-free semitransparent electrodes based on ultra-thin metal layers (e.g. SnO_x/Ag/SnO_x)[5]. Based thereon, semi-transparent perovskite solar cells with about 70% average transmittance in the near-infrared region (λ > 800 nm) and an average transmittance of 17% in the visible region (λ = 500-750 nm) have been realized [5]. For SnO_x as EEL, we unravel the critical importance of the of the oxidant used in the growth of the SnO_x, e.g. the use of ozone is essential for optimizing the fill factor of the solar cells by minimizing the potential barrier in the SnO_x-perovskite boundary layer. These results provide a general avenue to design PSCs incorporating indium-free transparent top- and bottom electrodes based on corrosion sensitive metals [6]. Finally, tin oxide growth by spatial ALD at atmospheric pressure is presented and its compatibility to replace its low-pressure analogs is shown. With this findings, an all-step roll-to-roll fabrication of highly stable, indium-free PSCs could be realized.

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4:15pm **AA1-TuA-12 Nano-Structured Ceramic ALD Coatings to Stabilize SiC Against Reaction in High Temperature Steam***, **Amanda Hoskins**, A Coffey, C Musgrave, A Weimer,* University of Colorado - Boulder

Silicon Carbide (SiC) is an ideal material for many high-temperature applications due to its resistance to thermal shock and high thermal conductivity. However, SiC degrades in water-rich environments limiting its applications in extreme oxidative environments such as combustion engines, heat exchangers, and high temperature reactor materials. Current deposition methods for environmental barrier coating (EBCs) such as plasma spraying and aerosol spraying generate micron-scale films with inherent grain boundaries and cracks. Atomic layer deposition (ALD) generates nano-scale films that are dense, crack-free, and chemically bonded to the surface without the use of excess precursor. We have found that the application of mullite nanostructured films grown with ALD significantly improves the oxidation resistance of SiC in extreme environments with a film much thinner than standard applications. In addition to mullite, we have targeted a variety of high temperature coating materials chosen based on thermal properties, structural characteristics, and stability in oxidative environments. We have grown ALD layers of our desired materials on high surface area SiC particles using a fluidized bed particle ALD reactor. Using thermogravimetric analysis, it has been shown that these coatings improve the oxidation resistance of SiC by up to 64% at 1000^{o}C. We have applied density functional theory (DFT) to model the performance of these mullite coatings in an oxidative environment. Computational modeling of oxygen diffusion through mullite and other candidate materials allows identification of promising coatings to further extend the lifetime of SiC. We expect to use this understanding to develop more advanced stabilizing coatings for SiC and the myriad of other applications that require high-temperature oxidation resistant materials.

4:30pm **AA1-TuA-13 Mechanical, Physical, and Electrical Properties of Plasma-Enhanced Atomic Layer Deposition of TiVN***, **Mark Sowa**,* Ultratech*; N Strandwitz, L Ju,* Lehigh University*; A Kozen,* U.S. Naval Research Laboratory*; B Krick,* Lehigh University

Specific ternary transition metal nitrides are known for their excellent mechanical, electrical, and chemical properties. TiVN thin films for hard, wear-resistant coating applications have been deposited by sputtering[1,2] and arc ion plating[3]. Compared to pure TiN and VN, TiVN films of intermediate stoichiometry are reported to be harder (H = 32.1GPa for $Ti_{0.77}V_{0.23}N$ vs H = 20.2GPa for TiN and H = 5.6GPa for VN) and stiffer (E = 410GPa for $Ti_{0.87}V_{0.13}N$ vs E = 395GPa for TiN and 307GPa for VN).[4] Plasma-enhanced atomic layer deposition (PEALD) of TiN has been extensively studied[5,6,7] and PEALD VN has also been reported[8]. We will report on PEALD $Ti_xV_{1-x}N_y$ (x = 0 to 1) films deposited using tetrakis(dimethylamido)titanium and tetrakis(ethylmethylamido)vanadium with N_2 plasma. Stoichiometry has been varied through control of the TiN:VN deposition cycle ratio. Analyses include spectroscopic ellipsometry(thickness and optical properties), four point probe(resistivity), XPS(stoichiometry and impurities), XRD(crystallinity), XRR(density and thickness), and sliding wear testing(tribological properties).

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ALD Applications
Room Plaza E - Session AA2-TuA
ULSI, High-k and III-V I (1:30-3:30 pm)/ULSI, High-k and III-V II (4:00-5:00 pm)

Moderators: Scott Clendenning, Intel Corporation, Elton Graungard, Boise State University, Sven Van Elshocht, IMEC

1:30pm **AA2-TuA-1 ALD as an Enabler of Self-aligned Multiple Patterning Schemes***, **Sven Van Elshocht**, Z Tao, J Everaert, S Demuynck, E Altamirano-Sanchez,* IMEC, Belgium **INVITED**

Dimensional scaling is since many decades one of the main drivers of technological advancement. It is captured in what is often referred to as Moore's law: a doubling of the number of transistors every ~2 years for the same cost. The last couple of years this trend has been slowing down, but is still very much alive.

One of the main issues is the difficulty to keep printing ever smaller features in a well-controlled and reliable matter. While smaller wavelength lithography tools are not yet into mass production, alternative techniques are being used to extend the current 193nm litho capability.

As an alternative to single exposure, multipatterning techniques are employed. One approach is multiple litho-etch (LE), where the litho print is divided into multiple partial prints that together form the targeted image. The pattern can as such be split in for example 2 or 3 prints, i.e. LELE or LELELE. The biggest concern with this method is overlay or the alignment of the different partial prints to each other.

To circumvent the problem of overlay, one has implemented self-aligned multiple patterning (SAMP). The first print forms a pattern on which a conformal spacer is deposited. After removal of the first material, referred to as the core or mandrel, one obtains a pattern with twice the density and where the width of the features is determined by the deposited spacer thickness. This procedure can be multiple times and result in double or quadruple patterning schemes.

In this presentation, we will demonstrate that Atomic Layer Deposition (ALD) is highly suited to fulfill the requirements as spacer deposition technique for SAMP. In addition, we will discuss the requirements of patterning materials in general toward. As a concrete example we will discuss fin patterning for a 7-nm logic technology node using Self Aligned Quadruple Patterning (SAQP).

2:00pm **AA2-TuA-3 Thin Film Dopant Sources Grown by PALD for Shallow Semiconductor Doping***, **Bodo Kalkofen**, M Silinskas,* Otto von Guericke University, Germany*; M Lisker,* IHP GmbH, Leibniz-Institut für Innovative Mikroelektronik*; Y Kim,* Lam Research Corporation

Plasma-assisted atomic layer deposition (PALD) was carried out for growing thin oxide films containing dopants for silicon, germanium, and SiGe. The applicability of these films as dopant sources for shallow doping of those semiconductor materials using various rapid thermal annealing methods, such as RTP, flash lamp and laser annealing, was investigated. Remote conductively coupled plasma and inductively coupled plasma sources were applied for generating oxygen radicals in the PALD processes. Tris(dimethylamido)borane was used as boron containing precursor for p type doping, source layers for n type doping were grown using triethylphosphite and triethylantimony for phosphorus and antimony containing oxides, respectively.

The as-deposited films of boron oxide were highly unstable in ambient air and could be protected by capping with in-situ PALD grown antimony oxide films. Phosphorus containing films were stabilized by incorporating them into a silicon dioxide matrix by carrying out ALD processes with supercycles of phosphorus and silicon precursor reactions with oxygen radicals. Also capping of the phosphorus containing films was applied. Antimony oxide films were stable at ambient air conditions.

Boron and phosphorus doping of Si could be obtained using the respective oxide films as dopant sources. This was confirmed by SIMS and sheet resistance measurements. A phosphorus dopant level >1E20 cm^{-3} in silicon could be formed with ALD doping and short time annealing by laser or flash, while a level of >1E19 cm^{-3} was obtained with RTP (950 °C) annealing. Diffusion of antimony into SiGe and Ge from antimony oxide could be shown. The influence of source layer thickness and different annealing conditions during rapid thermal annealing processes on the doping results was investigated.

2:15pm **AA2-TuA-4 Effective Work-Function of PEALD Metal Nitrides and its Tuning by Co-deposition***, **Ekaterina Zoubenko**, I Krylov, B Pokroy, M Eizenberg,* Technion - Israel Institute of Technology, Israel

The implementation of nitride based metallic compounds (e.g. TiN, WN) as metal gate materials is attractive for complimentary metal-oxide-semiconductor (CMOS) applications. Tuning the effective work-function (EWF) is challenging. The effective work-function of metal nitride has a wide range of values and depends on the dielectric material, the metal microstructure and its chemical composition. Recently, plasma enhanced atomic layer deposition (PEALD) at high vacuum (10^{-6}torr) using amid-based metalorganic precursors has enabled the deposition of low resistivity metal nitrides. The ALD technique, which is based on self-limiting surface reactions, enables the co-deposition of various metals and provides an additional degree of freedom to EWF engineering. However this issue was not investigated systematically in literature.

In the current work, EWF on SiO_2 of pure metal nitrides (TiN, WN, TaN and MoN) is presented. In addition, EWF tuning by metal nitride alloying at various compositions (e.g. TiN+WN) and its evolution with thermal annealing temperature will be discussed. The thickness, microstructure, chemical composition and electrical resistivity of the films were determined by X-ray reflectivity (XRR), X-ray diffraction (XRD) and transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and four-point probe (4PP), respectively. The EWF of metal nitrides on SiO_2, using MOS structure, was studied using capacitance-voltage (CV) measurements and plotting the flat-band voltage (V_{FB}) versus the effective oxide thickness (EOT).

As an example, as deposited TiN films of 30[nm] have poly-crystalline FCC structure, as determined by XRD and TEM. XPS depth profiling indicated carbon and oxygen concentrations of 3at%, which leads to a low value of resistivity of 110 [μΩ·cm]. The EWF of TiN on SiO_2 was determined to be 4.6±0.1 [eV], namely that the position of Fermi level is close to Si midgap. This combined with the low resistivity make TiN a good candidate for CMOS applications. Similar systematic study will be presented for other metal nitrides and their alloys.

2:30pm **AA2-TuA-5 Surface Morphology, Crystallinity and Electrical Properties of Some Rare-earth Oxide ALD Films***, **Satu Ek**, R Ritasalo,* Picosun Oy, Finland*; T Sarnet,* Picosun Oy*; J Kalliomaki,* Picosun Oy, Finland*; E Østreng,* Picosun Oy*; S Vangelista, A Lamperti, S Spiga,* CNR-IMM - MDM Laboratory*; R Piagge, G Ghidini,* STMicroelectronics

Rare-earth oxides (REOs) have interesting optical and electrical properties that make them useful for several applications. Many REOs have high dielectric constant (k), which can easily reach values k > 20. Therefore, they are relevant for the microelectronics industry. At present, there is a growing need for thinner gate dielectrics of current materials, such as SiO_2, which might lead high leakage currents, subsequently leading to increased power dissipation, reliability problems and unaccepted electrical breakdown [1,2]. The implementation of high-k gate dielectrics is one of several strategies developed to allow further miniaturization of microelectronic components. A possible gate dielectric material needs to fulfill certain requirements [1]: (i) k-value high enough to fulfill the roadmap of components scaling, (ii) thermodynamically stable with Si, (iii) kinetically stable, and compatible with processing to 1000°C for few seconds, (iv) act as an insulator, by having band offsets with Si of over 1eV to minimize carrier injection into its bands, (v) form a good electrical interface with Si, and (vi) have few bulk electrically active defects.

In this work, we have succeeded in the deposition of various REOs, such as CeO_2, La_2O_3,Y_2O_3, and Y_2O_3-doped Al_2O_3 ($Y:Al_2O_3$), in a uniform manner on 200mm Si wafers using a Picosun R-200 Advanced atomic layer deposition (ALD) reactor. REO films were deposited using $Ce(thd)_4$, $La(thd)_3$ and $Y(thd)_3$ as metal-containing precursors, and ozone as oxidizer.

The surface morphology, crystallinity and grain size of the deposited layers were studied. Conformality maps, AFM surface morphology and XRD analysis of Y_2O_3 and $Y:Al_2O_3$ films are presented in Fig. 1 as an example. The results show that uniform ALD layers were deposited, i.e. 1.4-2.5% (1σ non-uniformity), with a very smooth surface, with 0.5 nm roughness. Additionally, electrical measurements of the REO films were studied. Fig. 2 shows an example of the effect of Y_2O_3 content in Al_2O_3 on the breakdown field and leakage current. The Y_2O_3 films exhibit a high dielectric breakdown field (>6 MV/cm), a relatively high k value (~11), and a low-leakage current density (<10^{-8} A/cm^2at 3 MV/cm) with 100nm layer deposited at 300 °C, well-comparable to the values obtained by de Rouffignac et al. [2]. By adjusting the amount of Y_2O_3 in Al_2O_3 a good compromise can be reached with relatively high growth rate, low leakage and high breakdown together with relatively high k-value.

[1] Robertson, Eur. Phys. J. Appl. Phys. 28 (2004) 265–291.

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Acknowledgements: This work received funding from TEKES and ECSEL-JU R2POWER300.

2:45pm **AA2-TuA-6 Atomic Layer Deposition of High-k Oxide Films from $La(NO_{33}\cdot 6H_2O$ Solution Oxidant***, **In-Sung Park**, S Kim, T Lee, S Seong, Y Jung, J Ahn,* Hanyang University, Republic of Korea*; J An, J Yun,* Korea Research Institute of Standard and Science (KRISS), Korea

High-k films have been widely applied on the gate dielectric, capacitor dielectric, insulator in resistive memory, and even optical layer. ALD is a leading method in the formation of ultrathin layer of nm scale and the uniform/conformal coating on the complex substrate structure. In the fabrication of binary metal oxide films, the complete cycle of ALD typically consists of four steps: (1) pulsing with metal precursor; (2) purging with inert gas; (3) pulsing with oxidant; and (4) purging with inert gas.

In the ALD of metal oxide, the choice of both metal precursor and oxidant is very important for a successful ALD process. Various oxidants have been reported such as H_2O, O_3, and plasma-O_2 for the fabrication of metal oxide films. The oxidant can change the characteristics of the deposited oxide films such as crystalline structure, growth rate, and electrical properties. In this work, the high-k metal oxide films of ZrO_2 and HfO_2 were synthesized by using atomic layer deposition method with $La(NO_3)_3\cdot 6H_2O$ solution as oxygen source. The high-k oxide films formed with $La(NO_3)_3\cdot 6H_2O$ have been investigated by comparing the films formed with H_2O oxidant on the material and electrical properties.

Several findings are highlighted by the alternative introduction of $La(NO_3)_3\cdot 6H_2O$ solution to H_2O.

La elements in the deposited high-k films are not detected using the X-ray photoelectron spectroscopy, meaning La plays like a catalyst during ALD process.

The introduction of $La(NO_3)_3\cdot 6H_2O$ solution effectively altered the crystalline structure, grain size, and surface roughness of the grown high-k films. For example [1], the crystalline structure of the ZrO_2 film changed from a mixture of tetragonal and monoclinic phases to monoclinic phase. The average grain size is doubled from 140 nm to 200-280 nm by using $La(NO_3)_3\cdot 6H_2O$ solution, and the resulting film surface became rougher.

However, the concentration of $La(NO_3)_3\cdot 6H_2O$ solution had little influence on the above crystalline properties.. The average grain sizes of the ZrO_2 films prepared from $La(NO_3)_3\cdot 6H_2O$ solution at concentrations of 10, 20, 30, and 40% were 280, 256, 208, and 200 nm, respectively.

Considering the relation between optical bandgap energy and crystalline properties of high-k films, the controlled properties of crystalline films using $La(NO_3)_3\cdot 6H_2O$ solution contribute to the optical and electrical devices.

[1] N. K. Oh et al., Applied Surface Science 394, 231 (2017).

3:00pm **AA2-TuA-7 Great Enhancement of Dielectric Constant via High Temperature Annealing ALD Bi-layered Oxides***, **Keng-Yung Lin**, L Young, C Cheng, Y Lin, H Wan,* National Taiwan University, Republic of China*; R Cai, S Lo,* Industrial Technology Research Institute, Republic of China*; M Hong,* National Taiwan University, Republic of China*; J Kwo,* National Tsing Hua University, Republic of China

To push the high-speed, low-power device performances beyond Si-based MOSFETs, incorporating high-mobility GaAs as the channel material onto Si wafers is a promising way. Moreover, by utilizing high dielectric constant (k) oxides as the gate stacks, enhanced drain current is expected by capacitance effective thickness (CET) scaling, without the severe gate leakage caused by tunneling. Thus, enhancement of the dielectric constant in the high-k/GaAs system is vitally important. In this work, we have *in-situ* deposited atomic-layer-deposited (ALD) Y_2O_3(2.3nm)/Al_2O_3(5.0nm) and HfO_2(1nm)/HfAlO(9nm) bilayers respectively on freshly grown molecular beam epitaxy GaAs(001), followed by *ex-situ* post-deposition rapid thermal annealing and top/back gate electrodes formation. The dielectric constants of the gate stacks and the high-k/GaAs interfaces are characterized by conventional frequency-dependent capacitance-voltage (C-V) measurements. The k value of the Y_2O_3/Al_2O_3 bilayer increased from 11.1 to 15.6, a 40% enhancement, for the 900°C-annealed sample, compared to that of the as-deposited one. Note that the thicknesses of the oxide films have been verified by scanning transmission electron microscopy (STEM). The interfacial electrical characteristics between Y_2O_3/Al_2O_3 and GaAs also significantly improved by having smaller frequency dispersion in accumulation/depletion region as shown in Fig.1. We have also discovered a dielectric constant enhancement for HfO_2/HfAlO on GaAs. We have used an initial HfO_2 layer to prevent direct inter-mixing between Al_2O_3 and GaAs, which was known to degrade the CV characteristics during high temperature annealing. After annealing over 850°C in helium ambience, the dielectric constant increased from 17.6 to 22, a 25% enhancement, as shown in Fig.2. In addition, the frequency dispersion at accumulation region was reduced from 18.3% to 10.7%, indicating a lower interfacial trap densities (D_{it}) and high thermal stability at the HfO_2/GaAs(001) interface. In summary, we have greatly increased dielectric constant of ALD oxides in Y_2O_3/Al_2O_3 and HfO_2/HfAlO bilayers by mixing them via a thermal approach. Note that no new phases formed, as were studied using high-resolution synchrotron radiation X-ray diffraction and STEM (Fig.3). The high temperature annealed high-k/GaAs(001) interfaces are significantly improved, showing excellent thermal stability. The method for the formation of high quality mixed high-k materials could be generic for other ALD bi-layered oxides for future applications.

[†] K. Y. Lin and L. B. Young have made equal contributions to this work.

* M. Hong and J. Kwo are the corresponding authors.

3:15pm **AA2-TuA-8 Atomic Layer Deposition of Novel Interface Layers on III-V Channel Devices***, F Tang, **Xiaoqiang Jiang**,* ASM*; Q Xie,* ASM, Belgium*; M Givens,* ASM*; J Maes,* ASM, Belgium*; S Sioncke, I Tsvetan, L Nyns, D Lin, N Collaert,* IMEC, Belgium

III-V compound semiconductors are considered promising transistor channel materials to enable further scaling beyond Si technology due to their high bulk electron mobility values. However, unlike Si, III-V materials have poor quality oxides, and high-k dielectric deposited directly on the III-V surface is problematic due to high density of interface states (D_{it}) and oxide traps. A surface treatment is typically required to passivate the semiconductor surface to minimize the interface states. In addition, a deposited interface layer (IL) is required for the integration with high-k dielectrics to reduce the impact of oxide traps while maintaining a low D_{it}. Although extensive study has been done on searching appropriate IL, commonly investigated high-k metal oxides appear limited in ability to meet the performance requirements for a robust III-V channel transistor.

In this work, a thermal ALD process of a novel material is demonstrated for application as IL in III-V channel devices. The IL material is deposited using a commercially available, hot walled cross flow reactor (ASM Pulsar 3000®). Saturated thickness is demonstrated over a wide range of pulse times in Fig. 1(a) and (b), indicative of operation in the ALD regime. The growth per cycle of is 0.23Å shown in Fig. 1(c). The $In_{0.53}Ga_{0.47}As$ MOSCAPs demonstrate superior D_{it} values $<1x10^{12}$ $cm^{-2}eV^{-1}$, low accumulation dispersion (<1%), and hysteresis (<30 mV) values, extracted from CV characteristic as shown in Fig 1(d). The device performance matches previously published benchmark device metrics for InGaAs channel devices [1]. By employing this novel IL, high performance InGaAs nanowire MOSFETs built on 300 mm silicon wafers is also demonstrated with transconductance reaching 2200 [2].

To further improve the hysteresis or reliability of device, a secondary lanthanum silicate ($La_xSi_{1-x}O$) IL is introduced prior to the deposition of HfO_2 high-k. This lanthanum silicate is deposited by a H_2O-based ALD processes. An ALD master cycle includes a lanthanum oxide sub cycle and silicon oxide sub cycle, shown in Fig. 2(a). Fig. 2(b) shows the growth per master cycle and [Si] content extracted from RI values of bulk films. By using novel IL/lanthanum silicate IL/HfO_2 gate stack, the InGaAs MOSFET demonstrates an excellent electron mobility with a reduced oxide traps meeting the reliability target for 10 years operation [3].

In a summary, we developed novel ALD films for IL application, yielding excellent electrical properties on III-V devices.

[1] M. Radosavljevic et al., IEDM Tech. Dig., 765 (2011)

[2] N. Waldron et al. IEDM Tech. Dig., pp 31.1 (2015)

[3] S. Sioncke et al. submitted to VLSI (2017)

4:00pm **AA2-TuA-11 ZrO_2 as a High-k Gate Dielectric for Enhancement-mode AlGaN/GaN MOS HEMTs***, **Charles R. Eddy, Jr.**, V Wheeler,* U.S. Naval Research Laboratory*; D Shahin,* University of Maryland*; T Anderson, M Tadjer, A Koehler, K Hobart,* U.S. Naval Research Laboratory*; A Christou,* University of Maryland*; F Kub,* U.S. Naval Research Laboratory

Advanced applications of AlGaN/GaN high-electron-mobility transistors (HEMTs) in high-power RF and power switching are driving the need for an insulated gate technology. We present here basic and early applied studies of the use of zirconium oxide (ZrO_2) as a high-k, high breakdown gate dielectric for reduced gate leakage and a fully-recessed barrier structure for enhancement-mode operation of AlGaN/GaN HEMTs. We include the study of GaN surface preparations for dielectric deposition, surface/interface characterization and device operation wherein a world record threshold voltage of +3.99V is achieved.

An optimum GaN surface preparation involving a piranha etch followed by a thermal oxidation of the surface has previously been shown [1] to result in smooth, clean GaN surfaces that exhibit the best electrical performance when ALD high-k dielectrics are deposited thereon. This same preparation is applied to ALD ZrO_2 dielectrics. ZrO_2 films were deposited by atomic layer deposition (ALD) using two different metal precursors [zirconium (IV) tert-butoxide (ZTB) and tetrakis(dimethylamido)zirconium(IV) (TDMAZ)] and water. For the former we also assessed both water and ozone as the oxygen precursor. ZrO_2 films grown by ALD with ZTB were found to be slightly oxygen rich whether ozone or water were used as the oxygen source. However, films grown with ZTB and ozone did have carbon contamination. Films grown with TDMAZ and water were found to be stoichiometric and free of carbon.

Films grown with ZTB and water on optimally prepared surfaces again shown the best electrical performance for the dielectric-semiconductor interface in terms of smoothness, low leakage in forward and reverse bias ($< 10^{-5}$ A cm^{-2}) and low hysteresis. Unlike in previous studies with ALD deposited Al_2O_3 and HfO_2, where total trapped charge was in the mid-10^{11} to low 10^{12} cm^{-2} range, ZrO_2 films show considerably higher trapped charge densities in the high 10^{12} to mid-10^{13} cm^{-2} range. The nature of this charge is uncertain at this time but believed to be due to excess oxygen in ZTB deposited films and is directly responsible for a 1.5 – 2 V positive shift in threshold voltage.

[1] C.R. English, et al., J. Vac. Sci. & Technol. B 32,03D106 (1-17) (2014).

4:15pm **AA2-TuA-12 Investigation of High-quality Silicon Nitride (SiN_x) Thin Film Grown by Low-temperature Hollow Cathode Plasma-Enhanced ALD as a Gate Dielectric for AlGaN/GaN MIS-HEMTs***, **Xin Meng**, Y Byun, J Lee, H Kim, J Lee, A Lucero, L Cheng, J Kim,* University of Texas at Dallas

AlGaN/GaN metal-insulator-semiconductor high electron mobility transistors (AlGaN/GaN MIS-HEMTs) have been studied for power device applications. To mitigate current collapse and address the instability in threshold voltage (V_{th}), silicon nitride (SiN_x) has been widely investigated as a gate dielectric and passivation layer. This attributes to the low density of SiN_x/III-N interface states, achieved by passivating the defects related with nitrogen-vacancy and suppressing the formation of interface traps related with the Ga-O bonds. Recently, AlGaN/GaN MIS-HEMTs using a PEALD SiN_x gate dielectric have shown improved device performance [1]. Nevertheless, the film properties of the low-temperature SiN_x employed in these studies (SiH_4/N_2 plasma: low refractive index 1.7-1.85 and low density ~2.5 g/cm^3) cannot compete with those of the high-quality films grown by a high-temperature CVD process (e.g. MOCVD or LPCVD).

In this work, we report AlGaN/GaN MIS-HEMTs using high-quality PEALD SiN_x as the gate dielectric. SiN_x was deposited at a calibrated wafer temperature of 310 °C (16 nm,1500 cycles, set temp. 400 °C) in a home-made ALD system equipped with a Meaglow™ hollow cathode plasma source (Figure 1). Tris(dimethylamino)silane (TDMAS or 3DMAS) and N_2 plasma were used. High-quality SiN_x films were obtained (e.g., high refractive index 2.0, high mass density 2.9 g/cm^3, very low wet etch rate 0.8 nm/min in 100:1 dilute HF, dielectric constant ~7, and high breakdown electric field 11 MV/cm). *Ex-situ* XPS analysis showed a low oxygen content (2 at. %) and a negligible carbon content (<1 at. %) in the bulk film. Growth per cycle (GPC) was approximately 0.11 Å/cycle. The AlGaN/GaN MIS-HEMTs (L_{SG}=4.5 µm, L_G=5 µm, L_{GD}=6.5 µm, V_{DS}=10 V) showed a maximum drain current ~550 mA/mm, a high on/off ratio 10^9, a large gate bias swing, and a steep subthreshold swing of 72 mV/dec. Furthermore, negligible V_{th} shift and a small hysteresis (~ 100 mV) were observed between forward and reverse sweep under a large gate bias ($V_{G,\ max}$= 10 V), as shown in Figure 2. The excellent stability of V_{th} indicated fewer interface/border traps near the dielectric/III-N interface. The capacitance-voltage characteristics also showed a negligible hysteresis (Figure 3) and small frequency dispersion. A detailed comparison with Schottky barrier HEMTs and thermal ALD Al_2O_3 MIS-HEMTs will be presented. Our work has demonstrated that PEALD is a suitable technique to grow high-quality SiN_x film for AlGaN/GaN MIS-HEMTs applications.

[1]. X. Meng et al., "Atomic Layer Deposition of Silicon Nitride Thin Films: A Review of Recent Progress, Challenges, and Outlooks," Materials, 9 (12), 1007 (2016)

4:30pm **AA2-TuA-13 Atomic Layer Annealing for Atomic Layer Epitaxy of AlN Ultrathin Films at a Low Growth Temperature***, M Chen, **Wei-Hao Lee**, H Shih, W Kao, Y Chuang,* National Taiwan University, Taiwan*; R Lin,* Chang Gung University, Taiwan*; H Lin,* National Taiwan University, Taiwan*; M Shiojiri,* Kyoto Institute of Technology, Japan

Atomic layer deposition (ALD) is an attractive technique for preparing high-quality nanoscale thin films, and has been widely exploited in a great variety of nanoscale applications including solar cells, memories, and transistors. However, the as-deposited thin films prepared by ALD are generally of amorphous-like structure due to the requirement of a low deposition temperature to keep the self-limiting chemical reactions in ALD. As compared with amorphous films, crystalline films or even single-crystalline epitaxial layers are more favored because of the significantly improved optical and electrical properties. Therefore, it is highly demanded to improve the crystallization of the ALD-deposited thin films. In this work, a novel concept and approach termed as “atomic layer annealing” (ALA) was proposed in the ALD process to realize the low-temperature atomic layer epitaxy, i.e., to achieve high-quality epitaxial growth of AlN at a low deposition temperature of 300°C on sapphire substrate. Rather than a high growth temperature which is needed in conventional epitaxial growth techniques, a layer-by-layer, in-situ Ar plasma treatment was introduced into each ALD cycle to realize the ALA effect. The Ar plasma treatment during each ALD cycle provides sufficient crystallization energy to the surface of thin films from the incident radicals or ions, leading to the dramatic transformation of the AlN ultrathin film from the amorphous phase to a single-crystalline epitaxial layer. The X-ray diffraction and high-resolution transmission electron microscopy clearly indicates a high-quality single-crystal AlN epilayer with only a few tens of nanometer in thickness. In addition, the two-dimensional electron gas (2DEG) characteristic of the AlN/GaN heterojunction was also observed by the ALA treatment on the AlN layer. The result demonstrates great potential for further extension of the ALD tools from the conventional deposition of amorphous thin films to high-quality epitaxial growth at a low temperature, which can be utilized in a variety of fields and applications in the near future.

ALD for Manufacturing
Room Plaza F - Session AM+EM-TuA

ALD for Manufacturing (1:30-3:30 pm)/MLD II (4:00-5:00 pm)

Moderators: Maarit Karppinen, Aalto University, Paul Ma, Applied Materials, Inc., Mike McSwiney, Intel, USA, Sean Smith, Sandia National Laboratories

1:30pm **AM+EM-TuA-1 Large Area Spatial Atmospheric ALD***, **Corné Frijters**, F van den Bruele, F Grob, A Illiberi, P Poodt,* TNO/Holst Center, Netherlands

Atmospheric spatial ALD (sALD) is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. First industrial applications of spatial ALD include passivation of c-Si solar cells and roll-to-roll manufacturing of flexible barrier foils. An emerging application for Spatial ALD are flat panel (OLED) displays. We have developed spatial ALD processes for making high mobility oxide semiconductors for the TFT backplane as well as thin-film encapsulation for the OLED front plane.

As today’s displays are fabricated using glass panels in the order of several square meters, a remaining challenge is the development of large-area sALD deposition technology that is able to combine high throughput with uniform performance across large areas.

As an intermediate step between the lab and the display fab, we have installed a large area sALD sheet-to-sheet tool which can handle up to 400x325 mm^2 sized substrates able to deposit uniform films across a deposition width of 300 mm. This large area sALD tool is comprised of an RTP oven to quickly heat up the substrate and an ALD reactor with a maximum deposition temperature of 350 °C. The whole system is operated under an inert N_2 atmosphere. The substrate is transported into the tool by an automatic conveyor system to the ALD reactor and placed on a substrate carrier which is operated by an air bearing to allow for fast and uniform motion underneath the injector head where the deposition takes place.

We will present the initial results achieved with this tool where layer thickness non-uniformities of <1% have been achieved for AlOx layers deposited at 125 °C and a substrate speed up to 21 m/min, equivalent to 30 ms exposure times as well as excellent compositional uniformities for binary oxides. Furthermore we will demonstrate excellent multilayer thin-film encapsulation results on polymer foil-on-carrier by the large area sheet-to-sheet tool.

1:45pm **AM+EM-TuA-2 Low Resistivity Titanium Nitride ALD: Low Temperature Enabled by the Use of Ultra-High Purity Hydrazine***, **Daniel Alvarez**, J Spiegelman, K Andachi, R Holmes,* RASIRC*; A Kummel, S Wolf, M Kavrik,* UCSD*; M Raynor, H Shimizu,* Matheson Tri-Gas

Introduction

Next generation channel materials (SiGe, Ge and InGaAs) place very difficult thermal constraints (<400°C) on metal nitride deposition methods. New low temperature methods are needed for ALD of TiN_x metal gate electrodes. Previous studies have shown viable reactivity for hydrazine but have been limited by hydrazine purity, specifically water contamination [1-3]. This has been attributed to the low purity of commercially available 'Anhydrous' Hydrazine, which has water concentration ranging from 0.2-2.0%. Also, high concentrations of oxygen found in the resulting Metal-Nitride films range from 4-15% for SiN_x and TiN_x.

We have previously reported the safe delivery of gaseous hydrazine from a solvent-based formulation and membrane delivery system. [4] Here we present our studies on water measurement and removal, as well as hydrazine-based low temperature TiN_x ALD to obtain films with low resistivity.

Hydrazine Measurement and Purification

New purification methods have led to water contamination levels of <50 parts-per-million (ppm) in the hydrazine source formulation as measured by Karl-Fischer and GC-MS methods. Gas phase moisture measurements by FT-IR have been developed to a lower detection limit of 0.83ppm. The gas phase output of the ultra-dry material has been measured to below this detection limit (Figure 1). This compares to 31ppm for a standard commercially available material.

TiN_x Film Deposition and Characterization

Atomic layer deposition of near stoichiometric TiN_x was achieved on an SiON substrate by sequential pulsing of $TiCl_4$ and N_2H_4 precursors at a substrate temperatures of 275°C-350°C, where growth rate is approximately 0.5A per cycle. Films have been characterized by XPS (Figure 2), AFM, KPFM, STM and Four-point sheet resistance measurements. A TiN_x film with near stoichiometric ratio of Ti/N and the absence of added oxygen was achieved. Most significant is an initial measured Resistivity of $R_{average}$ =130 ohm, R_{sheet} = 50 ohm. Additional optimization of these initial results will be presented.

References

[1] S. Wolf, M. Edmonds, T. Kent, D. Alvarez, R. Droopad, A.C. Kummel, AVS (2015) EM+NS+PS-MoA7.

[2] K. Bernal-Ramos, T. Chen, R. Kanjolia, Y. J. Chabal, AVS ALD (2014).

[3] B. Burton, S. Kang, S. Rhee, S. George, J. Electrochem. Soc. 155(7) (2008) D508-D516.

[4] D. Alvarez Jr, J. Spiegelman, E. Heinlein, R. Holmes, C. Ramos, M. Leo, S. Webb, ECS Trans. 72(4), (2016), 243-248.

2:00pm **AM+EM-TuA-3 Modeling Ampoule Performance for Low Vapor Pressure Precursor Delivery***, **James Maslar**, W Kimes, B Sperling,* National Institute of Standards and Technology*; W Kimmerle, K Kimmerle,* NSI

Low vapor pressure organometallic compounds are widely utilized as precursors for ALD processes. Such precursors are often delivered using an inert carrier gas that is passed through either a bubbler (an ampoule with a dip tube) or a vapor draw ampoule (no dip tube: the gas in and gas out ports open directly into the ampoule headspace), depending on the precursor properties and process requirements. However, it can be difficult to predict how much precursor will be delivered for a given carrier gas flow rate, or even the relationship between precursor and carrier gas flow rate. A number of factors may contribute to this difficulty, including a pressure drop between the ampoule and the pressure control location, sublimative/evaporative cooling of the precursor (i.e., cooling reduces the precursor vapor pressure and hence the amount of material entrained in the carrier gas), incomplete saturation of the carrier gas (i.e., the precursor sublimation rate is too low to permit saturation of the carrier gas for a particular residence time in the ampoule), or slow mass transport processes in the ampoule. Furthermore, the relative importance of the factors depends on the precursor, ampoule design, and process conditions. The goal of this work is to develop analytical and numerical models that can be utilized to characterize ampoule performance, including establishing the precursor and carrier gas flow rate relationship. Models for both bubblers and vapor draw ampoules were developed. A variety of low vapor pressure precursors, e.g., CCTBA and PDMAT, and precursor simulants, e.g., hexadecane, were employed in this investigation. The focus of this investigation was on commercial 1.5 L-volume ampoules (with a maximum fill of 1.2 L). All ampoule models were experimentally validated using data that was obtained with custom-designed optical mass flow meters located downstream of the ampoule. For selected ampoules, resistance temperature detector arrays were employed in order to characterize the liquid temperature distribution in the ampoule and level sensors were employed to confirm liquid level in the ampoule. It is expected that the development of such models can facilitate both process optimization and development of improved ampoule designs.

2:15pm **AM+EM-TuA-4 An innovative chamber designed for ALD, PECVD and FAST® SiO_2 processes: towards high throughput and conformal deposition at low temperature***, **Laetitia Bonnet**, F Piallat, J Vitiello,* KOBUS, France

Since transistors are employed into integrated circuits, miniaturization of the components is the driver of their evolutions. 3D packaging is already used to stack and interconnect the components thanks to vertical vias driving through the silicon substrate. To prevent important energy loss by leakage, a liner is used in these vias, thanks to its great electrical properties silicon oxide is the most used dielectric material. However, SiO_2 deposition in Through Silicon Via is currently facing a challenge: a thick and conformal layer is needed, with a deposition temperature as low as possible for integration in thermally sensitive devices.

The use of a high power plasma, in the plasma-enhanced CVD method (PECVD), allows to achieve suitable electrical properties, while decreasing the substrate temperature down to temperatures as low as 350°C[1]. Nevertheless, with sensitive substrates the plasma power generated is high enough to damage the devices. In an ALD mode, with or without plasma assistance, the substrate temperature can be down to room temperature when a catalyst is added to the deposition cycle[2]. However, the low deposition rate, characteristic of ALD, is not compatible with the production demands, where thick layers (> 100 nm) are used.

In this context and to merge CVD and ALD advantages, the Fast Atomic Sequential Technique (F.A.S.T.®) was developed. Dedicated hardware solutions were found to allow a complete separation of the reactant and precursor until the substrate[3]. FAST tool can be used in continuous mode, in pulse-purge mode or in pulse only mode (fig.1). Similar approaches were presented in the past and referred to “purge-less ALD” or “pulsed-CVD”, the novelty resides here in the possibility to process all three techniques: CVD (fig.1a), ALD (fig.1b) and FAST (fig.1c) in the same chamber. Moreover, the process window is now extended with a new parameter: the pulse position; i.e. pulses can overlap for a CVD-like process or be well separated for ALD-like process.

For this study, the well known silicon precursor TetraEthyl OrthoSilicate (TEOS) was employed in all three deposition modes. A comparison of the growth rate (fig.2), conformality (fig.3) and films properties of the SiO_2 deposited by ALD, PECVD and FAST in the same reactor and with similar process conditions will be discussed. For example, SiO_2 deposited by FAST mode shows a growth rate 10 times faster than in ALD mode while the conformality reaches at least 70% for vias with aspect ratios up to 8:1 (compared to only 30% obtained in CVD). Additionally, optical and electrical properties were investigated and will be presented, as optical index, breakdown voltage and leakage current.

2:30pm **AM+EM-TuA-5 Growth Rates During Silicon Spatial Electron-Enhanced Atomic Layer Deposition: Role of Dangling Bond Lifetime***, **Andrew Cavanagh**, S George,* University of Colorado

Electron enhancement can dramatically reduce the temperatures required for ALD. Electrons can desorb surface species, such as hydrogen, by electron stimulated desorption (ESD) and create “dangling bonds”. These dangling bonds can then facilitate precursor adsorption leading to low temperature thin film growth. However, other residual species can also consume the dangling bonds and reduce the dangling bond lifetime. Film growth rates may then be reduced after longer times between the generation of the dangling bonds and their consumption by precursor adsorption.

Silicon films were grown using spatial electron-enhanced ALD (SEE-ALD). There was linear motion of the 6” wafer back and forth between the electron source and the disilane (Si_2H_6) precursors (see supplemental Figure S1). A DC glow discharge plasma was employed as the electron source. Si SEE-ALD growth rates were measured versus the electron dose time and the time between the electron dose and the subsequent Si_2H_6 exposure. In one experiment, Si thicknesses were measured versus position on the 6” wafer after 200 SEE-ALD cycles using two different wafer velocities under the electron source (see supplemental Figure S2).

Spectroscopic ellipsometry measurements revealed that the Si growth rate increased with electron dose time. The Si growth rate also decreased versus time between the electron dose and the subsequent Si_2H_6 exposure. A model was developed to explain the Si growth rates based on number of dangling bonds formed during the electron dose time, t_1, and the dangling bond loss during the time, t_2, between the electron dose and the subsequent Si_2H_6 exposure. The surface coverage of dangling bonds from hydrogen ESD is $\Theta = 1-\exp[-t_1\Phi\sigma]$, where Φ is the electron flux and σ is the hydrogen desorption cross-section. The dangling bond coverage is proportional to $\exp[-t_2/\tau]$ where τ is the dangling bond lifetime.

A dangling bond lifetime of $\tau = 113$ s and hydrogen desorption cross-section of $\sigma = 8 \times 10^{-20}$ cm^2 were determined by fitting the model to the growth rates versus t_1 and t_2. The results indicate that a higher wafer speed to lower t_2 is needed to minimize the effect of the dangling bond lifetime. This higher wafer speed will not produce a lower growth rate if the electron flux is also higher. We are currently working to increase the electron flux by using a hollow cathode plasma electron source.

2:45pm **AM+EM-TuA-6 Spatial Atomic Layer Deposition of Gate Encapsulation Silicon Nitride for Self-Aligned Contact Enablement***, **Jiehui Shu**, S Mehta, J Chang, X Qiu, J Liu,* GLOBALFOUNDRIES U.S. Inc.

Aggressive gate pitch scaling and shrinking contact CDs beyond 14nm node require precise control of contact to gate overlay to avoid S/D contact to gate shorts [1]. Therefore, Self-Aligned Contact (SAC) process is widely used for 14nm node and beyond for gate to contact overlay margin improvement. This is achieved by recessing the gate (W) and work function (TiN) metals post W CMP selective to oxide, and filling the space above W with a robust dielectric capping material. The dielectric fill is polished to be coplanar with oxide. The contact plugs are then opened by high selective SiO2 etch to Si3N4. Enough Si3N4 thickness is needed to prevent gate to contact shorts due to Si3N4 erosion during contacts open etch [2]. The key requirements for such a gate capping application are, a) defect free fill, b) adhesion to the gate metal and low-k spacer, c) low deposition temp (< 500C) with reduced in-film hydrogen for gate Vt stability, d) compatibility with downstream wet and dry etch processes e) selectivity in contact etch (selective in oxide dry etch process) and f) low leakage and high Vbd (>6MVcm). In this paper, we present the results of low temperature spatial atomic layer deposition (ALD) gate encapsulation Si3N4 process for 7nm self-aligned contact enablement. Blanket Si3N4 film properties at different process temperatures were characterized, such as etch selectivity, wet etch rate, growth rate, uniformity, etc. In-film Hydrogen content is associated with various film properties such as etch selectivity, wet etch rate. The lower the hydrogen content in Si3N4 film, higher its etch selectivity and lower the wet etch rate. HFS and FTIR are used for hydrogen content analysis in this work. By changing different precursor exposure sequence in spatial ALD process, we are able to modulate the hydrogen content in Si3N4 film. I-V curves and Vbd were obtained using MOS structures.

[1] S. Demuynck et al., IITC 2014

[2] C. Auth et al., VLSI2012

3:00pm **AM+EM-TuA-7 Fast Atomic Layer Deposition Process for Thin-Film Encapsulation of Organic Light-Emitting Diodes**, ***Tony Maindron**, C Lopez, S Meunier Della-Gatta, M Tournaire, B Caulfield, M Gontier,* CEA-Leti, France; *J Kools, L Baril,* Encapsulix, France

Thin-film encapsulation Organic Light-Emitting Diodes (OLED) consists in the addition of vacuum deposited thin mineral barrier like oxides, nitrides or oxi-nitrides layers directly onto the organic pixel. The main challenge today is to achieve high encapsulation levels with WVTR ~ 10^{-6} g/m²/day. The ALD technology is well-suited to reach that goal because the technology allows the deposition of defect-free oxide barrier films. The main limitation of the ALD technology is the stability of the oxide barriers, mainly aluminum oxide, to humid atmospheres. Due to its composition, as AlxOy:H, resulting from the low temperature deposition used to deposit onto the fragile OLED circuits (< 100 °C), an additional passivation is mandatory in order to protect the aluminum oxide from water condensation onto its surface. Different works have illustrated the benefits of depositing an additional ALD layer [i], or using metalcone solutions [ii] or PVD-deposited passivating SiO layers [iii]. In each case, the stability of the aluminum oxide is improved because the sensitive film is not exposed directly to moisture condensation. Another limitation with ALD technology is the low deposition rate of the materials. Former applications of ALD were dedicated to the microelectronics world, where very thin layers of oxides (< 5 nm) were deposited as gate insulating materials. For encapsulation purposes, thicker films (typ. > 30 nm) are mandatory, leading to very high deposition times in standard reactors at low temperatures (typ. 30 s/cycle with 1 Å/cycle leads to ~ 2.5 h processing time).

The CEA-Leti has acquired in 2016 an Infinity 200 ALD system from the company Encapsulix SAS. The reactor is a parallel precursor wave architecture [iv] which allows to deposit thin film barriers at high speed (1.5 s/cycle), at temperatures below 100 °C. In the framework of our OLED developments for microdisplay applications, we have qualified the Infinity 200 reactor for OLED circuits. The materials that have been deposited were Al_2O_3 and TiO_2. In this work a systematic study of the material deposition parameters onto 8'' Si wafers and film characteristics will be presented. Performances of these materials deposited onto OLED as thin-film barriers will also be evaluated, for single Al_2O_3 and TiO_2 layers as well as bilayers Al_2O_3/TiO_2.

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[i] A. A. Dameron et al. J. Phys. Chem. C 112 (2008) 4573-4580

[ii] P. Minwoo et al. Thin Solid Films 546 (2013) 153-156

[iii] T. Maindron et al. J. Vac. Sci. Technol. A 34 (2016) 031513

[iv] J. C. S. Kools, US patent 8,721,835 (2014)

3:15pm **AM+EM-TuA-8 Flexible Functional Devices at Mass Production Level with the FLEx R2R sALD Platform**, ***Diederick Spee**, W Boonen, E Clerkx, D Borsa,* Meyer Burger B.V., Netherlands

Atomic layer deposition has been around for quite some time. Only recently however, the link to mass production has been made, with the introduction of spatial atomic layer deposition (sALD), which allows for deposition rates in a range similar to established coating techniques like plasma enhanced chemical vapor deposition.

Simultaneously, flexible devices have gained increased popularity due to a huge diversity of applications. For such devices and their market introduction, sALD offers a unique opportunity: it combines high quality materials, from protective to functional coatings or active layers, with competitive costs and high throughput. At Meyer Burger (Netherlands) B.V. we have paved the road to sALD mass production of flexible devices with the introduction of the FLEx R2R sALD platform.

Our equipment is designed as a fully modular platform, allowing for integration of a sALD coating step with pre-and-post sALD steps (eg. surface treatment and activation, planarization and protective layers) for the production of high quality flexible functional foils. The design of the R2R platform, which is the result of dedicated gas flow modeling and web transport simulations, allows for a significant throughput of over 40 m^2/hour of 20 nm AlO_x coating on foil and already takes into account the scalability to larger web widths (currently 600 mm). Extensive process testing proves that layer growth corresponds to pure ALD both in terms of growth per cycle and saturation curves, even at such a high throughput. Furthermore, layer thickness uniformity is excellent: over a width of 500 mm, deviations are less than 1%. A 20 nm AlO_x moisture barrier deposited on 125 micron PET foil, without any additional surface treatment, has a water vapour transmission rate (WVTR) of 10^{-5}g/m^2/day at 20°C and 50% relative humidity, proving its high quality.

A detailed introduction of the R2R platform and the performance of our functional foils as well as a brief discussion on the scalability will be presented.

4:00pm **AM+EM-TuA-11 All-Organic Spatial MLD: Troubleshooting Deposition onto Porous Substrates**, ***Daniel Higgs**,* ALD NanoSolutions, Inc.; *Y Wang,* GE; *E Chan,* National Institute of Standards and Technology; *H Wang,* GE; *C Stafford,* National Institute of Standards and Technology; *S George,* University of Colorado - Boulder

Thin film polymers are used in many applications including sacrificial layers, passive and active biosurfaces, separation membranes, lubrication and friction modification, and sensors. Several of these applications require thin membranes on porous mechanical supports. As these membranes become thinner, polymer deposition techniques are being pushed to their limits. Current state of the art techniques for producing thin film membranes, such as interfacial polymerization, can produce films down to ~50-100nm, but new techniques are required for thinner membranes. MLD can produce polymer thin films at thickness <50nm, but gas-phase deposition of these thin MLD films onto porous supports is very challenging as unwanted coating occurs inside the pores. This talk will describe the various attempts to produce a uniform, thin MLD film on a porous support.

This work was part of a program funded under the DOE Innovative Manufacturing Initiative, to explore scale-up methods for producing model polyamide membranes for reverse osmosis water purification. As part of this project, we have developed a new spatial molecular layer deposition (MLD) reactor that is capable of sequentially depositing reactive monomers in the vapor phase on flexible substrates at speeds of up to 3 m/s. In this talk, we will describe the challenges and approaches for creating these thin film polymers. We will then compare the MLD films with solution-phase films. We will look at swelling behavior, internal structure, functional group density, and transport. We will also examine the various strategies employed to produce a thin MLD film on porous substrates. This understanding will enable companies to develop and manufacture next generation, energy-efficient membrane materials.

4:15pm **AM+EM-TuA-12 Graphene Oxide Functionalization by Molecular Layer Deposition**, ***Mercedes Vila Juarez**,* Coating Technologies S.L., Spain; *A Jaggernauth, M Neto,* CICECO, University of Aveiro; *M Hortiguela, G Gonçalves, M Singh,* TEMA-NRD, University of Aveiro, Portugal; *F Oliveira, R Silva,* CICECO, University of Aveiro

The functionalization of graphene oxide (GO) with organic molecules is one of the investigated routes for increasing the interface compatibility of GO, thereby enabling its use in a variety of applications such as biomedical platforms, composite filler in conductive polymers or in energy storage solutions. Wet chemistry processes are commonly used to achieve this polymer functionalization of GO, but they have limitations of high heterogeneity, time consumption, and difficult purification processes implying a significant loss of material.

Two approaches for dry functionalization of the nano-GO surface are therefore proposed, utilizing an atomic layer deposition (ALD) reactor: (i) vaporization− condensation of polyethylene glycol amine (PEG-NH_2) and (ii) molecular layer deposition (MLD) of a polymer hybrid from trimethylaluminum (TMA) and ethylene glycol (EG).

The dry functionalization of GO−COOH was successfully accomplished by the MLD growth of a hybrid polymer using TMA and EG precursors. 100 °C is sufficient for this deposition with at least 20 TMA-EG cycles showing a change in the surface of GO and depositing a minimum thickness of 5.0 nm. FTIR confirmed the presence of −Al− O−, −C−H−, and −C−O− bonds being formed on GO- TMA-EG. In addition, XPS highlighted the existence of native oxide Al and the increasing thickness of the hybrid polymer layer with number of cycles, confirming bond formation between EG and −Al−. The resulting hybrid polymer also resulted in an increase in the thermal stability of GO−COOH with an increasing number of cycles, according to TGA data.

The route for dry functionalization of GO−COOH with PEG-NH_2, via pulsed depositions in an ALD reactor, proved to be more challenging. FTIR demonstrated a changing GO surface with increasing number of cycles, with the main result being the presence of amide and −N−H− bonds, suggesting the reaction between −COOH functional groups of GO and −NH-terminating groups of PEG-NH_2. A temperature of 130 °C resulted in pegylated GO within a relatively short time of about 5 h, although control over the formation of double reactions will have to be investigated if the resulting nanoparticles are to be further activated.

4:30pm **AM+EM-TuA-13 Contrast Enhancement of Biological Nanoporous Materials with Zinc Oxide Infiltration for Electron and X-ray Nanoscale Microscopy***, **Leonidas Ocola,*** Argonne National Laboratory*; V Sampathkumar,* University of Chicago*; N Kasthuri, R Winarski,* Argonne National Laboratory

Most biological materials have problems with charging when imaging with electrons and low contrast when imaging with hard X-rays. Standard protocols for sample preparation include coating techniques, using sputtering of a conductive metal such as gold, platinum, or gold/palladium alloy, or non-coating perfusion techniques using glutaraldehyde, tannic acid and osmium tetroxide.

In this paper we describe the use of infiltrated ZnO as a means to address both charge dissipation in electron microscopy and contrast enhancement for X-ray microscopy. With ZnO infiltration it is feasible to coat a 2 – 3 nm thick conductive metal oxide film throughout a porous biological sample, and image both the surface and the interior of a sample without any further sample recoating. ZnO is a conductive oxide and the precursors required for its synthesis (water and diethylzinc) easily penetrate nanoporous materials that exhibit water intake. The samples imaged by electron microscopy were a canine tooth from a dog, and brain tissue that was fixated and supercritically dried ahead of time. Both samples were pre-treated in a vacuum oven, initially at room temperature, ramped to 95 ^{o}C, and then baked at 95 ^{o}C for several hours. The temperature of the vacuum pre-treatment matches that of the infiltrated ZnO process used in our Arradiance Gemstar ALD tool. Both tooth and brain tissue samples were inspected by optical microscopy before and after the vacuum oven pre-treatment to determine if the samples were compatible with the infiltration process. Given that no sample changes were observable, we proceeded with running an infiltration ZnO process of 18 cycles of [H_2O:DEZ], which would be the equivalent of a 2-3 nm coating on a flat surface. No further processing was needed for both electron and X-ray microscopy imaging. We show that high resolution X-ray tomography can be performed on biological systems using Zn K edge (1s) absorption to enhance internal structures, and obtained the first nanoscale 10 KeV X-ray absorption images of the interior regions of a tooth.

- Use of the Center for Nanoscale Materials and the Advanced Photon Source, both Office of Science user facilities, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. Additional funding by IARPA, (ARIADNE) under Contract D16P00002

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