Sunday Afternoon, July 16, 2017

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 $Si-CH_3$ 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 $Si-CH_3$ 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 $Si-CH_3$ 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 $Si-CH_3$ 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 $Si-CH_3$ 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 $(O)_2$-Si-$(NMe_2)_2$ 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$(O)_2$-Si-$(NMe_2)_2$. 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).

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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.

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.

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

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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.

[1] Y. H. Chang, et al, Microelectronic Eng. **88**, 440 (2011).

[2] Y. H. Lin, et al, Materials **8**, 7084 (2015).

[3] C. P. Cheng, et al, Appl. Surf. Sci. **393**, 294-298 (2017)

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.

[1] Kormondy, K.J., *et al.* Nanotechnology 28 (2017) 075706 doi: 10.1088/1361-6528/aa53c2

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.

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.

[1] Berdova et al. Acta Materialia 66, 370 (2014)

[2] Berdova et al. Journal of Vacuum Science and Technology A 33, 01A106 (2015)

[3] Ylivaara et al. Thin Solid Films 552, 124 (2014)

[4] Lyytinen et al. Wear 342-343, 270 (2015)

[5] Kilpi et al. Journal of Vacuum Science and Technology A 34, 01A124 (2016)

[6] Ylivaara et al. Journal of Vacuum Science and Technology A 35, 01B105 (2017)

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, $In--_2O_3$, 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.

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[2] T.D. Lin, *et. al.*, *Appl. Phys. Lett.***100**, 172110 (2012).

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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 ^{o}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 ^{o}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.

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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 devices$^{1)}$. 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 processes$^{2)}$.

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.

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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.

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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.

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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.

This research was supported by ARPA-E through the SWITCHES program.

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°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 °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°C. When the reactor temperature increase to larger than 250°C, 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

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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 resulting 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*, **Kristian Knemeyer**, V Strempel, P Ingale, R Naumann d'Alnoncourt,* BasCat, UniCat BASF JointLab, Technische Universität Berlin, Germany*; A Thomas, M Driess,* Institut für Chemie, Technische Universität Berlin, Germany*; F Rosowski,* BASF SE, Germany

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*, **Tian-Bao Zhang**, J Xu, Y Wang, L Chen, Q Sun, H Zhu, S Ding, D Zhang,* Fudan University, China

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*, **Philipp Brüner**,* ION-TOF GmbH, Germany*; T Grehl,* ION-TOF GmbH*; R ter Veen,* Tascon GmbH, Germany*; M Fartmann,* Tascon GmbH*; T Blomberg, M Tuominen,* ASM, Finland

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.

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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.

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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, *Christian Hill, S Rahimi, D Brown, A Dzarasova,* Quantemol Ltd, UK; *J Hamilton, K Wren-Little,* University College London, UK; *S Mohr,* Quantemol Ltd, UK; *J Tennyson,* University College London, UK

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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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, *Mira Park, J Kwon, Y Lee, J Park, S Kim, H Ahn, S Yun, J Park,* Hansol Chemical, Republic of Korea

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, *J Łobaza, M Kot,* Brandenburg University of Technology Cottbus-Senftenberg, Germany; *F Naumann,* ***Hassan Gargouri,*** Sentech Instruments, Germany; *K Henkel, D Schmeißer,* Brandenburg University of Technology Cottbus-Senftenberg, Germany

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 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.

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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 °C and completely volatilizes at 140 °C 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 ($<10^{-3}$ Ω 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 ($\rho < 10^{-4}$ Ωcm) 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 μΩcm 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 $(9\pm0.2)\cdot10^{-1}$ Ωcm whereas a decrease of the film resistivity by more than two orders of magnitude to $(3.3\pm0.1)\cdot10^{-3}$ Ωcm 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 $(4.1\pm0.1)\cdot10^{-4}$ Ωcm 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.

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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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