Monday Morning, July 30, 2018

Plenary Session
Room Grand Hall A - Session PS1-MoM

ALD Plenary Session

Moderators: Jin-Seong Park, Hanyang University, Han-Jin Lim, Samsung Electronics, Hyun-Chul Choi, LG Display

8:30am **PS1-MoM-2 Evolution of Memory Technology and Future Scaling Challenges***, Seung Ho Pyi,* SK Hynix, South Korea **INVITED**

In the ever-changing world of ICT, due to the emergence of Internet of Things (IoT), big data, and the cloud, demand for Memory IC is growing exponentially. Therefore, in this session, development trend of two memory Ics, DRAM and NAND Flash memory, and the role of key technologies, ALD in particular, in the development of Memory IC will be discussed. In both DRAM and 3D NAND, technologies have continued to drive innovation. In DRAM, a remarkale progress has been made in technologies related to spacer pattering, cell transistor, and high-k cell capacitor. In 3D NAND, to overcome the challenge of stacking multiple layers, technologies related to etching holes/lines with high aspect ratio, increasing channel mobility, and achieving device reliability were developed. In developing such innovative technologies, ALD processes for SiO_2, high-k dielectric and metal made a considerable contribution, and the need for ALD processes for various materials is expected to rise. Currently, continued scaling is expected to be increasingly difficult as manufacturing processes become more difficult and manufacturing cost increases due to the rising number of process steps and decreasing equipment throughput. Therefore, considering such scaling challenges, productivity enhancement should be incorporated into developing current and future ALD technologies.

9:30am **PS1-MoM-6 A Road to Damascus, ALD Technology***, Jinsung Chun,* Wonik IPS, Republic of Korea **INVITED**

Semiconductor industry is at the point of the big conversion. It is crucial to find the right path to reply to market needs. Through a series of analysis on the evolution of patterning technology, new materials, and device structure it was reached to the conclusion that future scaling will be driven by the transition to complete vertical structure in conjunction with the geometrical scaling and new materials. Moreover, ALD technology will play a key role in the 3D structure fabrication and new material process. Wonik IPS, one of the frontiers of ALD equipment, has been focusing on ALD technology development since the successful introduction of high-volume-manufacturing ALD system in 1996. We are ready to provide various ALD solutions and try to do the right thing right for new ALD era.

Plenary Session
Room Grand Hall A - Session PS2-MoM

ALE Plenary Session

Moderators: Geun Young Yeom, Sungkyunkwan University, Korea, Ankur Agarwal, KLA-Tencor

10:45am **PS2-MoM-11 Learning from ALE Mechanism Researches and Considerations for Future Demands***, Masayuki Tomoyasu,* Samsung Electronics Co., Inc. **INVITED**

There are continuously many challenges in dry etching process for Semiconductor device manufacturing such as High Aspect Ratio Structure Etching, Precise control of depth loading, Highly selective etching, LER/LWR minimization, Etching damage reduction, and so forth. ALE(Atomic Layer Etching) technology can relax a part of burden of the challenges.

Furthermore, mechanism analysis of ALE will also help understanding conventional etching processes. That will enlighten or emphasis necessity of even deeper understanding of plasma physics/chemistry and demand more precise design and control of plasma etching equipment as well. Several expectations from industry to academy to address future demands will be discussed.

ALD Applications
Room 116-118 - Session AA1-MoA

Memory Device & Materials I

Moderators: Steven M. George, University of Colorado at Boulder, Christophe Vallee, LTM - MINATEC - CEA/LETI, France

1:30pm **AA1-MoA-1 Atomic Layer Deposition as a Key Technology for Manufacturing 3D V-NAND Flash Memory***, **Jaeyoung Ahn**,* Samsung Electronics, South Korea*; J Jee, P Nam, B Kim, J Yang, D Kim, H Choi,* Samsung Electronics **INVITED**

The introduction of 3D V-NAND enables the high capacity, fast processing storage solutions to implement the emerging technologies such as cloud computing, big data, internet of things and mobile devices. Since the memory array size of 3D V-NAND has been increasing over the years, it is inevitable to stack more cells vertically, which builds stumbling blocks in deposition of various materials on the cell structures. ALD has been successfully adopted in the process integration as the key technology for CTF dielectric layers, gap-filling dielectrics, and word-line metals due to its superior step coverage and uniformity. However, since the surface area of the structures is expanding rapidly, it is very challenging to maintain good step coverage and uniformity for future generations of 3D V-NAND. During the process flow of 64-stacked V-NAND Flash devices, patterned wafers frequently show over 30 times larger surface area compared to blanket wafers and very high vertical and lateral aspect ratios. Consequently, we need advanced technologies employing new hardware platforms, more efficient precursors, and optimized process conditions. At the same time, we also need selection criteria to identify the right solution for each ALD step in the process flow. For these purposes, we propose numerical simulation of mass transfer using computational fluid dynamics approach as a tool for developing advanced ALD hardware and materials as well as optimizing existing processes.

2:00pm **AA1-MoA-3 Room-temperature Resonant Tunneling by Band-offset Engineering of Nanolaminated High-k Oxides Deposited by Atomic-layer Deposition***, **Hector Uribe-Vargas**, J Molina-Reyes,* National Institute of Astrophysics, Optics and Electronics

Due to the continuous scaling of advanced CMOS technology, high-k oxides became very important due to a low leakage current and high dielectric constant (k>8). These oxides are often deposited by atomic-layer deposition (ALD), which has a high reproducibility, conformality, outstanding control (to atomic level) on the thickness and stoichiometry and a low deposition temperature (T≤250°C). Because of these characteristics and taking advantage of the band offsets between silicon and different high-k oxides, a double barrier resonant tunneling (RT) diode could be formed. In this regard, RT devices have shown promise at achieving very high speed in wide-band devices and circuits that are beyond conventional transistor technology, nevertheless, this effect is often seen in highly complex crystalline heterostructures (usually fabricated by epitaxial growth), and only at very low temperatures (T<77 K).

In this work, 2 sets of 2 samples of metal-insulator-insulator-insulator-semiconductor (MIIIS) devices were fabricated. The first set of 2 samples is a stack of ultra-thin Al_2O_3, HfO_2 and Al_2O_3 (AHA stack with 2nm, 1nm and 2nm in thickness) deposited by ALD. After gate deposition, one sample was subjected to post metallization annealing (PMA) at 450°C for 30 minutes in an H_2/N_2 ambient. For the second set of 2 samples, a stack of ultra-thin Al_2O_3, TiO_2 and Al_2O_3 (ATA stack with 2nm, 1nm and 2nm in thickness) was also deposited by ALD and similarly, one sample was also subjected to PMA. These devices were designed in order to promote quantum-well (QW) formation at the intermediate oxide layer, having QW of 1.3 eV and 3.1 eV respectively and promoting RT conduction during substrate injection of electrons.

After Ig-Vg measurements at room temperature, experimental proof of RT via negative differential resistance (NDR) was demonstrated in MIIIS structures fabricated using ALD, putting this deposition technique as a powerful tool to obtain this phenomena after atomic control of all high-k layers. Due to the difference in the band gaps of different high-k materials, it is possible to promote quantization of discrete energy levels in intermediate layers of stacked ultra-thin high-k oxides. For the case of the AHA ($Al_2O_3/HfO_2/Al_2O_3$) structure, 3 distinctive NDR zones are observed after substrate injection. For the case of the ATA ($Al_2O_3/TiO_2/Al_2O_3$) structure, even though no evident NDR is present, RT is a strong possibility due to a high non-linearity (~20), high asymmetry and low dynamic resistance. When PMA is performed, no sign of RT/NDR is obtained in both AHA and ATA structures, due to an inner diffusion of atomic elements within the stacked oxides.

2:15pm **AA1-MoA-4 Atomic Layer Deposition of HfO_2 Thin Films using $Hf(BH_4)_4$ and H_2O***, **Devika Choudhury**, A Mane, R Langesley, M Delferro, J Elam,* Argonne National Laboratory

High dielectric constant (high-k) metal oxides and their silicates have been extensively studied as alternatives to SiO_2 for electronic and optoelectronic applications [1]. Excellent dielectric properties coupled with high thermal stability has made HfO_2 one of the most popular replacements for SiO_2 in CMOS and DRAM devices. HfO_2 thin films have been deposited using various methods including CVD, ALD, sputtering, and sol-gel techniques [2]. However, with the decreasing size of devices and increasing demand for ultrathin conformal films with precise thickness and composition control, ALD has emerged as the preferred method.

ALD of HfO_2 has so far been successfully implemented using different precursors. $HfCl_4$ and HfI_2 are two of the most commonly used Hf sources, which however require high deposition temperatures (>300°C) and generate corrosive byproducts (HCl and HI). Although alternative precursors like metalorganics or amides have also been used, the possibility of carbon contamination has restricted their use in electronic applications [3].

In this work, we demonstrate the relatively low temperature ALD of HfO_2 thin films using a carbon free precursor, tetrakis(tetrahydroborato)hafnium [$Hf(BH_4)_4$], and H_2O. As both precursors have substantial vapor pressure at room temperature, low temperature deposition growth is possible. Self-limiting, linear growth of HfO_2 is obtained at 200°C, and experiments on the feasibility of lower temperatures deposition are underway. The refractive index of the as-grown films measured at 632 nm is found to be 1.91, which indicates the formation of HfO_2. Stronger confirmation for HfO_2 is obtained by elemental analysis using X-ray photoelectron spectroscopy (XPS). The doublet of the Hf 4f orbital electrons obtained at binding energies of 18.4 and 20.1eV can be assigned to the Hf $4_{7/2}$ and Hf $4_{5/2}$ electronic states of Hf in Hf-O bonds respectively. Moreover, the O1s peak obtained observed at 531.9eV also corresponds to formation of Hf-O bonds in the as-deposited film. XRD analysis showed the films deposited at 200°C to be amorphous, but rapid thermal annealing at 750°C for 60s yields crystalline, monoclinic HfO_2 films.

References:

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[2] K. Kukli, M. Ritala, T. Sajavaara, J. Keinonen and M. Leskela; Thin Solid Films 416 (2002) 72–79.

[3] K. Kukli, M. Ritala, J. Sundqvist, J. Aarik, J. Lu, T. Sajavaara, A. Harsta and M. Leskela, Journal of Applied Physics; 92 (2002) 5698-5703.

2:30pm **AA1-MoA-5 TaN Based Multi-Vth Devices for 7nm and Beyond Technology***, **Donghun Kang**, T Abrams, V Chhabra, S Han, H Parvaneh, B Kannan, G Xu, R Lu, M Ozbek, S Krishnamurthy, P Mennell, H Wang, J Liu,* GLOBALFOUNDRIES U.S. Inc.

Multiple Vth (Multi-Vth) have been one of key components in RMG to meet different industry demands. To extend it to future technologies, several issues need to be resolved; lowering nFET Vth, developing etching process and mitigating TaN loading at different macros. In this study, we demonstrated TaN based multiple Vth devices with 12% better Toxgl adopting higher Al contained nFET work function, selective TiN etching and improved TaN micro-loading.

Fig.1 illustrated simplified process flow in RMG area. Etch of TiN/TaN stack were carried out by using different chemistries (Fig2). Chemistry A removes completely both TiN and 99% of TaN, which is good one for none-selective etching. On the other hand, other chemistries show reasonable selectivity with TaN, which could be a potential selective TiN removal process. Among them, chemistry D is chosen for the selective removal, considering RIE effect on TaN etching rate in Fig.3

Micro-loading was evaluated at three locations, flat, short channel and long channel regions. Each location has its own unique physical structure and surrounds, which could influence source population. Fig.4 compares deposited TaN thickness with different TaN deposition conditions. Significant loading (short/long channel thickness, >50%) was observed from control process. To compensate geometry effect, precursor flow, pule and purge time have increased, expecting better delivery to FIN in trench. With this approaches, loading short to long channel dramatically reduces to 15% in Fig. 4.

Fig.5 and Fig 6 summarize key device results. In Fig 5, both high Al conditions can lower nFET Vth than that of baseline process, demonstrating the ability to push nVTh down further. Fig. 6 shows the benefit of Toxgl for different Al content devices. High Al conditions achieves around 12% better Toxgl than control due to high K protection by TaN during patterning process. TaN based multi-Vth has successfully demonstrated with resolving, 1) nFET Vth lowering by higher Al content in NWF, 2) development/optimization of selective and none-selective etch, and 3) improvement in TaN micro-loading associated with physical shapes of macros. Higher Al nWF process is very effective to lower nFET Vth with matching device parameters. Improved source delivery is a key factor to reduce micro-loading up to 15%. Toxgl benefit of 12% has confirmed by better HfOx protection from patterning process.

2:45pm **AA1-MoA-6 Atomic Layer Deposition: A Few Prospective Applications Aiming Mass-production after Current Si-based Semiconductor Process***, **Tae Joo Park**,* Hanyang University, Republic of Korea **INVITED**

ALD (atomic layer deposition) is one of the most advanced thin film coating or deposition technique in the current vacuum science or electronic device fabrication processes. Recently, the matured ALD technique begins to look for new applications with its strong advantages such as the superior step coverage (conformality) on complicated 3D structures and extremely-precise film thickness controllability. Up to now, there have been a few feasible applications of ALD technique aiming at mass production; electrical and chemical passivation of the assorted solar cells and organic/inorganic flat panel displays, of which fabrication process and physics are familiar with those of semiconductor devices.

This presentation starts with the introduction of modified/advanced ALD process for current Si based industry; discrete feeding method (DFM) and electric field-assisted ALD (EA-ALD) technique for efficient metal film growth to achieve ultrathin and continuous thin film. Next, new-type 2-dimensional electron gas (2DEG) field-effect transistor comprised of only two ALD binary oxide films and wafer-scale uniform ALD growth of 2D chalcogenides will be introduced as part of post-CMOS technology. ALD applications for energy system are also briefly discussed such as Li-based composite thin films for secondary batteries and catalytic/protective layer for photoelectrochemical cells. Another important application of ALD technique could be the design of core-shell structured nano/micro particles for multifunctional applications. A specially designed ALD reactor enables the successful fabrication of core-shell structured nano/micro particles irrespective of the chemical reaction conditions (pH, temperature etc). This technique is also applicable to passivation of various quantum dots and microparts.

3:15pm **AA1-MoA-8 Atomic Layer Deposition of NbO_x Films with Tunable Stoichiometry Using Hydrogen Plasma Reduction***, **Alexander Kozen**, T Larrabee, M Twigg, H Cho, S Prokes,* U.S. Naval Research Laboratory

The Niobium oxide system has seen recent interest, particularly due to its potential use as both a non-volatile, in the case of Nb_2O_5, or volatile, in the case of NbO_2, memristor material. Nb_2O_5 is a high k dielectric (k~41) with a high refractive index (n~2.2) and a wide bandgap (3.6 eV), while NbO_2 is a thermochromic material that undergoes a first order crystalline phase transition at a critical temperature (T_c) of 800˚C. Both of these phases, along with their intermediate sub-oxides, can serve as material components of memristors to facilitate low-power neural computing hardware.

Using the same metalorganic precursor, $^tBuN{=}Nb(NEt_2)_3$, we demonstrate deposition of NbOx films containing tunable ratios of Nb^{4+} and Nb^{5+} by incorporating additional H_2 plasma steps into the ALD process to selectively reduce Nb^{5+} atoms to a lower oxidation state. The ability to produce NbOx thin films with specific metal to oxygen ratios is critical to understanding the memristive switching behavior of the NbOx materials system, while use of one chemical precursor to deposit a spectrum of varying material stoichiometry and phase can greatly simplify fabrication and design of neuromorphic circuits.

We will examine the impact of plasma chemistry, number, and duration of both single and multiple H_2 plasma steps in the Nb_2O_5 ALD process on film growth, chemistry, and morphology, and will discuss how these additional steps can be used to reduce the resulting film from pure phase amorphous Nb_2O_5 to a NbO_2-rich amorphous film. Additionally, we elucidate the relationship between overall film stoichiometry and electrical properties, with a focus on memristive switching behavior of these materials.

ALD Applications
Room 116-118 - Session AA2-MoA

Memory Device & Materials II

Moderator: Ji-Hoon Ahn, Korea Maritime and Ocean University

4:00pm **AA2-MoA-11 Effects of Fluorine in ALD W on Dielectric Properties***, **Hyung Chul Kim**, S Lee, H Cho, S Jin,* SK Hynix, Republic of Korea **INVITED**

Recently, it has been recognized that both achieving low resistivity at the gate electrode and suppressing poly-Si gate depletion are key factors for developing deep submicron metal–oxide–semiconductor field effect transistors (MOSFETs). The tungsten (W) metal gate electrode is a good candidate for solving simultaneously the problems mentioned above. However, it has been known that pure tungsten gate is unstable when it is deposited on the SiO_2 and that fluorine (F) diffusion into SiO_2 during the deposition and annealing process causes many undesirable effects . Little is known about the effect of the impurity present in the metal on the properties of the oxide . In this paper, we show the changes of the capacitance equivalent thickness (CET) by the F in atomic layer deposition (ALD) W on the oxide in the W / barrier metal / oxide / Si metal oxide semiconductor capacitor (MOSCAP) . The CET increased by 4 ~ 5 Å in ALD W compared to PVD W, and the change of oxide by F was confirmed. As the barrier metal thickness increases, the CET decreases. Also when the RTA proceeds after the W deposition, the CET increases . F reacts with SiO_2 in Al_2O_3/SiO_2 stack to increase CET. The SiO_2 reacted with F makes a defect source inside SiO_2, leading to the increase of the frequency dispersion and the leakage current. The results of this study can be usefully used as the basic data for metal development and oxide reliability in DRAM and Flash devices.

4:30pm **AA2-MoA-13 Low Temperature Atomic Layer Deposition of Ru for Copper Metallization***, A Mane, **Yan Zhang**,* Argonne National Laboratory*; A Kumar, J Allgair,* BRIDG*; J Hryn, J Elam,* Argonne National Laboratory

Contact metallization in large-scale semiconductor devices such as logic, memory, MEMS, and SoC using 2.5D and 3D interposers requires a high quality and conductivity metal barrier/seed layer for subsequent metal electroplating. Ruthenium metal has a bulk resistivity of 7.1 μΩ cm, a work function of 4.7 eV, and a low solid solubility with strong adhesion to Cu, making Ru an attractive contact metal barrier metal or seed layer for Cu electroplating. There have been numerous reports of Ru ALD using a variety of precursors. However, technical challenges remain including the need for high growth temperature, very long nucleation delay, and the use of plasma that limits Ru conformality in high aspect ratio features. Currently, there is a strong desire and demand for 3D-devices where high quality, uniform, and conformal metal growth on high aspect ratio structures for ultra largescale integration (ULSI) process flow including for 2.5D and 3D interposer substrates creation.

Here we have developed a low temperature (200^{o}C) Ru atomic layer deposition process using $Ru(DMBD)(CO)_3$ and O_2 precursors. To enhance the Ru nucleation and growth, especially at low temperature, we performed low temperature Pt ALD using $Pt(MeCp)Me_3$ and O_2 to deposit a sub-monolayer Pt seed layer that greatly accelerates the subsequent Ru nucleation. High quality Ru films were deposited on a variety of substrates including Si(100), fused silica, Al_2O_3 and TiN. The ALD Ru films were uniform across the 18” deposition zone of our tubular ALD reactor. Thin Ru films were characterized by XPS, SEM, TEM, four point IV measurements, XRD and XRF. We have also performed Cu electroplating on the ALD Ru layers and found that the Ru films deposited using the Pt seed layer exhibited excellent Cu electroplating. Here we will present details of the Ru ALD and Cu electroplating.

4:45pm **AA2-MoA-14 Conformal Growth of Low-resistivity Ru by Oxygen-free Thermal Atomic Layer Deposition***, **Guo Liu**, J Woodruff, D Moser,* EMD Performance Materials

Ru has been widely investigated as an alternative material for metallization applications in semiconductor devices to replace the Co adhesion layer or as a filling material to replace Cu without the need for a barrier layer. ALD deposition of low resistivity Ru is typically achieved using O_2 as the co-reactant or by plasma enhanced ALD using N_2/H_2 or NH_3 in an oxygen-free process. However, for certain semiconductor applications, the strongly oxidizing O_2 co-reactant can cause damages to other layers especially metal films, while a PEALD process has limited capability for step coverage. An oxygen-free thermal ALD process for Ru would be desirable. Current oxygen-free thermal ALD processes for Ru generally suffer from low growth rate and high resistivity problems due to high impurity levels and/or low film density because of limited reactivity of common O_2-free co-reactants with most Ru precursors below their thermal decomposition temperatures.

In this work, we present an oxygen-free thermal ALD process that can deposit low-resistivity Ru thin films down to a few nm thick with a short nucleation delay of less than 30 cycles as shown in Fig. 1. The methods include ALD growth of a ruthenium film at lower temperatures using an oxygen-free co-reactant and post-deposition annealing at higher temperatures. The deposition step was carried out in the temperature range of 150-250°C using a thermally stable high vapor pressure precursor, dimethylbutadiene ruthenium tricarbonyl or (DMBD)$Ru(CO)_3$. The annealing step was performed at 300°C or higher in an oxygen-free atmosphere. The deposition and annealing conditions have been optimized for high growth rate and low resistivity. Under optimal deposition and annealing conditions, low resistivity of about 20 μΩ-cm comparable with the O_2 ALD process of the same precursor (1) has been achieved. Conformal step coverage has also been demonstrated as shown in Fig. 2.

References:

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5:00pm **AA2-MoA-15 Plasma Enhanced Atomic Layer Deposition of Nickel and Nickel-based Alloy Thin Films for High-quality and Thermally Stable Nickel Silicide***, S Kim, **Shunichi Nabeya,*** Yeungnam University, Republic of Korea

Metal silicides are silicon compounds with metals, and they have low resistivity like metals as well as good compatibility with Si and metals. So, metal silicides, which have been formed by metal deposition on Si followed by post silicidation annealing, have been used for contact materials in Si devices. $TiSi_2$ have been widely used for contacts, however NiSi and $CoSi_2$ are applied to sub-100 nm Si devices since $TiSi_2$ shows narrow line width effect that is increase in $TiSi_2$ resistivity with decreasing linewidth. In order to overcome limitations of current Si devices in downscaling, emerging nanodevices have been intensively studied, and their structures are moved from 2D planar to 3D structure. So, the schemes of contact fabrication used for 2D devices are changed in 3D emerging nanodevices, and conformality of metal thin films is the most important requirement to be achieved. In view of this, ALD is a good alternative to conventional PVD techniques for fabricating the silicide contact. Earlier, there are few reports on nickel deposition by thermal ALD process due to the lack of suitable Ni precursors for it [1, 2]. Though ALD of nickel oxide processes are relatively easy to develop, a rather complex step is needed to obtain nickel silicides from this oxide. In our previous research, we successfully obtained metallic Ni film by using thermal ALD process using a Ni metalorgarnic precursor and H_2 or NH_3 molecules as reactants. One drawback of thermal ALD Ni process is that much amount of impurities of O and C are included in as-deposited film, leading to a relatively high resistivity of ~1700 μΩ-cm and a post annealing process at 480˚C was needed to obtain high-quality Ni film. In order to obtain NiSi with a simpler process, it is necessary to realize a high-purity Ni film by ALD. Generally, plasma enhanced ALD (PEALD) is a better method for obtaining high-quality metal thin films as compared to the thermal ALD. In this study, PEALD Ni processes are developed by using various reactants including N_2, H_2 or NH_3 plasma. The properties of PEALD-Ni films depending on the reactants used are compared using various analysis such as XRD, XPS, 4-point probe, TEM etc. We also evaluate the silicidation behavior of PEALD-Ni films deposited with optimized condition. Finally, Ni-based alloy films where a noble metal is incorporated in them are also prepared using PEALD for improving the thermal stability of the nickel silicide film.

Acknowledgement

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References

[1] J. Chae, H.-S. Park, S.-W. Kang, Electrochem. Solid State Lett. 5 2002 C64-66.

[2] K.-W. Do, C.-M. Yang, I.-S. Kang, et al., Jpn. J. Appl. Phys. 45 2006 2975-2979.

5:15pm **AA2-MoA-16 Ternary Thin Film Alloys of Ti-Si-N as Low Resistance Diffusion Barrier for Memory Applications***, **Somilkumar Rathi,** J Mack, Z Karim, N Mukherjee,* Eugenus, Inc.

The rapid advances in memory technology, coupled with decreasing feature sizes and increasing aspect ratios, have imposed stringent requirements on the physical and electrical properties of metal-to-semiconductor interfaces. This has resulted in several integration and material challenges for low-resistance contacts and diffusion-barrier films. Reactively-sputtered titanium nitride (TiN) is widely used as diffusion-barrier layer due its high thermal and chemical stability, low electrical resistivity, and process maturity. However, the columnar and polycrystalline grain structure provides a pathway for diffusion during higher-temperature anneal steps. This undesirable effect, which leads to device degradation and failure, has led to the search for alternative films. In this work, we report recent advancements on the amorphous ternary alloy films composed of titanium, silicon and nitrogen (TSN), an excellent alternative to TiN films. These TSN films were grown using Atomic Layer Deposition (ALD) technique on the Eugenus 300mm QXP commercial reactor. In order to understand the feasibility and tunability for a variety of applications, the films were grown over a wide temperature window of 400-620°C and using several different chlorine-based Si precursors. Film thickness and silicon content were varied and corresponding electrical characterization was performed. X-ray photoelectron spectroscopy and Rutherford Back Scattering techniques were utilized for compositional analysis. The results indicate that ALD-based TSN films are not only high volume manufacturing compatible, but have excellent mechanical, thermal and electrical properties and are scalable to the next technology nodes.

5:30pm **AA2-MoA-17 Atomic Layer Deposition of Mixed Phase TiN_xC_y using Highly Reactive Substituted Hydrazines and Tetrakis(dimethylamido)Titanium***, **Jaime DuMont,** M Knez,* CIC nanoGUNE, Spain

Tribology, in spite of being one of the most traditional industrial sectors, is in great demand of innovation. At over 6% of the worlds GDP, corrosion and wear represent significant expenses in the global economy and yet they seldom receive the attention they require. The development of protective coatings that can suppress both factors at the same time is therefore of great economic interest. Among the materials which have demonstrated superior hardness, strength and chemical stability are titanium nitride (TiN) and titanium carbide (TiC). The protective capability of these materials is not, however, without limitation. When exposed to high temperature applications or high-speed machining these coatings can become brittle and easily fracture because of poor resistance to high temperature oxidation. Inclusion of carbon atoms in the TiN lattice has been shown to substantially increase the hardness and lower the friction coefficient. These beneficial properties are a result of the TiN_xC_y composition and can be adjusted by controlling the material's C-N ratio to a precise level. When tuned correctly, TiCN films can display anti-wear capabilities and higher hardness that far surpass those of TiN and TiC alone.

Next generation TiN_xC_y coatings will require a deposition strategy that 1) functions at temperatures low enough to keep critical tool dimensions within tolerance 2) circumvents corrosive hydrogen halide by-products 3) maintains a strong chemical binding of the coating to the substrate and 4) can be easily scaled for large-area applications. Atomic layer deposition is a technique primed to meet these requirements. In this work we develop a new low-temperature, halide-free, mixed phase TiN_xC_y thermal atomic layer deposition (ALD) process. We exploit the high reactivity of substituted hydrazines, including tertiary butyl hydrazine (TBH) and monomethylhydrazine (MHH), together with the amide based precursor, TDMATi. These superior precursor combinations circumvent the corrosive hydrogen halide by-products of conventional metal nitride ALD processes, provide the required C and N atoms and further lower the deposition temperature through transamination-like exchange reactions. We will discuss process parameters (substrate temperature and precursor exposure times) as well as ex situ characterization studies (X-ray diffraction (XRD) and reflectivity (XRR) and scanning electron microscopy (SEM)) of the TiN_xC_y materials deposited as well as their effectiveness as next generation protective coatings.

ALD Fundamentals
Room 107-109 - Session AF1-MoA
Precursor and Process I

Moderator: Taek-Mo Chung, Korea Research Institute of Chemical Technology (KRICT)

1:30pm **AF1-MoA-1 Forcing Timescale: Can Monolayer Stability Be Built Into a Precursor?***, **Sean Barry,*** Carleton University, Canada **INVITED**

Presently, there are two processes for depositing gold metal ALD: the Carleton example uses trimethylphosphinegold (III) to allow gold metal to be deposited under 130°C using plasma-assisted ALD using oxygen, while the Helsinki process uses an aminocarbodithiolatedimethylgold (III) and ozone to deposit gold metal at 180°C. Although both processes are viable, a truly thermal deposition process with a robust and easily synthesized precursor has yet to be developed.

We have been studying Au(I) compounds using a variety of ligands to understand how to improve the thermal stability of gold precursors while maintaining a sufficient volatility and reactivity. Here we maintain the phosphine coordinative ligand but alter the covalent ligand to affect its ability to stabilize a gold compound through electron donicity and protect it using steric bulk. Can the judicious application of these principles allow a gold(I) centre enough kinetic stability at the growing surface to permit saturative growth?

This presentation will discuss the effect of ligand modification on volatility, thermal stability, and deposition kinetics. Volatility and thermal stability were measured using thermogravimetric analysis, while deposition kinetics were measured using a quartz crystal microbalance. These trends will be discussed under the theme of precursor modification, and some general strategies for improving precursor characteristics will be considered.

2:00pm **AF1-MoA-3 Comparative Study on New Heteroleptic Zirconium ALD Precursors***, **Sanni Seppälä**, K Mizohata,* University of Helsinki, Finland*; W Noh,* Air Liquide Laboratories Korea*; J Räisänen, M Ritala, M Leskelä,* University of Helsinki, Finland

Heteroleptic approach has gained wide interest in the development of ALD precursors in the recent years. By combining different ligands enhancement in properties, such as thermal stability and growth rate, is pursued compared to homoleptic counterparts. For example, replacing an alkoxide ligand of a homoleptic compound with cyclopentadienyl may enhance the thermal stability of the compound. However, it is not always easy to predict the properties of the heteroleptic compounds and sometimes the result can be a combination of the undesirable properties of the different ligands. Thus it is important to study different heteroleptic compounds to understand the benefits they can offer compared to traditional ALD precursors.

Zirconium oxide is a very interesting material for several applications, the most important at the moment being memory devices in microelectronics. In this work, three heteroleptic zirconium precursors, namely cyclopentadienyl N,N-bis(tertbutyl)ethene-1,2-diaminato isopropylalkoxo zirconium Zr(Cp)(^{t}BuDAD)(O^{i}Pr), methylcyclopentadienyl tris[2-(methylamino)ethyl] aminate zirconium Zr(MeCp)(TMEA) and pentamethylcyclopentadienyl triethoanolaminate zirconium Zr(Me$_5$Cp)(TEA) were evaluated as Zr sources in the atomic layer deposition of ZrO$_2$. Ozone or water was used as the oxygen source. Films were deposited at 200 – 425 °C with an F-120 ALD reactor (ASM Microchemistry). Growth saturation, crystal structures, compositions and electrical characteristics of the films were thoroughly studied. Zr(Cp)(^{t}BuDAD)(O^{i}Pr) and Zr(MeCp)(TMEA) were found to be more reactive than Zr(Me$_5$Cp)(TEA) since they produced uniform films with both tested oxygen sources at all studied temperatures whereas with Zr(Me$_5$Cp)(TEA) films could not be deposited with water below 400 °C. The main crystalline phase of the films was the highest permittivity tetragonal ZrO$_2$. Very low impurity levels were detected in the films deposited with ozone.

The research leading to these results has received funding from the Finnish Centre of Excellence in Atomic Layer Deposition (Academy of Finland).

2:15pm **AF1-MoA-4 A New Class of ALD Precursors for Aluminum Oxide – Potential Alternative to TMA!***, **Lukas Mai**, N Boysen, D Zanders,* Ruhr-University Bochum, Germany*; T de los Arcos,* University of Paderborn*; F Mitschker,* Ruhr-University Bochum, Germany*; G Grundmeier,* University of Paderborn*; P Awakowicz, A Devi,* Ruhr-University Bochum, Germany

Due to its chemical inertness and wear resistance, thin films of Al$_2$O$_3$ are often employed as protective coatings. In particular gas barrier layers (GBLs) of Al$_2$O$_3$ are used in organic light emitting diodes (OLEDs) or on polymers to protect degradable compounds or goods from air. For high quality GBLs, the thin films should be very uniform and conformal over the whole surface especially on demanding geometries. Moreover, the films should be dense and amorphous to avoid diffusion path ways. With atomic layer deposition (ALD) it is possible to fabricate such thin films at low temperatures, as the self-limiting nature of this process leads to highly uniform, conformal and dense films with a precise thickness control. For the ALD of Al$_2$O$_3$, trimethylaluminum ([AlMe$_3$], TMA) is the most commonly used precursor. Despite the inherent advantages of TMA in terms of high volatility and reactivity toward a range of co-reactants at low temperatures, there are certain issues with TMA such as its pyrophoric behavior and not well-defined ALD window. Therefore, we attempted the synthesis of alternative Al precursors.

Here, we present the synthesis of the *3-(dimethylamino)propyl* (DMP) substituted aluminum complexes[AlMe$_2$(DMP)] (**1**, DMAD) and[Al(NR$_2$)$_2$(DMP)] [R = Me (**2**), Et (**3**), ^{i}Pr (**4**)] as an alternative class of precursors for ALD of Al$_2$O$_3$.[1]In these complexes, the DMP ligand stabilizes the Al center atom by a dative bond from the amine to the Al (Fig. 1). This yields thermally stable, non-pyrophoric new complexes, whose thermal properties, in terms of evaporation behavior, can be tuned by systematic variation of the alkyl side chains within the ligands (Fig.1). As compounds **1** and **3** exhibits a high evaporation rate at only 45 and 60°C, new plasma enhanced (PE)ALD processes employing oxygen plasma were developed. The two processes are self-limiting at substrate temperatures between 60°C and 220°C on Si(100) with growth rates of 0.92 Å cycle^{-1} using **3** and 0.60 Å cycle^{-1} employing **1** (Fig. 2). The resulting Al$_2$O$_3$ thin films are conformal, uniform, smooth, dense and of high purity even at low deposition temperatures. For the investigation of the Al$_2$O$_3$ films as GBL, thin films of various thicknesses were deposited on PET substrates at 60°C and the improvement of the gas barrier of the PET by a factor of 90 for a 15 nm thin film using **1** and a factor of 25 for an only 5 nm thin film using **3** was obtained by oxygen transmission rate (OTR) measurements (Fig. 3). The thin film properties are of the same quality as for layers obtained from TMA, rendering our new intramolecular stabilized precursors to be a promising and safe alternative for ALD of Al$_2$O$_3$ coatings.

2:30pm **AF1-MoA-5 Atomic Layer Deposition of Aluminum Metal Using a Thermally Stable Aluminum Hydride Reducing Agent***, **Kyle Blakeney**, C Winter,* Wayne State University

We report the thermal atomic layer deposition (ALD) of highly conductive aluminum metal thin films at temperatures as low as 100°C. The precursors used are AlCl$_3$ and a new aluminum dihydride reducing agent. Self-limiting growth is demonstrated for both precursors with a growth rate of about 3.5 Å/cycle within an ALD window of 120-160°C. Film resistivities were as low as 3.03 µΩ·cm and the films were crystalline by X-ray diffraction. Film composition as determined by X-ray photoelectron spectroscopy showed Al (> 94 at%) with low Cl impurities (<0.5 at%). To our knowledge, this is the first thermal ALD process for aluminum metal films and aluminum has the most negative electrochemical potential ($Al^{3+} \leftrightarrow Al^0 E° = -1.676$ V) of any element deposited by thermal ALD to date. Accordingly, the new aluminum dihydride reducing agent used in this study should enable ALD processes for many challenging elements and materials.

2:45pm **AF1-MoA-6 Low Temperature PE-ALD of Copper Films using Copper Aminoalkoxides Precursors with Hydrogen***, **Akihiro Nishida**, A Sakurai, T Yoshino, M Okabe, M Enzu, A Yamashita,* Adeka Corporation, Japan

Copper is well-known as an interconnect material for semiconductor devices having a high electrical conductivity, high thermal conductivity, and comparatively good electromigration resistance. Physical vapor deposition (PVD) has been used as the most popular method to deposit thin copper seed layers for microelectronic devices. However, it is difficult to deposit a conformal and continuous film on the high aspect ratio substrate. Copper atomic layer deposition (ALD) is required in order to deposit thin copper seed layers which have good coverage, high film continuity, and low resistivity.

In this study, we have carried out the investigation of several types of copper ALD precursors preferred for industrial uses, and found that some copper aminoalkoxides precursors have low melting points. As an example, the melting point of bis(1-ethylmethylamino-2-propoxy)copper (CTA-5) was observed at 38°C by DSC measurement. CTA-5 showed a very clean TG curve without decomposition and residue at 10 Torr. Additionally, we demonstrated PE-ALD of thin copper metal film using CTA-5 and hydrogen as the co-reactant, and succeeded in making shiny metallic copper films at 40°C. The growth rate was at 0.30 Å/cycle and 0.41 Å/cycle on the Si and SiO$_2$ substrates, respectively. Each of resistivity was measured at 3.7 µΩ·cm and 4.1µΩ·cm. It was also found that carbon, nitrogen, and oxygen contamination was not detected in each copper metal film by XPS measurement. Regarding film morphology, we verified that continuous films were deposited by FE-SEM measurement. Therefore, we finally conclude that CTA-5 is better suited for manufacturing copper ALD processes compared to conventional copper ALD precursors.

3:00pm **AF1-MoA-7 Atomic Layer Deposition of Rhenium Selenide Thin Films**, *J Hämäläinen, K Mizohata, K Meinander, M Mattinen, J Räisänen, M Leskelä,* ***Mikko Ritala,*** University of Helsinki, Finland

2D materials research is evolving at a high pace as new layered materials are synthesized and their properties studied towards various applications. A group of these 2D materials that has raised major attention since 2010 is transition metal dichalcogenides (TMDCs). An addition to this 2D materials family is $ReSe_2$ which was fabricated by CVD only very recently [1]. In many respects $ReSe_2$ is not a typical TMDC material though. It has been reported to have distorted 1T´ structure with low symmetry that leads to anisotropic electronic, optical and mechanical properties similar to ReS_2 [2]. $ReSe_2$ monolayers are more weakly coupled than in typical TMDCs, but not so strongly decoupled as in case of ReS_2 because the structural distortions are not as severe [3].

ALD is a very attractive method for making thin films with precise control on film thickness, composition, and structure. We have recently reported ALD of ReS_2 using $ReCl_5$ and H_2S in a wide deposition temperature range up to 500 °C [4]. Here, we introduce deposition of rhenium selenide thin films by ALD using the same Re metal precursor with bis(trimethylsilyl)selenide as a co-reactant. Successful film growth was achieved at deposition temperatures up to 450 °C. The ALD process development and characterization will be discussed.

[1] M. Hafeez, L. Gan, H. Li, Y. Ma, and T. Zhai, *Adv. Mater.* 28 (**2016**) 8296.

[2] M. Hafeez, L. Gan, A. S. Bhatti, T. Zhai, Mater. *Chem. Front.* 1 (**2017**) 1917.

[3] B. Jariwala, D. Voiry, A. Jindal, B. A. Chalke, R. Bapat, A. Thamizhavel, M. Chhowalla, M. Deshmukt, A. Bhattacharya, *Chem. Mater.* 28 (**2016**) 3352.

[4] J. Hämäläinen, M. Mattinen, K. Mizohata, K. Meinander, M. Vehkamäki, J. Räisänen, M. Ritala, and M. Leskelä, *Adv. Mater.* (**2018**) Early View Online. https://doi.org/10.1002/adma.201703622

3:15pm **AF1-MoA-8 Plasma Enhanced Atomic Layer Deposition of Silicon Nitride Films with Inorganic Disilane Precursors**, ***Xiaobing Zhou,*** *B Hwang, X Wang, B Ketola, J Young, C Lee, M Telgenhoff, B Rekken, Y Ahn, W Chung,* Dow Chemicals; *X Meng, Y Byun, J Kim,* University of Texas at Dallas

Di or higher silanes containing one or more than one Si-Si bonds were reported to improve growth-per-cycle (GPC) rates in the atomic layer deposition (ALD) of silicon-based dielectric films. We studied this phenomenon by depositing silicon nitride (SiN) films from two inorganic disilanes without organic functionalities under different plasma enhanced ALD conditions. ALD type of film formation was observed for pentachlorodisilane (PCDS)-ammonia plasma and tris(disilanyl)amine (TDSA)-nitrogen plasma systems at 270 – 360°C. The SiN film properties including refractive indices, compositions and wet etch rates were determined. These results will be discussed in the presentation.

ALD Fundamentals
Room 107-109 - Session AF2-MoA
Mechanism and Surface Science

Moderators: Charles H. Winter, Wayne State University, Sang Woon Lee, Ajou University

4:00pm **AF2-MoA-11 Different Growth Mechanism of SiO_2 Layer on Various High-*k* films by PE-ALD using Tris(dimethylamino)silane and Oxygen Plasma**, ***Toshihide Nabatame,*** *M Inoue,* National Institute for Materials Science, Japan; *M Takahashi, K Ito,* Osaka University, Japan; *N Ikeda, A Ohi,* National Institute for Materials Science, Japan

GaN power devices with metal-oxide-semiconductor (MOS) structure have been widely investigated to suppress the leakage current properties. Various silicate materials such as $HfSiO_x$ and $AlSiO_x$ have been characterized as gate insulator. To fabricate silicate films, a HfO_2/SiO_2 laminate was generally deposited by atomic layer deposition (ALD). The SiO_2 films grown by ALD using Tris(dimethylamino)silane (TDMAS) precursor and ozone oxidant gas had high-quality as gate insulator [1]. However, the growth mechanisms of the SiO_2 film on various High-*k* materials have not been fully understood. In this study, we systematically investigate growth rate of SiO_2 layer on various High-*k* layer by plasma-enhanced ALD (PE-ALD) using TDMAS precursor and oxygen plasma gas, and also discuss about different growth rate.

The SiO_2 films were deposited on SiO_2, HfO_2, Al_2O_3, and TiO_2 films/Si substrates by PE-ALD at 300 degree C. The HfO_2/SiO_2 laminate films were also grown by PE-ALD at 300 degree C with Tetrakis(dimethylamino)hafnium and TDMAS precursors. The various composition ratios (Hf/Si = 3/1, 2/1, 1/1, 1/2, and 1/3) of the HfO_2/SiO_2 laminate films were prepared by changing each number of ALD cycle.

The growth per cycle (GPC) of the HfO_2 and SiO_2 films on SiO_2/Si substrates were found to be 0.083 and 0.038 nm/cycle, respectively, from the relationship between the number of ALD cycles and the film thickness. On the other hand, the experimental data of the HfO_2/SiO_2 laminate thickness as a function of the number of ALD cycle satisfied a linear relationship regardless of Hf/Si composition ratio. The GPC was 0.082 nm/cycle. Considering to the GPC of the HfO_2 (0.083 nm/cycle), the estimated GPC of a SiO_2 layer was 0.081 nm/cycle, which was unexpected, but increased by about 2 times compared to a single SiO_2 film. To recognize the different GPC of the SiO_2 layer between HfO_2/SiO_2 laminate and a single SiO_2 films, the GPCs of the SiO_2 films on SiO_2/Si and HfO_2/Si substrates were examined up to 10 cycles. Noted that the GPC of the SiO_2 films on HfO_2/Si substrate was much higher than that on SiO_2/Si substrate. Furthermore, the Hf content of HfO_2/SiO_2 laminate film with Hf/Si=1/3 shifted to the Hf rich side from the relationship between the designed Hf/Si composition ratio and the estimated Hf/Si ratio of the deposited film using TEM and EDS analysis. These suggest that an initial adsorption of TDMAS precursor on the surface of SiO_2 and HfO_2 films must be different and strongly affects to the GPC.

Reference

[1] L. Han, and Z. Chen, ECS J. of Solid Sate Sci. and Technol., 2 N228 (2013).

4:15pm **AF2-MoA-12 In-situ Surface Science Studies of Atomic Layer Processes of GaN Surfaces in Preparation for Atomic Layer Epitaxial Growth**, ***Samantha Rosenberg,*** U.S. Naval Research Laboratory; *D Pennachio,* UCSB; *M Munger,* SUNY College at Brockport; *C Wagenbach,* Boston University; *V Anderson,* Kennesaw State University; *S Johnson, N Nepal, A Kozen, J Woodward,* U.S. Naval Research Laboratory; *Z Robinson,* SUNY College at Brockport; *J Hite,* U.S. Naval Research Laboratory; *K Ludwig,* Boston University; *C Palmstrøm,* UCSB; *C Eddy, Jr.,* U.S. Naval Research Laboratory

We have previously shown that using our low temperature plasma-assisted atomic layer epitaxy (ALEp) method we can grow AlN and InN for various applications.[1-3] The materials we have grown using our ALEp method have shown good crystalline quality, but suffer from an incorporation of carbon. Theory has led us to believe that the substrate preparation plays a significant role in the remediation of carbon, as that surface becomes the interface for the growth of the III-N film. Therefore, using surface science techniques, we strive to develop not only a fundamental understanding of the ALEp growth process but also atomic layer processes that will result the best cleaning method for a pristine starting surface for ALEp.

Here we employ *in-situ* surface studies of *in-situ* and *ex-situ* GaN substrate preparation and InN ALEp growth to advance fundamental understanding of the ALEp process. We conduct *in-situ* grazing incidence small angle x-ray scattering (GISAXS) experiments at the Cornell High Energy Synchrotron Source utilizing morphological evolution monitoring to investigate the growth surface during sample preparation, a gallium-flash-off atomic layer process (ALP) at varying temperatures, and film deposition. GISAXS information is complemented with *in-vacuo* x-ray photoelectron spectroscopy, reflection high-energy electron diffraction, and *ex-situ* atomic force microscopy studies conducted at the Palmstrøm Lab at UCSB, where we consider different *ex-situ* sample preparation methods in contrast to our standard preparation method as a way to produce the most suitable GaN surface for our ALP/ALEp-based approach. We have been able to determine with GISAXS that ALP-based gallium-flash-off experiments performed at higher temperatures (500°C) produce a smoother starting surface than lower temperatures. Additionally we have determined that we should only perform ~10 cycles instead of 30 as was empirically chosen previously. We have also been able to observe repeating cycles in our ALEp process with GISAXS, leading us to insights on the underlying chemical process of the gallium-flash-off ALP. With the Palmstrøm Lab at UCSB, we have determined with *in-vacuo* XPS and *ex*-situ AFM that a combination of UV/ozone exposure followed by an HF dip produces the cleanest and smoothest GaN surface. Combining these two results, *ex-situ* and *in-situ* cleaning preparation, should lead us to the best GaN starting surface to grow high quality crystalline III-N materials.

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

[2] C. R. Eddy, Jr, et al., J. Vac. Sci. Technol. A 31(5), 058501 (2013)

[3] R. S. Pengelly, et al., IEEE Trans. Microwave Theory Tech. 60, 1764 (2012)

4:30pm **AF2-MoA-13 Surface Chemistry during Atomic Layer Deposition of Zn(O,S)***, **Bonggeun Shong**,* Hongik University, Republic of Korea

Ternary compound zinc oxysulfide (Zn(O,S)) is a semiconductor whose band gap is tunable with the composition. Thin films of Zn(O,S) can be deposited with atomic layer deposition (ALD) using diethylzinc ($Zn(C_2H_5)_2$) and mixed pulses of H_2O and H_2S as O and S sources, with an advantage of tunable O to S atomic ratio. However, it is known that the fraction of S incorporated in the ALD Zn(O,S) thin films is higher than its ratio in the reactant pulses [1]. Recently, the reason for such growth behavior has been suggested as exchange reactions between *ZnOH and H_2S to yield *ZnSH at the surface of the growing film [2]. In this work, the surface chemical reactions involved in ALD of Zn(O,S) is investigated using density functional theory (DFT) calculations. It is observed that while ALD reactions of both ZnO and ZnS would be facile, the reactions involving H_2S are both kinetically and thermodynamically favored over those with H_2O. As a result, surface *ZnOH can be replaced by H_2S, but reaction of *ZnSH with H_2O is less likely. Our results confirm the chemical mechanism governing the composition of ALD Zn(O,S), and suggest factors needs to be considered in ALD of ternary compounds.

[1] Bakke et al., JVSTA 2012

[2] Lancaster et al., JPCC 2017

4:45pm **AF2-MoA-14 Surface Reaction Mechanism of Atomic Layer Deposited Metal on Organic Textiles***, **Jong Seo Park**,* Yonsei University, Republic of Korea*; H Lee,* Incheon National University, Republic of Korea

Electronic textiles (e-textiles) are electrically conductive textiles which are potentially important for future wearable electronic systems. Recently, we reported that atomic layer deposition (ALD) could be a good route to functionalize conventional non-conductive textiles to conductive textiles just by depositing Pt on Cotton without any damage. In this work, we deposited Pt via ALD on various thermally weak textiles, such as Cotton, Silk, Nomex, Nylon, Wool and Kevlar fibers. Pt was successfully deposited on Cotton, Silk, Nomex, Wool, Kevlar fibers except Nylon fibers. We investigated the growth characteristics and surface reactions mechanism of ALD Pt on various textiles by using different techniques, such as X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and density functional theory (DFT) calculation. Pt ALD on the various textiles seems to be hard since it has rare reactive sites of ALD reaction such as surface hydroxyl group. From results of XPS and DFT calculation, it was found that Pt precursor molecules directly react with chemical species of the reactive sites of Cotton and Silk fibers, while Nylon fibers did not react with Pt precursor molecules. The activation energies for the reactions of the Pt precursor with cellulose of Cotton (26.3 kcal/mol for –OH) or Silk fibroin (19.5 kcal/mol for –OH, 26.1 kcal/mol for –NH) are smaller compared to that with Nylon 66 (36.9 kcal/mol). Therefore, the reactivity of Nylon toward adsorption of HDMP is considerably smaller than those of Cotton and Silk. Thus, we found that ALD Pt layer forms with very high durability on surface of Cotton and Silk fibers through organic-inorganic hybridization. We believe that the functionalized flexible textiles which were obtained by Pt ALD are promising candidates for various wearable and smart fabric industries as a new platform for future textile electronics.

5:00pm **AF2-MoA-15 Insight in Surface Dependence and Diffusion-mediated Nucleation Mechanism of Ruthenium Atomic Layer Deposition on Dielectrics***, **Job Soethoudt**,* KU Leuven, Belgium*; Y Tomczak,* IMEC, Belgium*; F Grillo, R Van Ommen,* Delft University of Technology, Netherlands*; E Altamirano Sanchez,* IMEC, Belgium*; A Delabie,* KU Leuven, Belgium

Area -Selective Deposition (ASD) is of interest for a variety of applications including bottom-up patterning for nano-electronic device fabrication, yet its industrial implementation has been limited by unwanted nucleation on the non-growth surface. ASD of Ruthenium is of interest for bottom-up patterning, as a thin Ru hardmask is not attacked by etchants typically used to pattern dielectrics or TiN hardmasks (eg. C_xF_y, NF_3, BCl_3). In order to control and reduce defectivity in Ru ASD, the surface dependence and nucleation mechanisms of Ru Atomic Layer Deposition (ALD) need to be understood.

We have investigated the nucleation mechanism of (ethylbenzyl)(1-ethyl-1,4-cyclohexadienyl)ruthenium (EBECHRu) and O_2 ALD at 325ºC on different dielectric surfaces. The Ru nucleation behaviour is strongly affected by the dielectric surface, and is governed by adsorption, diffusive aggregation and coalescence. Precursor chemisorption proceeds most rapidly on -OH terminated dielectrics, followed by Si-O-Si bridges and finally Si-CH_3 terminated organosilicate glass (Figure 1). On hydrophilic and hydrophobic SiO_2 the average nucleus is significantly larger compared to values predicted from the inherent deposition rate on existing Ru nuclei (0.03nm/cycle), indicating Ru species aggregate through surface diffusion during nucleation resulting in an island growth mode (Figure 2a, b, c). Less reactive surfaces not only result in fewer, larger nuclei because of the reduced adsorption rate on the substrate, but the nucleus size distribution also becomes more polydisperse because surface diffusion promotes aggregation (Figure 2d). The nucleation behaviour on organosilicate glass is explained through a growth model [1, 2] which takes into account the impact of diffusive aggregation on the nucleus size distribution (Figure 3). The experimental results are best described if the Ru precursor adsorption initially occurs only on the organosilicate glass substrate, and the Ru nuclei are active towards precursor chemisorption only after reaching a critical size (~0.85 nm). This result is consistent with the notion that catalytic decomposition of the ligands by oxygen requires a minimum Ru island size. The initial stages of growth are therefore dominated by the diffusive aggregation of Ru nuclei rather than direct Ru growth on the islands. These findings provide new fundamental insight in the nucleation mechanism of Ru ALD. Moreover, the impact of surface diffusion may be relevant for ASD as surface diffusion could mitigate defectivity caused by nucleation on dielectrics.

[1] F. Grillo et al., J. Phys. Chem. Lett. 8, 975-983 (2017).

[2] F. Grillo et al., Catal. Today (2018)

5:15pm **AF2-MoA-16 Surface Oxidation Model in Plasma-enhanced ALD for Silicon Oxide Films Including Various Aminosilane Precursors***, **Kosuke Yamamoto**, A Suzuki, M Kagaya, M Matsukuma, T Moriya,* Tokyo Electron Technology Solutions Ltd., Japan

Plasma-enhanced atomic layer deposition (PEALD) attracts much attention for semiconductor manufacturing processes because it permits both low process temperature and high film uniformity. Deposition of silicon oxide (SiOx) films is one of the most successful applications in PEALD. The conformal, uniform and low-temperature deposition of PEALD-SiOx thus enables self-aligned multiple patterning in high volume manufacturing. Based on this technical and industrial significance, many research groups have already discussed surface reaction mechanisms of PEALD-SiOx deposited by using aminosilanes and O_2 plasma. However, previous researches mainly focused on the adsorption step of the silicon precursors and there are fewer studies published on the oxidation step. In this work, we therefore aim to clarify the surface oxidation mechanism of PEALD-SiOx processes by employing both experimental and computational approaches.

Firstly, we calculated the main chemical species present in an Ar/O_2 plasma by using numerical simulation in order to narrow down the potential reactions between oxidants and surface functional groups. We determined that triplet oxygen atom (^3O) and singlet oxygen molecule ($^1O_2$) are expected to be the main oxidants under our experimental condition. To compare the energy barriers for the specified reactions with ^3O and $^1O_2$, we analyzed oxidation pathways by using density functional theory (DFT) calculations, as shown in Figure 1. No energy barrier was observed in the ^3O oxidation pathway in contrast with $^1O_2$ oxidation, which has an energy barrier of 0.1~0.6 eV. These computational results support the conclusion that surface oxidation is dominated by ^3O; in view of both the generation of oxidizing species and the energy barrier for oxidation. Subsequently, PEALD experiments were systematically examined with various aminosilanes, substrate temperatures (T_{subs}) and oxidation times, as shown in Figure 2. We found that the number of amino ligands (R) on the precursors affected saturation trends with oxidation time. Moreover, a more rapid increase was observed with increasing substrate temperature for SiH_3R precursors compared to the results for precursors which have more amino ligands. We have thus developed a surface oxidation model for explaining these experimental results considering just two reactions: Si-H bond oxidation and Si-R bond oxidation. Even with this simple reaction model, the differences in surface oxidation trends can be explained simply by considering the ratio of surface densities of Si-H and Si-R groups before the oxidation step.

5:30pm **AF2-MoA-17 Thermal and Plasma Enhanced Atomic Layer Deposition of Al_2O_3 and HfO_2 Films Investigated by using in situ Auger Electron Spectroscopy***, **Haiping Zhou**, Y Fu, M Mirza, X Li,* University of Glasgow, UK

Al_2O_3 and HfO_2 are well-established high-k materials to replace SiO_2 in transistor and capacitor applications. To grow high quality atomic layer deposition (ALD) films with high dielectric breakdown electric field and low leakage current, it is important to understand the impact of both plasma enhanced ALD (PEALD) using O_2-plasma and thermal ALD using H_2O on the interface between ALD film and substrate surface, and also the impact of the interface on the quality of ALD films.

We have studied the influence of both thermal and PEALD processes on the electrical properties of Al_2O_3 and HfO_2 films, and found that both the Al_2O_3 and HfO_2 films grown by the PEALD with O_2-plasma have higher dielectric breakdown electric fields and lower leakage currents than that grown by the thermal ALD with H_2O.

To further understand and optimize the ALD processes, we have used in situ Auger electron spectroscopy (AES) and high-resolution scanning Auger microscope (SAM) of a NanoSAM system, which is vacuum connected with an ALD chamber, to investigate the surface chemical compositions and distributions in the interface between the ALD Al_2O_3 and HfO_2 films and Si, Au and Ti substrate surfaces without exposing the ALD films to air. We have found (a) for the Al_2O_3 films grown with H_2O, the AES spectra show significant peaks of Al and O, but slight peak of C, which means the Al_2O_3 film deposited on Si, Au and Ti surfaces, but some C impurities remained unreacted in the film; (b) for the HfO_2 films grown with H_2O, the AES spectra show significant peaks of C and O, but very slight peak of Hf, which suggests that HfO_2 film hardly deposited on Si, Au and Ti surfaces, but many C impurities remained unreacted in the film; (c) for both Al_2O_3 and HfO_2 films grown with O_2-plasma, the AES spectra show significant peaks of Al and O, and Hf and O, respectively, but no peak of C is observed within the detecting limit of the NanoSAM. This indicates the Al_2O_3 and HfO_2 films deposited on Si, Au and Ti surfaces, high purity and free of carbon contamination from unreacted ligands when deposited at the optimized PEALD processes conditions.

The AES investigations of Al_2O_3 and HfO_2 films are well in agreement with the studies on their electrical properties, and again confirm the superior qualities of the PEALD Al_2O_3 and HfO_2 over the thermal ALD Al_2O_3 and HfO_2.

Atomic Layer Etching
Room 104-106 - Session ALE1-MoA
Plasma and/or Energy-enhanced ALE I

Moderators: Bert Ellingboe, Dublin City University, Satoshi Hamaguchi, Osaka University, Japan

1:30pm **ALE1-MoA-1 Investigation of Atomic Layer Etching Process and UV Damage for AlGaN/GaN HEMT**, ***Hiroyuki Fukumizu,*** Toshiba Memory Corporation, Japan; *K Kanomaru,* Toshiba Corporation, Japan; *T Kikuchi,* Toshiba Corporation **INVITED**

Gate-recess type of AlGaN/GaN for high electron mobility transistor (HEMT) is one of the devices which can operate normally-off for high power electronics applications. This gate-recess structure demands precise control of etching depth and minimization of etching damage to AlGaN film. In previous atomic layer etching (ALE) studies for GaN or AlGaN, it was first reported that the surface was oxidized by O_2 plasma and then subsequently this surface was removed by BCl_3 plasma [1]. Recently, a directional type of ALE for GaN and AlGaN films using Cl_2 or BCl_3/Cl_2 plasma and Ar ion bombardment was investigated and the surface roughness of GaN film etched by ALE was more suppressed than RIE [2]. We investigated the etching process property and UV damage on AlGaN film and compared them between ALE and conventional RIE.

AlGaN films were etched by Cl_2/Ar chemistry for RIE. In case of ALE, a modified layer was formed by exposure to Cl_2 plasma and then, this modified layer was removed by Ar ion bombardment. The etched surface roughness was evaluated by AFM and the surface roughness etched by RIE increased with etching. On the contrary, the surface etched by ALE showed a relatively smooth surface regardless of the etched depth. The increase of surface roughness etched by RIE is supposed to be due to lack of nitrogen of AlGaN film, which is confirmed with XPS. To evaluate plasma induced damage, the etched surfaces were analyzed by cathode luminescence (CL). CL intensity of near band edge (NBE) of AlGaN decreased after RIE and ALE. The degradation of NBE intensity of AlGaN etched by ALE was more serious than RIE. This indicated that ALE process introduced higher damages on AlGaN film than RIE. CL intensity of NBE of GaN, which was located under AlGaN film, also decreased after RIE and ALE. This degradation etched by ALE was larger than RIE. The residual thickness of AlGaN film was thick enough to protect the penetration of ions into GaN film underneath the AlGaN film. From this result, it was supposed that damage of GaN film was introduced not by ions but UV photon radiation and this UV induced damage on GaN film brought by ALE was larger than RIE. This is supposed that ALE process time was longer than RIE and UV radiation amount of ALE was also larger than RIE.

[1] S. D. Burnham, K. Boutros, P. Hashimoto, C. Butler, D. W. S. Wong, M. Hu and M. Micovic, Phys. Status Solidi C **7**, 2010 (2010).

[2] T. Ohba, W. Yang, S. Tan, K. J. Kanarik and K. Nojiri, Jpn. J. Appl. Phys. **56**, 06HB06, (2017).

2:00pm **ALE1-MoA-3 Plasma-assisted Atomic Layer Etching of Si-based Dielectric Films Studied using *in situ* Surface Diagnostics**, ***Sumit Agarwal,*** *R Gasvoda,* Colorado School of Mines; *S Wang,* Lam Research Corp.; *R Bhowmick,* Colorado School of Mines; *E Hudson,* Lam Research Corp. **INVITED**

The shrinking device dimensions in integrated circuits combined with the introduction of 3-D device architectures has created a need for atomic layer etching (ALE) processes for a variety of materials including Si-based dielectrics such as SiN_x and SiO_2. Development of new ALE processes that can meet the demands for semiconductor manufacturing requires an atomistic-level understanding of the surface reaction processes. In our geoup, in collaboration with Lam Research Corporation, we have pioneered the use of *in situ* optical diagnostic techniques including highly surface sensitive attenuated total reflection Fourier transform infrared spectroscopy and multi-wavelength ellipsometry to study the surface processes that occur during ALE.

In this presentation, I will discuss the atomistic–level details of an SiO_2 and SiN_x ALE process consisting of CF_x deposition from a C_4F_8/Ar plasma, and an Ar plasma activation step in which the CF_x film is activated, and the underlying substrates are etched. Sequential cycles of ALE of SiO_2 show a drift in the etch per cycle (EPC) with increasing cycle number. We attribute the drift in EPC to excess CF_x that is liberated from the reactor walls in the Ar plasma step. This increase in the EPC occurs even though the infrared spectra confirm that the CF_x deposition onto the SiO_2 film is reproducible from cycle to cycle. To minimize the drift in EPC, Ar plasma half–cycles of twice the length are employed, which allows for the removal of CF_x from the reactor walls during each cycle, thus creating more reproducible chamber wall conditions. To further control the EPC, and obtain selective etching of SiN_x over SiO_2, we have explored selective attachment of surface functional groups such as hydrocarbons of different chain lengths. We have demonstrated that attachment of hydrocarbons to the surface priot to the start of ALE retards the EPC.

2:30pm **ALE1-MoA-5 Silicon Atomic Layer Etching by Two-step Plasma-enhanced Atomic Layer Deposition Consisting of Oxidation and $(NH_4)_2SiF_6$ Formation**, *E Song,* Korea Institute of Materials Science, Republic of Korea; ***Ji-Hye Kim,*** ISAC Research Inc., Republic of Korea; *J Ahn,* Korea Maritime and Ocean University, Republic of Korea; *J Kwon,* Korea Institute of Materials Science, Republic of Korea

The process of precise silicon etching on the atomic scale was investigated by examining the formation of an $(NH_4)_2SiF_6$ thin film as an intermediate phase followed by the removal of this layer by sublimation. An amorphous $(NH_4)_2SiF_6$ thin film was formed on a Si substrate via a two-step plasma-enhanced atomic layer deposition (PEALD) process consisting of an oxidation step involving an O_2 plasma and a transformation step to deposit an $(NH_4)_2SiF_6$ thin film using an NH_3 / NF_3 plasma, where the deposited thin film was removed by a sublimation process. Because the thickness of the $(NH_4)_2SiF_6$ thin film could be linearly controlled by altering the number of PEALD cycles, the etching depth could be successfully controlled on the sub-nanometer scale.

2:45pm **ALE1-MoA-6 Factors in Selectively Etching SiO_2 over Si_3N_4 Using C_4F_8/Ar Atomic Layer Etching**, ***Chad Huard,*** *M Kushner,* University of Michigan

Atomic layer etching (ALE) using fluorocarbon gas passivation offers several benefits over conventional etching, including increased selectivity enabled by low ion energies and increased control over polymer buildup.[1,2] This polymer is important in obtaining selective etching using fluorocarbon gases. During continuous etching the passivating fluorocarbon radical fluxes are generated by the same plasma as the activating ions, creating a close coupling between polymerizing and etching fluxes. These conditions result in limited operating conditions which produce selective etching of SiO_2. ALE offers a method to decouple the passivation/polymerization phase from the activating ions, enabling a new avenue to control selectivity.

In this presentation results will be discussed from a new computational model of the etching of silicon nitride and silicon dioxide by C_4F_8 containing plasmas. This new model, developed within the Monte Carlo Feature

Profile Model (MCFPM), takes into account the transport of ion energy and radical species through a finite thickness polymer capping layer, including mixing and etching processes at the interface between the polymer and the material being etched. Applications to ALE in the context of self-aligned-contacts will be discussed.

Results from this model indicate that infinite selectivity to SiO_2 (over Si_3N_4) may be achievable in a pulse-periodic steady state ALE. This selectivity is possible because SiO_2 consumes more polymer during etching than Si_3N_4. When reactions with polymer by SiO_2 consumes all of the polymer deposited in each passivation phase of ALE, but the polymer consumed by Si_3N_4 is less than the amount deposited, a thick layer of polymer will form on a cycle to cycle basis on Si_3N_4. This thickening will eventually prevent etching of Si_3N_4, while SiO_2 continues to etch. Before reaching this state, there is a transient period where the polymer on Si_3N_4 is not yet thick enough to prevent etching, limiting the ability of ALE to provide perfect selectivity. In this initial period, the selectivity depends on many factors, including the ALE pulse times and the ion energy during the etching phase. Since ALE is often used to manage very thin films, the physics of this transient period where a finite amount of material is etched from both SiO_2 and Si_3N_4 takes on heightened importance.

[1] D. Metzler et al., J. Vac. Sci. Technol. A **32,** 20603 (2014).

[2] T. Tsutsumi et al., J. Vac. Sci. Technol. A **35,** 01A103 (2017).

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

3:00pm **ALE1-MoA-7 Bias System for Controlling Ion Energy Distributions***,* ***Dan Carter****, V Brouk, H Nguyen,* Advanced Energy Industries, Inc.

Radio frequency voltage is commonly applied for generating bias in ALE and other traditional plasma processes. As device scaling drives the need for atomic precision, techniques for improving ion energy control continue to evolve. While methods combining frequencies[1] or harmonics[2], with and without phase control[3] and even dynamic frequency variation[4] have shown promise, the very nature of sine wave excitation is conflicting for achieving narrow or freely controlled Ion Energy Distributions (IEDs)[5]. We investigate a new power system utilizing optimized asymmetric voltage waveforms combined with a novel control system specifically designed for controlling wafer surface potential. Using this bias voltage application we evaluate the ability to directly manipulate surface bias and resulting IED's for producing single or multiple peaks with narrow or broad energy spread. We assess a metrology approach that allows the measurement of ion energy, ion current and sheath capacitance in real time. Near mono-energetic control across a wide energy range is demonstrated. Capability down to 10's of eV is shown for plasmas in the 10 to 100 mT range making this method suitable for many energy-sensitive, atomic scale plasma processes.

1. S. Shannon et al.; J. Appl. Phys. 97, 103304 (2005)
2. P. Diomede et al.; Plasma Sources Sci. Technol. 23 (2014)
3. Y. Zhang et al.; J. Appl. Phys. 117, 233302 (2015)
4. S. Lanham et al.; J. Appl. Phys. 122, 083301 (2017)
5. E. Kawamura et al.; Plasma Sources Sci. Technol. 8 (1999)

3:15pm **ALE1-MoA-8 Reactions of Hexafluoroacetylacetone (hfac) and Metal Surfaces under Low-energy Ion Irradiation***,* ***Tomoko Ito****, K Karahashi, S Hamaguchi,* Osaka University, Japan

In recent years, atomic layer etching (ALE) by the formation of volatile organic transition-metal compounds has been expected to establish low-damage and atomically controlled etching processes for metallic thin films. Hexafluoroacetylacetone (hfac: $CHF_3COCH_2COCF_3$) is one of the candidates of organic ligands that may be used for atomic layer etching of Ni and Cu. Nigg et. al. have reported that Ni organic compounds desorb from a pre-oxidized Ni surface by hfac exposure and a control of the substrate temperature [1]. For the development of a highly anisotropic etching process, it is important to understand and control surface reactions of metal with an organic compound layer under low-energy ion bombardment. Therefore, our objectives of this study are to understand surface reactions by hfac exposure to a metal surface and to clarify effects of ion-induced reactions on hfac adsorbed metal surfaces. In this study, we have developed an atomic layer process (ALP) surface analysis system which consists of two parts: a high-resolution XPS analysis chamber and an ALP reaction chamber. After reactive gas exposure to a sample in the ALP reaction chamber, the sample can be transferred to the XPS chamber without air exposure of the sample. The hfac exposure was in the range of 100 - 10000L (in the units of L: Langmuir: 10-6 Torr ・ s) and Ni and Cu substrates are used in this study. The substrate temperature was set at room temperature. The hfac adsorbed surfaces were irradiated by low-energy Ar^+ ions (15- 50eV) and the changes in the chemical states were observed by XPS. It is found that, for pre-oxidized Ni and Cu surfaces, hfac molecules adsorbed without C-O and C-F bond braking. It is also found that hfac adsorbed Ni-O surfaces are fluorinated by low-energy Ar^+ ion bombardment.

[1] H. L. Nigg and R. I. Masel, J. Vac. Sci. Technol. A, 17, 3477 (1999).

Atomic Layer Etching
Room 104-106 - Session ALE2-MoA
Plasma and/or Energy-enhanced ALE I

Moderators: Tetsuya Tatsumi, Sony Semiconductor Solutions Corp., Eric Joseph, IBM T.J. Watson Research Center

4:00pm **ALE2-MoA-11 Application of ALE Technology to <10nm Generation Logic Device Fabrication***,* ***Jongchul Park,*** Samsung **INVITED**

As the design rule decreased gradually the dry etching technology has confronted with the severe limitations of etch loading and mask etch selectivity. Since the single RF powered CCP (Capacitively Coupled Plasma) was developed high frequency dual CCP, ICP (Inductively Coupled Plasma), DCS (DC Superposition) and RF pulsing have developed continuously to overcome those limitations. ALE technology was introduced recently as next generation etching technology to obtain very high performance at SAC (Self Aligned Contact) module of the high density logic device. But as the ALE consists of repeated deposition and etching the process controllability is very worse than the previous etching. We analyzed the control knobs for contact not-open and SAC shoulder fail to obtain much better performance for the mass production, and suggest the superior advantages of ALE over the conventional etching on the point of the fundamental limitations of the dry etching and also recommend very essential technologies for better process capability of ALE technology.

4:30pm **ALE2-MoA-13 Isotropic Atomic Layer Etching of ZnO on 3D Nanostructures, using Acetylacetone and O_2 Plasma***, A Mameli, M Verheijen, A Mackus, W Kessels,* Eindhoven University of Technology, Netherlands*;* ***Fred Roozeboom,*** Eindhoven University of Technology and TNO, Netherlands

The continuous driving force from the semiconductor industry for realizing smaller features and device structures with higher density and higher-aspect ratio poses increasing challenges in traditional etching techniques. Atomic layer etching (ALE) provides the opportunity to overcome the shortcomings of more conventional etching processes. Extensive research in this field has led to the development of two main classes: plasma ALE to achieve anisotropic etching and thermal ALE for the isotropic counterpart. Besides anisotropic etching, plasma can also be applied for achieving isotropic etch profiles. Yet, this process option has not been explored extensively.

In this work, we demonstrate isotropic ALE of ZnO on a regular array of vertical nanowires, using the alternated doses of O_2 plasma and acetylacetone (Hacac). A linear ZnO thickness decrease with increasing number of cycles was measured by *in-situ* spectroscopic ellipsometry, and saturation behavior was demonstrated for both Hacac and O_2 plasma, at 250^{o}C. The etch rates per cycle were found to increase from 0.5 to 1.3 Å/cycle with process temperature increasing from 100 to 250^{o}C. Transmission electron microscopy (TEM) studies conducted on ZnO-coated nanowires before and after ALE proved the isotropic character of the process. Moreover, the ALE process produced no surface damage/amorphization, as demonstrated by high resolution TEM inspection. *In-situ* infrared spectroscopy measurements were conducted to elucidate the mechanism underlying self-limited etching. Based on these measurements, a preliminary reaction mechanism is proposed in which Zn(acac)-$_2$ is assumed to be the etching product and persisting acac-species on the ZnO surface provide the self-limiting character. Finally, a high etch selectivity over SiO_2 and HfO-$_2$, and the possibility to extend the process to other oxides such as Al_2O_3 are also demonstrated.

We believe that this plasma-based ALE process represents a valuable addition to the ALE toolbox and opens-up new possibilities for using plasma-processing to achieve isotropic etch profiles. Furthermore, similar approaches can be used to extend the process to other materials, such as nitrides, by tuning the plasma chemistry accordingly.

(1) Lee, C. G. N. *et al.,* The Grand Challenges of Plasma Etching: A Manufacturing Perspective. *J. Phys. D. Appl. Phys.* **2014**, *47*, 273001.

(2) Lill, T. *et al.,* Directional Atomic Layer Etching. *Encycl. Plasma Technol.* **2016**, 133–142, Taylor & Francis.

(3) George, S. M. *et al.,* Prospects for Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions. *ACS Nano* **2016**, *10*, 4889–4894.

4:45pm **ALE2-MoA-14 Etching Reactions of Halogenated Layers Induced by Irradiation of Low-energy Ions and Gas-clusters***, **Kazuhiro Karahashi,** T Ito, S Hamaguchi,* Osaka University, Japan

In recent years, in microfabrication of various new devices such as MRAM, PRAM, RRAM, etc., damage-free, high-precision etching technologies of various materials are required. Some promising atomic layer etching processes use the formation of a halogenated layer on a metal surface and an adsorption layer of an organic molecule. If one uses ion irradiation to achieve etching anisotropic in atomic layer etching (ALE), it is necessary to reduce the incident ion energy and minimize damage formation to the surface. It is therefore important to understand surface reactions induced by low-energy ion irradiation. Similarly surface reactions by the irradiation of gas clusters or free radicals are also causes low or no damage to the surface. Therefore such processes may also be used for ALE.

In this study, fluoride layers formed on the surfaces of silicon, copper, nickel and cobalt were evaluated by exposure to XeF_2 using XPS. In addition, the process of removing fluoride layers by low energy ions and clusters was discussed. XeF_2 was exposed to the cleaned surface of the sample (Si, Cu, Ni, Co) and the chemical state of the surface layer after irradiation by in-situ photoelectron spectroscopy (XPS) was evaluated. The desorption reaction was evaluated by measuring changes in the surface fluorinated layer by irradiation with low-energy Ar ions (30, 50, 100 eV) and Ar cluster ions (3,000 atoms / ion, 3 keV / cluster). A fluoride layer with metal-fluorine bonds was formed on the surface by exposure to XeF_2. The fluoride layer formed on the Ni surface was almost saturated at 1000 L exposure. The adsorption process was a self-limiting process. The fluoride layer was removed by Ar + ion irradiation with an energy of 30 eV. In this single step of ALE, the substrate surface was etched and the etched depth was limited to the depth of the fluoride layer.

5:00pm **ALE2-MoA-15 Optimization of Atomic Layer Etch Process for Fabrication of Dual Barrier GaN-based Power Device using *in-situ* Auger Spectrometric Surface Ananlysis***, **Xu Li,** H Zhou, K Floros, S Cho, D Hemakumara, D Moran, I Thayne,* University of Glasgow, UK

ALE (Atomic Layer Etch) as a precisely etching technique removes very thin layers of materials has attracted extensive attentions in semiconductor processing, which is particularly suitable for fabricating GaN-based e-mode power devices in cascode module. For GaN-based power transistors employing a gate recess process, ALE has the potential to offer the etching precision required to precisely control device threshold voltage. In this work, an ALE process developed for etching group III nitrides in a dual barrier device materials consisting of a 2 nm GaN cap layer, a 4-8 nm InAlN barrier layer, another 1 nm GaN cap layer for the following 3 nm AlGaN barrier layer above a 250 nm GaN channel and 4 µm C-doped buffer layer on Si wafer grown by MOCVD based on a cycled procedure of HBr bromination of the semiconductor surface followed by argon plasma removal of the modified surface layer has been optimized using i n-situ Auger spectrometric analysis which supplies the information of the etching progress through different layers in the device materials via analyzing the surface composition during ALE processing.

A cluster tool from Oxford Instrument Plasma Technology has been used for ALE etching and in-situ analysis, which includes (amongst other process chambers and in-situ metrology) an inductively coupled plasma (ICP) etching chamber with repeat loop function, a basic requirement of an ALE process, and an Scienta Omicron NanoSAM surface analysis tool (including an Auger spectrometer). The clustered arrangement enables samples and wafers to be subjected to plasma processing before transfer into the analysis chamber under vacuum. The etching chemistry was based on the formation of self-limited Ga, In and Al bromides on the sample surface as a consequence of exposure to a short HBr gas pulse in the plasma etch chamber. This modified surface was then removed using an Ar plasma with an optimized RF power level which removes only the surface bromides and is not going to induce damage to the underneath materials. Etching could be suspended at any ALE steps in order to transfer the sample into analysis chamber to carry out Auger spectrometric analysis for determining which layer the etching was in. Experiments showed that the Auger spectrum could clearly and sensitively indicate the layer where the etching is going on, which is useful in fabricating e-mode transistors in the cascode module devices.

5:15pm **ALE2-MoA-16 ALE to Enable Memory Scaling***, **Alex Schrinsky,** C Huffman, M Koltonski, A Wilson,* Micron **INVITED**

Aggressive pitch scaling for both DRAM and non-volatile memory devices is pushing etch loading and precision control outside the limit of conventional continuous subtractive etch processing. Extreme control in removal and selectivity is required to enable forward looking devices. Atomic Layer Etching (ALE) techniques propose to achieve control at an atomic scale and could offer solutions to many of the key scaling challenges now faced by developers of next Gen IC's.

Emerging Materials
Room 113-115 - Session EM-MoA

Laminate, Multicomponent, and Nitride Materials

Moderators: Nicholas Strandwitz, Lehigh University, Ji Hye Kim, ISAC Research Inc.

4:00pm **EM-MoA-11 Comparisons Between TiO_2/Al_2O_3 Nanolaminates Grown by Thermal and Plasma Enhanced Atomic Layer Deposition: Growth Mechanism and Material Properties***, G Testoni,* Universidade do Vale do Paraíba, Brasil*; **Rodrigo Pessoa**, M Fraga,* Universidade Brasil, Brasil*; N Galvão,* Instituto Tecnológico de Aeronáutica*; W Miyakawa,* Instituto de Estudos Avançados*; H Maciel,* Instituto Tecnológico de Aeronáutica

Nanolaminate coatings can offer significant improvements to traditional single-layer materials. An interesting class of nanolaminate materials is one based on alternatively ordered thin films of transition metal oxides with nanoscale thickness [1]. Using the TiO_2/Al_2O_3 nanolaminate concept of our previous work [1], it is possible to obtain at high temperature a 'stable amorphous film' which is very attractive for applications in microelectronics and optics. It is known that amorphous films of certain materials 'crystallize' during the various processing steps (deposition, metallization and lift-off) required for manufacturing a device. This crystallization modifies the fundamental properties of the film, which makes it suitable for the application. Herein, the thermal atomic layer deposition (ALD) and plasma enhanced atomic layer deposition (PEALD) of TiO_2/Al_2O_3 nanolaminates on silicon(100) and glass substrates were studied in order to discuss the growth mechanism and material properties of the films. We use the nanolaminate concept where each TiO_2/Al_2O_3 nanolaminate incorporates a certain number of Al_2O_3 partial-monolayers (between 10 to 90) during 2700 total reaction cycles of TiO_2 under temperature of 250ºC [1]. TiO_2/Al_2O_3 films were deposited by a TFS-200 ALD system from Beneq. TMA and TTIP were used as metallic precursors, while H_2O or O_2 plasma were used as ligand. The growth mechanisms and fundamental properties of the TiO_2/Al_2O_3 nanolaminates were inferred from measurements of the film thickness, chemical composition, microstructure and morphology. In addition, some optical and mechanical characteristics were determined and correlated with fundamental properties. Results evidenced that the model proposed for thermal ALD TiO_2/Al_2O_3 nanolaminate is valid for PEALD, however it was necessary a higher number of Al_2O_3 layers for stop the TiO_2 crystallinity. This allows obtaining a nanolaminate with improved properties in comparison with thermal ALD, as for example higher transmittance, lower refractive index (near the value of 3.2 eV), low resistivity, and higher hardness and young modulus. These properties are interesting for sensing application, such as UV detection.

[1] J. Azadmanjiri, C. C. Berndt, J. Wang, A. Kapoor, V. K. Srivastava, C. Wen, J. Mater. Chem. A 2 (2014) 3695–3708

[2] G. E. Testoni, W. Chiappim, R. S. Pessoa, M. A. Fraga, W. Miyakawa, K. K. Sakane, N. K. A. M. Galvão, L. V. Santos, H. S. Maciel. Journal of Physics D: Applied Physics, 49 (2016) 375301.

4:15pm **EM-MoA-12 Texture Control of ALD $PbTiO_3$ and $PbTi_xZr_{1-x}O_3$ Films by Hot Chuck and Rapid Thermal Annealing***, **Nicholas A. Strnad,*** University of Maryland*; D Potrepka, J Pulskamp,* U.S. Army Research Laboratory*; Y Liu, J Jones,* North Carolina State University*; R Phaneuf,* University of Maryland*; R Polcawich,* U.S. Army Research Laboratory

$PbTi_xZr_{1-x}O_3$ (PZT) is a perovskite ferroelectric material that is widely studied for its high dielectric constant and piezoelectric coefficients. Thin-film PZT has found several commercial uses, namely ink-jet print heads, ferroelectric random access memory (FRAM), MEMS gyroscopes, and more recently PZT-MEMS based speakers. Niche technological applications include MEMS resonators, actuators, and transducers. Thin-film PZT is currently deposited by primarily 2-dimensional (2-D) deposition techniques such as sol-gel, sputtering, and MOCVD. Thin-film PZT-based devices could benefit greatly from an atomic layer deposition (ALD) PZT process capable of transitioning traditionally 2-D architectures to 3-dimensional (3-D) architectures utilizing etched high aspect-ratio sidewalls to greatly enhance areal density especially for actuator technologies. The literature on PZT deposited by ALD is sparse and falls short of providing industry with an off-the-shelf solution. Additionally, there is little effort dedicated to controlling the texture of ALD PZT films, which is a desired component for many of the aforementioned technologies. Here we explore several techniques for controlling the texture of ALD PZT by depositing nucleation seed layers. First, we attempt to deposit 1-3nm of ALD grown TiO_x followed by 1-5nm ALD grown PbO_x and anneal in a PZT sputter chamber which has a PbO_x partial pressure. The PbO_x is expected to react with the TiO_x to form $PbTiO_3$ (PTO), but will be self-limited to what can be chemically incorporated because excess lead oxide will boil off the surface with the chuck maintained at 600° C or hotter. Second, we deposit 1-5nm of ALD grown TiO_x and anneal in an RTA that is expected to have a small PbO_x partial pressure due to re-deposition of lead oxide from prior processing of chemical solution deposited PZT films onto a quartz glass liner that is within 1 cm of the wafer surface. Third, as a control we deposit 40nm of PTO by sol-gel with 30% lead excess which crystallizes primarily in the 100/001 orientations following post-deposition anneal. Each of the ALD PZT films are deposited in an amorphous state and later crystallized by rapid thermal anneal in an O_2 atmosphere. To further evaluate the contribution of the nucleation layers to the texture, sol-gel PZT films are deposited in the first and second cases to be analyzed alongside the ALD PZT films. The films are characterized primarily by spectroscopic ellipsometry for film thickness, scanning electron microscopy for film thickness and microstructure, x-ray diffraction for phase identification and texture, and for select samples STEM with EDS for detailed structure and chemical analysis.

4:30pm **EM-MoA-13 Optical and Electrical Properties of $Ti_xSi_{(1-x)}O_2$ Films Prepared by ALD***, **Lenka Zajickova**, P Ondracka, D Necas,* Masaryk University, Czech Republic*; M Elias,* CEITEC, Brno University of Technology, Czech Republic*; J Vida,* Masaryk University, Czech Republic*; D Holec,* Montanuniversitat Leoben*; A Goullet,* University of Nantes

The mixed TiO_2-SiO_2 oxides have multiple possible optical applications with demonstrated use in waveguides, laser mirrors and rugate filters. They are also considered as an alternative dielectric for high-k applications and they attracted considerable attention in the area of photocatalysis because they are more active than pure TiO_2. $Ti_xSi_{(1-x)}O_2$ were deposited on Si substrate by plasma enhanced atomic layer deposition using tetrakis(dimethylamido)titanium and tris(dimethylamino)silane precursors for Ti and Si, respectively. The overall stoichiometry of the final thin film was varied by changing the relative number of TiO_2 and SiO_2 cycles as 1:1, 2:1, 1:2 and 3:1. The chemical bonding in the films was confirmed by X-ray photoelectron spectroscopy (XPS). Optical properties were determined in the wide spectral range from the ellipsometry (NIR-UV spectroscopic ellipsometer J. A. Woollam V-VASE, 0.6-6.4 eV, angles of incidence 60, 65, 70 and 75°) and reflectance (VUV spectrometer McPherson VUVAS 1000, 5.6–10.3 eV, near-normal incidence) measurements. The results on dielectric function and band gap were in good agreement with the density functional theory (DFT) predicted optical properties of amorphous $Ti_xSi_{(1-x)}O_2$ solid solutions. The electrical properties of the films were investigated in the MOS capacitor structures using a wafer probe station and the 4200 Keithley semiconductor parameter analyzer. The mixed oxide dielectric constant is deduced from the C-V curves measured at 1 MHz in accumulation regime whereas the film stability is assessed from the C-V loops recorded by accumulation (A) to inversion (I) and I to A. The dielectric layer insulating characteristics were assessed from the measured leakage current and breakdown voltage.

4:45pm **EM-MoA-14 Concerted Coating and Reduction for the Fabrication of Magnetic Fe_3O_4/TiO_2 Core-shell Nanoparticles***, **Sarai Garcia**, A López-Ortega, A Chuvilin, M Knez,* CIC nanoGUNE, Spain

Composite nanoscale materials are under intense investigation, opting for merging the functionalities of the constituting materials. Fe_2O_3-TiO_2 core-shell nanoparticles (NPs) are among the intensely investigated composite NPs for their application potential in a broad variety of fields, such as, sensing, selective separation, biomedicine, or photocatalysis [1,2]. The combination of a titanium dioxide (TiO_2) shell and a magnetic iron oxide core can provide added value to the composite by tuning the biocompatibility, stability and/or photocatalytic properties through the TiO_2 shell and at the same time, the possibility to use the materials for hyperthermia, imaging or controlled positioning through magnetic fields [3].

In this work, Fe_2O_3 nanoparticles are coated with TiO_2 and concertedly turned magnetite Fe_3O_4-TiO_2 core-shell NPs through atomic layer deposition (ALD) at moderate temperatures (Figure 1). The generated coatings prevent agglomeration of the nanoparticles and re-oxidation to γ-Fe_2O_3 even at high temperatures, allowing for the use of post-process annealing and thus crystallization of the amorphous TiO_2 to anatase. The occurring reduction of Fe_2O_3 to Fe_3O_4 is a function of the applied precursor and the processing temperature. This presentation will detail on our process and the characterization of the materials by means of X-ray diffraction (XRD), magnetometry, Energy Dispersive X-Ray analysis (EDX) and electron microscopy.

[1] M. Stefan *et al.*, "Synthesis and characterization of Fe_3O_4-TiO_2 core-shell nanoparticles," *J. Appl. Phys.*, vol. 116, no. 11, 2014.

[2] W. Wu, X. Xiao, S. Zhang, F. Ren, and C. Jiang, "Facile method to synthesize magnetic iron oxides/TiO_2 hybrid nanoparticles and their photodegradation application of methylene blue," *Nanoscale Res. Lett.*, vol. 6, pp. 1–15, 2011.

[3] S. Exhibit, C. Strobel, R. Herrmann, A. A. Torrano, and I. Hilger, "Biocompatibility of titanium dioxide nanoparticles for diagnostic and therapeutic purposes in personalized nanomedicine," pp. 1–17, 2013.

5:00pm **EM-MoA-15 Aluminum Nitride – From Amorphous to Highly Oriented Hexagonal Thin Films***, Z Chen, M Bosund, I Tuoriniemi, V Malinen, Z Zhu, **Emma Salmi**, K Härkönen,* Beneq Oy, Finland

Aluminum nitride (AlN) has a wide band gap, good thermal and chemical stability, thermal conductivity and interesting electro-acoustic properties. It is used in several applications, of which many depend on the crystalline structure of the material. Barrier, passivation and dielectric layers benefit from amorphous structures [1]. However, highly oriented crystalline films are needed for instance in optoelectronic and surface acoustic wave devices [2].

In this work the aim was to deposit AlN films with varying crystallinities to separately address the needs of different application areas. TMA and $AlCl_3$ were utilized as the metal precursors, while NH_3 or NH_3 plasma were used as the nitrogen source. The deposition temperatures were varied from 220 to 550°C.

PEALD AlN films were deposited at 220°C from TMA and NH_3 plasma in a Beneq TFS 200 ALD reactor. On a 200 mm wafer a uniformity of 1.7% was achieved. The films were amorphous and had a refractive index of 1.88.

Thermal ALD process from TMA and NH_3 was studied at 350–475°C with a Beneq P400 batch ALD reactor. Significant effect of the pulsing sequence on the growth characteristics and film properties was observed. With the optimized process at 350°C, a GPC of 1.37 Å/c and refractive index of 2.10 were measured. The bulk oxygen and carbon contents were 1.0 and 0.4 at.%. The films were polycrystalline with randomly oriented hexagonal structure, and the degree of crystallinity was increased with increasing deposition temperature (Figure 1).

The Beneq P400 batch ALD reactor is equipped for studying ALD processes at high temperatures. This enabled us to increase the temperature range of the thermal ALD $AlCl_3$–NH_3 process from the previously reported 500 up to 550°C [3,4]. Significant improvement on the film quality was observed with increasing deposition temperature. The GPC and refractive index increased from 0.67 to 0.76 Å/c and 1.99 to 2.06. Simultaneously the bulk oxygen and chloride impurity contents decreased from 3.2 to 2.5 and 1.8 to 0.7 at.%. Furthermore, these results were achieved with a uniformity of 2.5% on a batch set-up with a planar surface area of 20 000 cm^2. All the films were polycrystalline with highly oriented hexagonal [001] structure as the only observed peak was (002) (Figure 2).

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[2] G.F. Iriarte at al., Mater. Res. Bulletin 45 (2010) 1039-1045.

[3] K.-E. Elers et al, J. De Phys. IV France 5 (1995) C5-1021–C5-1027.

[4] V. Rontu, J. Vac. Sci. Technol. A 36 (2018) 021508.

5:15pm **EM-MoA-16 Purely Thermal Deposition of Polycrystalline Gallium Nitride Films at 400^{o}C***, **Sourish Banerjee**, S Dutta, A Aarnink, J Schmitz, D Gravesteijn, A Kovalgin,* University of Twente, Netherlands

In the field of III-V semiconductor materials, research is focused mostly on epitaxially grown films. Developing their polycrystalline counterparts (e.g., polycrystalline gallium nitride or poly-GaN) may lead to their more widespread adoption in application areas, such as in microelectronics and lighting. Unlike traditional epitaxy, atomic layer deposition (ALD) of poly-GaN films allows for less stringent growth requirements such as reduced temperatures, atomic-level thickness control and direct growth on a variety of substrates without the need of buffer layers.

The majority of reports on low temperature deposition of poly-GaN from trimethylgallium (TMG) and ammonia (NH_3) precursors mention an additional means of activation (e.g., plasma) to dissociate NH_3. This is done to increase the chemical activity of ammonia (by forming radicals) with the TMG-chemisorbed surface. However, in this work, we have used a different (radical-free) chemistry to deposit GaN films by a purely thermal route; i.e., without plasma or other radical-production means. Such a deposition approach can be beneficial, for example, in industrial-scale batch-type reactors where uniform radical delivery is a challenge.

We have utilized the strong adduct-forming chemistry of the Lewis-acid TMG and the Lewis-base NH_3 on the growth surface (Fig. 1). At the deposition temperature of 400^{o}C the TMG-NH_3 adduct dissociates into a Ga-NH_2-Ga linkage, thereby forming the first monolayer of GaN in a self-limiting fashion. Due to the reversible nature of this adduct formation, at optimal gas-pressure conditions, alternate pulses of TMG and NH_3 with in-between purges result in the efficient film growth. This pressure-dependency of adduct formation is revealed by in-situ monitoring the growth with spectroscopic ellipsometry (SE), which shows a strong dependence of the growth per cycle (GPC) with the NH_3 partial pressure (Fig. 2). Using this approach, we obtained GPC values as high as 0,045 nm/cycle.

The efficient removal of all methyl groups of TMG during GaN deposition in the adduct-assisted mechanism is revealed from the low carbon content (1 at. %) in the films, as obtained from depth profiled X-ray photoelectron spectroscopy (Fig. 3). The cross-section scanning electron microscope (SEM) image (Fig. 4) shows a 23-nm GaN film deposited on aluminium nitride (AlN). Grazing-angle X-ray diffraction (GIXRD) spectrum (Fig. 5) reveals that the GaN film is polycrystalline and has a wurtzitic structure.

In our presentation, the purely thermal radical-free deposition of poly-GaN films will be detailed: focussing on the growth mechanism, determining the ALD window, and presenting several film properties.

5:30pm **EM-MoA-17 ABC-type pulsing for group 13 nitrides**, *P Rouf,* ***Henrik Pedersen,*** Linköping University, Sweden

The group 13 nitrides (13-Ns) are essential electronic device materials for present and future technologies. Thin film deposition of AlN and GaN are well explored by CVD at relatively high temperatures (800-1000°C). The high temperature aids epitaxial growth and ligand removal, rendering high crystalline quality films with low impurity levels. As 13-N CVD almost exclusively uses the trimethyl complexes of the group 13 metals, carbon is a major impurity with concentrations in the 10^{17} cm^{-3} range.

ALD is less explored for the 13-Ns but would open to topographically more advanced 13-N structures, higher control when depositing multilayer superlattice 13-N structures and possibly low deposition temperatures. A major challenge for ALD is the limitation in deposition temperature set, mainly by the thermal stability of the monolayers formed by the surface chemical reactions in the ALD cycle. The thermal stability of the group 13 precursors also limits the deposition temperature; $AlMe_3$ decomposes at about 330°C and previous studies have shown that the carbon content in the films increases rapidly when deposition temperature starts to approach the decomposition temperature [1]. The lower temperatures used in ALD compared to CVD hampers the crystalline quality and the removal of ligands leading to an increase in impurity levels, mainly carbon and oxygen, to the several atomic percentage levels.

Here we discuss the possibility to use the time-resolved precursor supply in ALD with an additional pulse between the precursor pulses, i.e. an ABC-type pulsing, to decrease impurities and increase crystalline quality. To improve the crystalline quality, we intentionally move out of the ALD temperature window and did time-resolved CVD of 13-Ns at 480°C, allowing thermal decomposition of the $13Me_3$ precursors. We then introduced a pulse of H_2 or N_2 gas or H_2-, N_2- or Ar plasma as B-pulse between the $13Me_3$ (A-pulse) and NH_3 (C-pulse) to study how it can aid the removal of ligands, as probed by the impurity levels in the deposited films. XPS measurements shows that the carbon content in AlN can be reduced from about 3 at. % to below 1 at. % (which is on the detection limit of XPS) by a H_2 gas or H_2 plasma as the B-pulse. H_2 gas as B-pulse also increases the GIXRD peak intensity, which is likely an effect of a higher crystalline quality, and the growth per cycle. Initial results do not show any improvement on the carbon content for N_2 plasmas as B-pulse in AlN deposition.

Financial support from the Swedish Foundation for Strategic Research (SSF RMA 15-0018) is gratefully acknowledged.

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Nanostructure Synthesis and Fabrication
Room 113-115 - Session NS-MoA

2D Materials

Moderators: Yo-Sep Min, Konkuk University, John Conley, Jr., Oregon State University

1:30pm **NS-MoA-1 Low-temperature Growth of 2-D SnS Thin Films by Atomic Layer Deposition**, ***In-Hwan Baek,*** *J Pyeon,* Korea Institute of Science and Technology, Republic of Korea; *T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea; *J Han,* Seoul National University of Science and Technology, Republic of Korea; *C Hwang,* Seoul National University, Republic of Korea; *S Kim,* Korea Institute of Science and Technology, Republic of Korea

Many efforts have been dedicated to 2-D metal chalcogenides because of their characteristic properties which can hardly be expected from bulk materials. A challenging task for implementation of 2-D metal chalcogenides in emerging devices is to synthesize the well-crystallized layer on large area substrates at low temperatures which are compatible with the current fabrication processes for electronic devices are. SnS, a p-type layered semiconductor with high hole mobility, is a promising candidate for the realization of the large-area growth at low temperature because of its low melting point (882^{o}C). Several techniques such as spray pyrolysis, chemical vapor transport, sulfurization and e-beam evaporation have been introduced to synthesize 2-D SnS thin films. However, There are difficulties in synthesizing phase-pure SnS thin films because tin sulfides exist in various phases such as SnS, Sn_3S_4, Sn_2S_3, and SnS_2.

Here, we demonstrate a successful synthesis of single phase and impurity-free p-type SnS thin films using an ALD technique at low temperatures (< 240^{o}C). The use of a Sn precursor with an oxidation state of +2, bis(1-dimethylamino-2-methyl-2propoxy)tin(II), enabled the synthesis of single phase SnS(II) thin films at temperatures ranging from 90ºC to 240ºC, which is an exceptionally wide window for an ALD process. The SnS grain size increased with increasing the growth temperature. It was also found out that the SnS van der Waals interlayers were well aligned in parallel to the substrate at 240ºC. Impurities such as carbon, oxygen, and nitrogen were negligibly detected in the SnS(II) films and other phases such as Sn_2S_3 and SnS_2 are not incorporated. Furthermore, we investigated the feasibility of the SnS(II) thin films as a functional material in emerging devices such as thin film transistors and gas sensors.

1:45pm **NS-MoA-2 Atomic Layer Deposition of 2D Semiconductor SnS_2**, ***Miika Mattinen,*** *P King, L Khriachtchev, K Meinander,* University of Helsinki, Finland; *J Gibbon, V Dhanak,* University of Liverpool, UK; *J Räisänen, M Ritala, M Leskelä,* University of Helsinki, Finland

Two-dimensional (2D) materials have attracted broad interest due to their unique properties and wide range of applications stemming from their layered crystal structures. In particular, semiconducting 2D materials, such as MoS_2, have been extensively studied for applications including field-effect transistors (FETs), photodetectors, catalysis, energy storage, and sensing. Tin disulfide (SnS_2) has recently emerged as a promising alternative for MoS_2 as a 2D semiconductor. It has an indirect band gap ranging from 2.2 eV in bulk[1] to approximately 2.6 eV in monolayer[2] and it has shown performance comparable to MoS_2 in FET and photodetector applications.[3] Furthermore, SnS_2 appears to have potential for low-temperature processing compared to the dichalcogenides of refractory metals, such as MoS_2.

We have developed a new process for atomic layer deposition of 2D SnS_2 films using tin(IV) acetate and H_2S at 150 °C combined with mild post-deposition annealing at 250 °C in H_2S/N_2 atmosphere. Deposition of continuous, uniform, and conformal ultrathin (2 to 11 monolayers) SnS_2 films is demonstrated for the first time (Supplementary Figure 1). The annealed films exhibit good crystallinity with the expected, layered SnS_2 structure and are very smooth, stoichiometric, and show n-type semiconducting behavior (Supplementary Figure 2). Using the present method, SnS_2 films can be deposited on a range of different substrates.

[1]Burton et al., *J. Mater. Chem. A*, **2016**, *4*, 1312–1318

[2]Ye et al., *Nano Res.*, **2017**, *10*, 2386-2394

[3]Huang et al., *ACS Nano,* **2014**, *8*, 10743–10755

2:00pm **NS-MoA-3 Wafer-scale Growth of Single Phase SnS$_2$ Thin Films by Atomic Layer Deposition**, ***Jung Joon Pyeon***, *I Baek,* Korea Institute of Science and Technology, Republic of Korea; *T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea; *J Han,* Seoul National University of Science and Technology, Republic of Korea; *C Kang, S Kim,* Korea Institute of Science and Technology, Republic of Korea

Two-dimensional (2-D) metal chalcogenides have received great attention because of their unique characteristics which are not expected from bulk materials. In order to implement the 2-D materials in nanoelecronic devices, it is imperative to develop a facile route for large-area synthesis with precise thickness controllability and excellent uniformity in a temperature range compatible to common fabrication processes for electronics. SnS$_2$ is great a great candidate material for meeting the above conditions. Because the melting point(T$_m$) of SnS$_2$ is 860^{o}C, lower than that of other 2-D mateirals such as MoS-$_2$ and WS$_2$ (>1000 ^{o}C). The low meliting point of SnS$_2$ renders the high crystallized growth below 400^{o}C that satisfies the device process temperature. In addition, this material has a few hundreds of cm^{2}V^{-1}s^{-1} and shows a indirect band gap ~ 2.4 eV, lager than that MoS$_2$ and WS$_2$. This larger band gap of SnS$_2$ allows that higher on/off current ratio and lower leakage currents of off state. Also SnS$_2$ materials is environmental friendly, abundant materials and nontoxic. However, tin sulfides exist various crystal phases such as SnS$_2$, SnS, and Sn$_2$S$_3$. The important point is that the electronic properties of tin sulfides are strongly dependent on the crystal phase. Therfore, it has been challenging to synthesize the pure SnS$_2$ single phase without the other crystal phase.

Here we demostrated a useful technique to form single phase SnS$_2$ thin films by Plasma Enhanced Atomic Layer Deposition (PEALD). The SnS$_2$ thin films were grown by PEALD using unstable 2$^+$ Sn(dmamp)$_2$ source and H$_2$S plasma. All the processes were performed below such a low temperature of 300^{o}C, which is compatible to current fabrication processes for electronic devices. Despite of low temperature, our SnS$_2$ has van der waals interlayer structure and these films have single phase of n-type SnS$_2$ without no oher phase. In addition, this method achieved great uniformity over large area (4-inch Si wafer) and excellent step coverage on the 3D structure. Moreover, field effct transtor devices using single phase SnS$_2$ channel layers were investigated. We expect that this SnS$_2$ process would provide decisive opportunities for realizing next genenration nano electronic devices.

2:15pm **NS-MoA-4 ALD Tin Sulfide Thin Films and Their Device Applications**, ***Hyeongsu Choi***, *S Shin, J Lee, H Park, N Lee, C Jung, H Cho, H Jeon,* Hanyang University, Republic of Korea

Tin disulfide (SnS$_2$) and tin monosulfide (SnS), two representative tin sulfide materials, are emerging as two-dimensional (2D) materials after appearances of graphene and black phosphorus. SnS$_2$, an n-type semiconductor, has hexagonal structure that individual layers consisting of three atomic planes, such as CdI$_2$. It has been studied, due to the same crystal structure and similar semiconductor characteristics with transition metal dichalcogenides(TMDCs) . In the case of SnS, it has been attracting attention as an absorber layer of solar cell due to its appropriate band gap and absorption coefficient. Recently, SnS is also studied as a 2D material due to orthorhombic double layer structure like black phosphorus. However, very few studies have been done to obtain tin sulfide thin films with current thin film fabrication methods such as chemical vapor deposition (CVD) and atomic layer deposition (ALD).

In this study, we will present about results of high crystalline tin sulfide thin films deposited by ALD method. High crystalline SnS$_2$ thin films were obtained by phase transition from the high crystalline SnS thin films. SnS thin films were deposited on Si/SiO$_2$ substrate with tetrakis(dimethylamino)tin (Sn[N(CH$_3$)$_2$]$_4$, TDMASn) and hydrogen sulfide (H$_2$S) at 170°C, and subsequent H$_2$S annealing was performed in the tube furnace at 450°C. We then characterized the crystal structures, chemical bonding states, and optical band structures with XRD, XPS, TEM and UPS. In addition, we fabricated the field effect transistors (FETs) with SnS and SnS$_2$ thin films, and compared their switching device characteristics. Consequently, changes in the crystal structure and chemical state from SnS to SnS$_2$ were examined by XRD and XPS, respectively. After transition from SnS to SnS$_2$, the optical bandgap was measured and increased from 1.35 to 2.70 eV, but absorption coefficient decreased from ~10^5 to ~10^4 cm^{-1} at visible region. Transition of electrical characteristic from p-type to n-type were also observed, and highly crystalline orthorhombic and hexagonal layer structures of two tin sulfide thin films were directly shown in the images of high resolution-transmission electron microscopy (HR-TEM). The electrical characteristics of FETs of SnS and SnS$_2$ thin films showed on-off current ratios of 8.8 and 2.1 X 10^3 and mobilities of 0.21 and 0.014 cm^2/Vs, respectively. These deference of switching device characteristics will be discussed based on the major carrier concentrations of the SnS and SnS$_2$ thin films.

2:30pm **NS-MoA-5 Synthesis of 2D MoS$_2$ and MoS$_2$-Graphene Heterojunction by Atomic Layer Deposition**, ***Youngjun Kim***, *D Choi, W Woo, J Lee,* Yonsei University, Republic of Korea; *G Ryu, Z Lee,* Ulsan National Institue of Science and Technology, Republic of Korea; *J Ahn, J Park, H Kim,* Yonsei University, Republic of Korea

The effective synthesis two-dimensional molybdenum disulfides (2D MoS$_2$) with atomically controlled thickness is essential for their use in electronic devices. In this work, 2D MoS$_2$ was grown directly on SiO$_2$ and Graphene using Atomic Layer Deposition (ALD) with MoF$_6$ and H$_2$S. We investigated the growth characteristics of the Molybdenum precursor (MoF$_6$) by Raman spectroscopy and microscopy. By using MoF$_6$ precursor, 2D MoS$_2$ synthesized also on the graphene forming MoS$_2$/graphene heterostructure. The optical microscopy, Raman spectroscopy, photoluminescence (PL), X-ray photoemission spectroscopy (XPS), and transmission electron microscopy (TEM) measurements indicate that the ALD MoS$_2$ is layered structure with good uniformity, stoichiometry and controlled layer number. Furthermore, we demonstrated the electrical properties of 2D MoS$_2$ and optical characteristics of MoS$_2$/Graphene 2D heterostructure. This fabrication process could also provide an opportunity for the production of burgeoning MoS-$_2$ and other Transition Metal Dichalcogenides (TMD) for nanoelectronics and optoelectronics.

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

Layered two dimensional (2D) transition-metal dichalcogenides (TMDs) are finding use in nanoelectronic and optoelectronic applications due to their thickness dependent optical and electrical properties. Scalable fabrication of TMD-based devices requires deposition routes that can produce continuous and uniform films with sub-nanometer thickness control. Atomic layer deposition (ALD) is a highly promising route for the synthesis of 2D TMDs and heterostructures due to digital thickness control achieved by sequential self-limiting chemistry. Another advantage of ALD is that thickness control and the structural development of the films can be decoupled by separating the deposition and crystallization steps. We take advantage of these process attributes to prepare ALD MoS$_2$/WS$_2$ nanolaminates that would be otherwise difficult to grow by conventional chemical vapor deposition approaches. We have recently characterized the self-limiting deposition of MoS$_2$-containing amorphous films from bis(tert-butylimido)-bis(dialkylamido)Mo and 1-propanethiol. Using the homologous W precursor, we now report on the development of MoS$_2$/WS$_2$ nanolaminates, which offer a convenient means to tune the optical and electronic properties of few-layer TMD systems.

We deposited thin films using (N^{t}Bu)$_2$(NMe$_2$)$_2$M and 1-propanethiol, where M=(Mo,W), at wafer temperatures of 300°C to 400°C on SiO$_2$/Si substrates. As-deposited and sulfur annealed films were evaluated using spectroscopic ellipsometry, grazing incidence X-ray diffraction (GIXRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and cross-sectional transmission electron microscopy (TEM). As-grown films were an amorphous matrix of metal sulfides mixed with unreacted ligands, evident as carbon and nitrogen impurities as measured by XPS. As-deposited films were annealed to produce 2H-MoS$_2$ and 2H-WS$_2$ under a sulfur atmosphere, which also removed residual ligands. Nanolaminates were prepared by alternating the injections of the two metal precursors at a fixed Mo:W ratio to achieve different film compositions. The overall Mo:W ratio in the film was found to follow the pulsing ratio of the two metal precursors. Upon annealing at 850°C, we obtained films that exhibit Raman modes associated with 2H-MoS$_2$ and 2H-WS$_2$, suggesting that distinct phases, rather than a solid solution, were favored. Relative changes in the overall Mo:W composition were also maintained in the annealed films, indicating that final material properties in TMDs could be controlled by implementing ALD nanolaminates. We will also discuss the implications of film incubation during laminate cycling and subsequent effects on film chemistry.

3:00pm **NS-MoA-7 Wafer-scale MoS$_2$ Monolayer Grown on SiO$_2$/Si Substrate by Modified Atomic Layer Deposition**, ***Dae Hyun Kim***, *D Kim, T Seok, H Jin, T Park,* Hanyang University, Republic of Korea

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) have gained great attention due to its potential applications in electronic and optical devices. Among the 2D-TMDCs family, MoS$_2$ monolayer has been extensively studied due to high carrier mobility over 200 $cm^2v^{-1}s^{-1}$and flexibility. The electronic band structure is transformed from indirect (~1.2 eV) to direct (~1.9 eV) with decreasing the thickness of MoS_2 from bulk to mono layer (0.6 nm), that is suitable for electronic and optical applications. However, most of studies on 2D MoS_2 have utilized small flakes prepared by mechanical exfoliation and chemical vapor deposition with a transfer technique onto SiO_2 substrate due to the difficulty of direct growth of uniform MoS_2 monolayer on SiO_2 substrate.

In this study, an uniform MoS_2 monolayer was grown directly on 4-in. SiO_2/Si substrate by modified atomic layer deposition technique with extremely-precise thickness controllability and uniformity, which were confirmed by various tools such as Raman shift, photoluminance (PL) mapping and atomic force microscopy. The detailed experimental results will be presented.

3:15pm **NS-MoA-8 X-ray Absorption Spectroscopy of Amorphous and Layered ALD Molybdenum Sulfide Films Prepared using MoF_6 and H_2S***, Steven Letourneau,*** Boise State University*; M Young,* Argonne National Laboratory*; N Bedford,* National Institute of Standards and Technology*; Y Ren, A Yanguas-Gil, A Mane, J Elam,* Argonne National Laboratory*; E Graugnard,* Boise State University

Atomic layer deposition of molybdenum disulfide has recently been demonstrated using various chemistries. Many of these ALD processes, when performed at low temperatures, yield amorphous films and require annealing to obtain layered MoS_2. Raman spectroscopy is one of the most widely used characterization techniques for 2D materials, but these amorphous structures typically do not show the in-plane and out-of-plane vibrational modes of a layered structure. Characterizing these amorphous films is difficult, but crucial if ALD is to succeed in making monolayer or few layer MoS_2. In this work, we use X-ray absorption spectroscopy (XAS) and pair distribution function (PDF) measurements to investigate the as-deposited structure of ALD MoS_2 films prepared using MoF_6 and H_2S at 200°C. Model fits of the extended X-ray absorption fine structure (EXAFS) regime were used to infer the local coordination around the Mo atom centers. While the Mo-S coordination in ALD MoS_2 films seems to fit well with MoS_2 reference structures, the Mo-Mo coordination number was much lower than expected. In addition, PDF measurements performed to examine the bonding pairs suggested small clusters of trigonally prismatic MoS_2 with polysulfides forming between the sulfur atoms. Annealing these films at 400°C in H_2S yielded layered MoS_2, which was confirmed by transmission electron microscopy and X-ray photoelectron spectroscopy, suggesting that thin, layered MoS_2 films are possible using MoF_6 and H_2S.

ALD Applications
Room Premier Ballroom - Session AA-MoP
ALD Applications Poster Session

AA-MoP-1 Highly Visible Light Photocatalytical Activity of Ozone-Assisted Atomic Layer Deposited Fe_2O_3 Coated TiO_2 Powders*, X Zhao,* Nanjing Unviersity, China*; **Yan-Qiang Cao**, A Li,* Nanjing University, China

With the rapid development of modern industry, environmental pollution has become a serious issue. TiO_2, as an efficient and safe photocatalyst, can only absorb ultraviolet light. In order to make full use of visible light, the doping and modification of TiO_2 powders have drawn great attention. Herein, Fe_2O_3 coated TiO_2 powders was prepared by ozone-assisted atomic layer deposition (ALD) strategy, taking advantage of its 3D conformality, precise control of film thickness and flexible surface modification. Fe_2O_3 coating with various ALD cycles of 200-800 was derived using $Fe(Cp)_2$ and O_3 as precursors of iron and oxygen at 250ºC, respectively. 400-cycle Fe_2O_3 coated TiO_2 sample exhibits optimal photocatalytic activity with ~72% degradation of methyl orange in half an hour under illumination of visible light, much higher than pure TiO_2 of less than 2%. X-ray diffraction results indicate that there is no significant change in the particle size and anatase structure of TiO_2 powder coated with 400 Fe_2O_3. Instead, ultrathin Fe_2O_3 amorphous layer is formed on the surface of TiO_2 with reduced bandgap from 3.2 eV to 2.9 eV and improved visible light adsorption. Mott-Schottky curves confirm the formation of Fe_2O_3/TiO_2 p-n junction could suppress the electron-hole recombination. Above all, compared to plasma-enhanced ALD, ozone-assisted ALD shows better depostion efficiency in powder samples and is more suitable for the surface modification of TiO_2 powders.

Keywords: Ozone-assisted atomic layer deposition; TiO_2 powders; Fe_2O_3 coating; Photocatalytic activity; p-n heterojunction

AA-MoP-2 Synaptic Behaviors of $Pt/HfO_2/HfO_x/TiN$ Bilayer-structure Memristors by Atomic Layer Deposition*, **Chang Liu**, Y Cao, A Li,* Nanjing University, China

HfO_x-based resistive random access memory shows remarkable potential for next-generation non-volatile memories, however it is not optimized as synaptic devices for neuromorphic system applications. Herein, we focused on the fabrication and synaptic behaviors of HfO_2/HfO_x bilayer-structure memristive devices. 4-nm nonstoichiometric HfO_x films on TiN-coated Si substrates were prepared using $Hf[N(C_2H_5)CH_3]_4$ (TEMAH) and hydrogen plasma by plasma-enhanced atomic layer deposition (PEALD), while 2-nm stoichiometric HfO_2 films were deposited using TEMAH and H_2O precursors via thermal ALD. X-ray photoelectron spectroscopy analyses shows that the atomic ratio of Hf: O in HfO_2 and HfO_x active layers is 1: 2.00-2.05 and 1: 1.60-1.74, respectively, indicating HfO_2/HfO_x bilayer-structure memristors have been obtained.. The $Pt/HfO_2/HfO_x/TiN$ memistive cells exhibit bipolar resistive switching features with 20 intermediate resistance states by applying 1 V to 3 V reset voltages with 0.1 V interval, based on the migration/diffusion of oxygen vacancies. Several essential synaptic functions are simultaneously achieved in such a bilayer-structure device, such as nonlinear transmission characteristics, spike-timing-dependent plasticity, and long-term/short-term plasticity.

Keywords: memristor, bilayer-structure, atomic layer deposition, oxygen vacancy, synaptic behaviors

AA-MoP-3 Wafer-scale Single-domain-like Graphene with Enhanced Electronic Transport Properties by Defect-selective Atomic Layer Deposition of Hexagonal ZnO*, M Sung, **JinWon Jung**,* Hanyang University, Republic of Korea

Large-area graphene films produced by means of chemical vapor deposition (CVD) are polycrystalline and thus contain numerous grain boundaries that can greatly degrade their performance and produce inhomogeneous properties. A better grain boundary engineering in CVD graphene is essential to realize the full potential of graphene in large-scale applications. Here, we used atomic layer deposition (ALD) technique to deposit ZnO selectively on grain boundaries of the CVD graphene so as to depress the highly resistive effect of the grain boundaries. The ZnO ALD / Graphene film showed the electrical properties—a sheet resistance of 68 Ω/□, a field effect mobility of 7,460 and 2,610 $cm^2 \cdot V^{-1} \cdot s^{-1}$ for hole and for electron, respectively. A defect-selective atomic layer deposition (ALD) for stitching grain boundaries of CVD graphene with conductive ZnO so as to increase the connectivity between grains. In the present ALD process, ZnO with a hexagonal wurtzite structure was selectively grown mainly on the defect-rich grain boundaries to produce ZnO-stitched CVD graphene with well-connected grains. For the CVD graphene film after ZnO stitching, the inter-grain mobility is notably improved with only a little change in the free carrier density. We also demonstrate how ZnO-stitched CVD graphene can be successfully integrated into wafer-scale arrays of top-gated field-effect transistors on 4-inch Si and polymer substrates, revealing remarkable device-to-device uniformity.

AA-MoP-4 Atomic Layer Deposition Under in situ Ultraviolet Radiation for Highly Conductive Air Stable ZnO Thin Film Fabrication*, **Hong-rho Yoon**, M Sung,* Hanyang University, Republic of Korea

Compounds of ZnO is very attractive compound semiconductors due to their wide band gap (~3.3eV) characteristics and large exciton binding energy (60meV). However, ZnO preparing by low temperature atomic layer deposition (ALD) has low conductivity. Here, we report the highly transparent, and highly conductive air-stable thin film of ZnO using ALD at low temperature under in situ UV irradiation of the growing film. X-ray photoelectron spectroscopy (XPS) was used to reveal that the UV irradiation generates oxygen vacancies, partially removes O–H bonds, and thereby improves the electrical conductivity. Thus, the in situ UV irradiated ZnO film shows an electrical resistivity of 5.5 × 10-4 Ω cm, compairing to 0.25 Ω cm resistivity of the pristine ZnO film, and an optical transparency of nearly 90%. In addition, even on prolonged exposure of the film to air, it maintains high stability and conductivity against the degradation of the electrical conductivity.

AA-MoP-5 Annealing Temperature Modulated Interfacial and Electrical Properties of PEALD-derived HfLaO/Si Stack*, **Duo Cao**, F Liu, H Shi, W Shi,* Shanghai Normal University, China*; X Cheng, L Zheng, L Shen, Y Yu,* SIMIT, Chinese Academy of Sciences, China*; J Wang,* University of California Los Angeles

HfLaO dielectric films have been shown to lead to significantly superior performance as the gate dielectric layer. Recent research on HfLaO has shown this material demonstrates a high crystallization temperature and a low leakage current while preserving a low equivalent oxide thickness (EOT) value. In this work, we investigated the effects of rapid thermal annealing on the interfacial and electrical properties of HfLaO films deposited on Si substrate. Films with different thicknesses were grown by plasma enhanced atomic layer deposition (PEALD) at 200°C with in situ pre-O_2, pre-NH_3 and post-O_2 plasma treatments. Films were treated with rapid thermal annealing (RTA) at a series of temperatures. The HfLaO films retain its insulating characteristics and are thermally stable even after annealing at 800 °C. X-ray photoelectron spectroscopy (XPS) spectra indicates that the main component of the interfacial layer is silicate without any silicide. Leakage current-voltage and capacitance-voltage characteristics of the MIS capacitors were obtained. Heat treatment can effectively improve the dielectric performance, such as increase of effective permittivity, reduction in ΔV_{fb} and no obvious frequency dispersion. However, the increase of annealing temperature leads to the increase of leakage current density, which is due to the decrease of the conduction band offset (ΔE_c) and further crystallization of the samples. These investigation results might provide the guidance for the performance optimization of high k gated dielectrics to meet the requirements of future complementary-metal-oxide-semiconductor (CMOS) devices.

AA-MoP-6 Atomic Layer Deposition of Yttrium Oxide using Heteroleptic Y Precursors*, **Daehyeon Kim**, J Lee,* Air Liquide Laboratories Korea, Republic of Korea

Rare earth based oxides are of interest for their potential application in future logic and memory technologies, and Yttrium oxide (Y_2O_3) is well-known as high-k material for metal gate transistor and a dopant for high-k materials. Not only semiconductor applications, usage for non-semiconductor applications (such as coating material) has been also considered. In past studies, heteroleptic precursors which have alkylcyclopentadiene and amidine ligands, $Y(RCp)_2(R'\text{-amd})$, have been developed to aim to be liquid and to enhance its volatility and thermal stability. In this work, two heteroleptic precursors, $Y(EtCp)_2(iPr\text{-amd})$ and $Y(iPrCp)_2(iPr\text{-amd})$, and one homoleptic precursor, $Y(EtCp)_3$, were evaluated and their physical properties and ALD results were compared. Both $Y(EtCp)_2(iPr\text{-amd})$ and $Y(iPrCp)_2(iPr\text{-amd})$ showed high thermal stability and clean TG evaporation. $Y(EtCp)_2(iPr\text{-amd})$ is liquid and showed the highest vapor pressure (1Torr at 150ºC) among three precursors. Atomic layer deposition (ALD) of Y_2O_3 films was performed using these precursors with various oxidant such as ozone, oxygen, and water. $Y(EtCp)_2(iPr\text{-amd})$ gave flat ALD window up to 450ºC with a growth rate of 0.8~1.0Å/ cycle. X-ray photoelectron spectroscopy (XPS) showed that obtained thin film was pure and carbon and nitrogen impurities were below the detection limits. Step coverage of the film was also good (~100%, AR= 1:20) at 350, 400°C.

AA-MoP-7 Atomic Layer Deposition Y_2O_3 on GeSn/III-V for Application to MOSFET Common Gate Process*, C Chu,* ***Guang-Li Luo****, S Chen, W Wu, W Yeh,* National Nano Device Laboratories, Republic of China

Integration technology between GeSn and GaAs is attractive due to high GeSn hole mobility (>1500 cm^2/Vs) and high III-V electron mobility (8500 cm^2/Vs, GaAs) as well as the CMOS compactness (GeSn p-channel and III-V n-channel MOSFETs [1, 2]. Sub-nm equivalent oxide thickness (EOT) gate stacks are required to keep the intrinsically high performance of GeSn and III-V. The focus here is on finding suitable high permittivity (k) dielectric (k>20) to form a gate stack with low interface state density and EOT. The most perilous issue is engineering a high-quality interface between GeSn /III-V and the high-k dielectric, that is, passivation of the GeSn /III-V surface. An interfacial layer (IL) either intentionally or unintentionally formed during the high-k dielectrics deposition process is usually necessary for achieving high electrical performance of Ge and III-V based MOS devices, but its presence could increase EOT, and is not beneficial to device performance. Therefore, the IL has to be as thin as possible, and permittivity for dielectric has to be as high as possible. Atomic layer deposition (ALD) is an important tool to fabricate these proposed IL because it offers precise, monolayer-level thickness control. In order to further improve on interface properties of Y_2O_3/ GeSn and III-V interface, it is quite important to clarify the dominant factor determining the interface properties. Therefore, studies on interface structures and electrical interface properties are necessary. This paper aims to grow Y_2O_3 film by atomic layer deposition (ALD). It can produce high quality, high smooth surface and good stoichiometry Y_2O_3 film due to the self-limited growth mechanism. In this work, Pt/Y_2O_3/GeSn and Pt/Y_2O_3/GaAs capacitors similar to MOSFET gate stack process were fabricated. High interface states density and capacitor leakage current can be reduced by chemistry treatment. Capacitance-voltage (C-V) was done to discuss the electrical characteristics, such as equivalent oxide thickness (EOT), hysteresis reduction.

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AA-MoP-8 Carbon Textile Decorated with Redox-Active Vanadium Hybrid for Flexible Supercapacitors*,* ***Do Van Lam****, S Lee, J Kim,* Korea Institute of Machinery and Materials

We demonstrate that, via V_2O_5 coating by low temperature atomic layer deposition and subsequent pyrolysis, ubiquitous cotton textile can readily turn into high-surface-area carbon textile fully decorated with pseudocapacitive V_xO_y/VC widely usable as electrodes of high performance supercapacitor. We found that carbothermic reduction of V_2O_5 ($C + V_2O_5 \rightarrow C' + VC + CO/CO_2(g)$) leads to chemical/mechanical activation of carbon textile, thereby producing high-surface-area conductive carbon textile. In addition, sequential phase transformation and carbide formation ($V_2O_5 \rightarrow V_xO_y \rightarrow VC$) occurred by carbothermic reduction trigger decoration of the carbon textile with redox-active V_xO_y/VC. Thanks to the synergistic effect of electrical double layer and pseudocapacitance, the supercapacitors made of the hybrid carbon textile exhibited far better energy density with excellent cycling stability than the carbon textile simply undergone pyrolysis. Our method could open up a promising and facile way to synthesize hybrid electrode materials for electrochemical energy storages possessing advantages of both electrical double layer and pseudocapacitive material.

AA-MoP-9 MAPS (Mecaro's Advanced Precursors System)-Ti Series: Atomic Layer Deposition of TiN or TiO_2 Films Using New Titanium Precursors*,* ***Ho Hoon Kim****, D Lee, S Cheon, Y Yoo, S Ha, J Kim, Y Byun,* MECARO Company, Republic of Korea

Size decrease demand in semiconductor devices has been increased for the last few decades. A thinner barrier layer with high uniformity and conformality and also excellent step coverage is needed for optimum layer filling.[1] For these reasons, atomic layer deposition (ALD) has been introduced as a method to deposit conformal thin films in a structure having high aspect ratio, and the famous materials deposited by ALD are Al_2O_3, HfO_2, ZrO_2, ZnO, and TiN. Selection of appropriate precursor plays a critical role in the success of final ALD process since high temperature deposition is required, high thermal stability precursors are required as well. Titanium dioxide (TiO_2) is an attractive candidate for several thin film applications, such as high dielectric constant material for electronic devices. TiO_2 is also a constituent of several important multi-metal oxide systems, such as strontium titanates (STOs), barium strontium titanates (BSTs), and lead zirconium titanates (PZTs), for dielectric and ferroelectric applications.[2] ALD processes for producing metal containing thin films comprise feeding into a reaction space vapor phase pulses of metal containing cyclopentadienyl-based ligands precursors as a metal source material. The quest for alternatives to cyclopentadienyl-based ligands has led to *N*-centered donor ligands in various fields of organometallic and coordination chemistry.

In this work, series of titanium complex (MAP-Ti series) having amine derivative have been synthesized and characterized as new precursors for ALD. The one of these new compounds was found to have properties well-suited for use as precursors for ALD of thin films. It has high volatility, high thermal stability, and high reactivity. The experimental details of film deposition and characterization will be reported briefly.

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AA-MoP-10 MAPS (Mecaro's Advanced Precursors System): Atomic Layer Deposition of TaN and NbN Thin Films using Noble Metal Precursors*,* ***Woori Bae****, Y Byun, S Cheon, H Kim, M Kim, S Ha, J Kim,* MECARO Company, Republic of Korea

New materials are needed to meet the requirements of the continuous downscaling of microelectronic devices. The copper-based interconnects in the next generation ultra large scale integration (ULSI) microelectronics is creating significant challenges for new barrier materials. Transition metal nitrides or metal silicides are considered the most promising diffusion barrier materials[1] for next generation ULSI microelectronics. In this work, tantalum and niobium nitride films were deposited with reducing agent or plasma and characterized, using newly designed MAP-Nb01 and MAP-Ta01 precursors which are characterized by various spectroscopies. The main goal of the present study was to deposit Nb and Ta metal nitride films by atomic layer deposition (ALD)[2,3] method. Films deposited by ALD have excellent conformality and large area uniformity in addition to accurately controlled film thickness.

Protonated lithium amides together with other synthetic strategies have been extensively used to generate the imido ligand, neutral niobium and tantalum complexes have been synthesized and their functionalities were used as both ancillary and reactive sites. The diffusion barrier performance and gate electrode properties of TaN and NbN will be described in some detail. After an account of the experimental details of film deposition and characterization, the results will be reported briefly.

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AA-MoP-11 The Impact of O_2/N_2 Ratio in O_3 Based TiO_2-Active Layer in Vacancy-modulated Conductive Oxide*,* ***Elie Schapmans****,* IMEC, Belgium

Ozone is an effective oxidant used in atomic layer deposition of dielectric oxides. At imec, we have successfully developed ALD processes such as TiO_2 ALD with both O_3 and H_2O. The O_3 based TiO_2 process resulted in high k Rutile phase when grown on Ru substrate or Anatase phase when grown on TiN substrate [1]. In both cases, applications in microelectronic devices have been demonstrated such as in MIM capacitors [1] and a resistive switching memory device with nonfilamentary switching mechanism called Vacancy-modulated conductive oxide VMCO [2]. Thermal ALD films were grown on blanket Si 300mm diameter wafers in a cross flow single wafer reactor at 250°C and 210°C deposition temperatures using Ti(OCH3)4 and O_3 as precursors. O_3 was delivered at a fixed density of 225g/m^3 and formed with a different O_2/N_2 ratio. The TMEIC O_3 generator made it possible to explore a complete range of O_3, formed from N_2 free up to highly N_2 doped O_3 at a fixed O_3 density. The saturation behavior and the growth per cycle of TiO_2 film were determined prior to the integration in the VMCO stack. This stack consists of a 10nm PVD TiN bottom electrode, a 5-10nm amorphous Si barrier layer followed by a ~ 8nm TiO_2 switching layer and 100nm PVD TiN top electrode. We observed a gradual increase in growth rate by lowering the N_2 gas flow used for O_3 generation, up to a value of 0.04nm/cycle in the case N_2 free O_3 based TiO_2. The growth rate also slightly decreases with deposition temperature reduction from 250°C to 210°C. All TiO_2 films were amorphous as deposited regardless the N_2/O_2 ratio or deposition temperature employed. (Fig1) However, significant differences can be demonstrated via electrical measurements depending on the process conditions. In terms of breakdown voltage, we see an improvement of more than 1V with an high N_2 flow during O_3 generation at 210°C. The robustness of the stacks decreases in the case of N_2 free O_3 based TiO_2.(Fig2)

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AA-MoP-12 Effect of O_2 Plasma Exposture Time on Al_2O_3/Si Interface Properties during Al_2O_3 Formation using PAALD

Kwan Hong Min, Korea Institude Energy Reseach, Republic of Korea*; J Lee, M Jeong, S Choi,* Korea Institute of Energy Research, Republic of Korea*; M Kang, J Lee, S Park,* Korea Institute Energy Research, Republic of Korea*; D Kim,* Korea University, Republic of Korea*; H Song,* Korea Institute Energy Research, Republic of Korea

Thermal ALD and PAALD(Plasma Assisted ALD) are widely used as methods for Al2O3 deposition on Si surface. PAALD has the advantage of faster deposition rate compare to thermal ALD. On the other hand, it has disadvantage of the damage to Si surface because of plasma intensity as reaction energy for O2 dissociation. In this study, the effect of O2 plasma exposure time on Si interface was investigated. O2 plasma exposure time was varied from 0.5 to 10 second. Passivation properties such as carrier lifetime, implied voltage were measured by Qusai-Steady-State Photoconductance(QSSPC) and interface properties were analyzed by Capacitance-Voltage(C-V) characteristics. According to increasing O2 plasma exposure time, it is confirmed that passivation properties were decreased. Especially, 'hump' property was observed, which is known to be caused by the interface trap during C-V measurement at low frequency. Therefore, we could expect that the interface properties would be decreased. To confirm interface properties, fixed charge density and interface trap density of Al2O3/Si interface were extracted by C-V and conductance method. As a result, it was found that an increase of O2 plasma exposure time little affected on the fixed charge density but the interface trap density was much affected. Therefore, optimization of plasma condition is important for Al2O3 deposition using PAALD.

AA-MoP-13 Effect of Mechanical Stress on Ferroelectric Properties of Fully-Atomic Layer Deposition Processed TiN/$HfZrO_x$/TiN Stacks

C Choi, ***Myeong Gyoon Chae,*** Hanyang University, Republic of Korea

Due to the device scaling limit, alternative materials and device structures have been investigated to continue performance enhancement and power consumption reduction. Among them, Ferroelectric Random Access Memory (FeRAM), Ferroelectric Field Effect Transistor (FeFET), and Negative Capacitance Field Effect Transistor (NC-FET) are being actively researched as promising alternatives to present DRAM, FINFET, and NAND Flash. As a result, ferroelectric materials have garnered strong interest further. In the early step of research, conventional ferroelectric materials (PZT, BTO, SBT) were actively studied. However, due to poor scalability and bad electrical stability such as higher leakage and breakdown, which are considered as fundamental problems of these materials, CMOS-compatible hafnium dioxide (HfO_2) based ferroelectric materials have been emerging actively.

In this study, we fabricated all atomic layer deposition (ALD) processed ferroelectric capacitor based on doped-HfO_2. To investigate the effect of mechanical stress on ferroelectricity, top electrode titanium nitride (TiN) thickness was controlled. In the case of a device with a thicker TiN, a larger switching polarization and lower ferroelectric saturation voltage were observed compared to a device with a thin TiN. It can be seen that the thick electrode acts as a stressor to inhibit the formation of the monoclinic phase during crystallization and generates a ferroelectric orthorhombic phase. Our finding indicates that performance of ferroelectric materials based devices can be improved by enhanced ferroelectricity as a result of optimizing mechanical stress and thermal budget.

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AA-MoP-14 Atomic Layer Deposition of SnTe for Dopant Application of Phase-change Materials

Eui Sang Park, *C Yoo, W Kim, Y Lee,* Seoul National University, Republic of Korea*; J Jung,* Soulbrain, Republic of Korea*; C Hwang,* Seoul National University, Republic of Korea

A phase-change random access memory (PCRAM) is one of the most promising candidates for the next-generation non-volatile solid-state memory. PCRAM is known for its low cost, high stability, and high compatibility with complementary metal–oxide semiconductor (CMOS) technology. Nevertheless, there are some commercialization issues that must be met such as reduction of switching power, faster phase transition speed, the stable resistivity in the amorphous state. Incorporation of phase-change materials (PCM) with 3D fabrication technology is another challenge to increase the memory density. The 3-D vertical structure was suggested for highly integrated array of cells in vertically integrated structure.[4] In this vertical geometry, atomic layer deposition (ALD) can deposit a PCM film with its excellent step coverage due to the self-limiting growth mechanism.

In this work, an ALD process to form SnTe films was developed . According to the previous reports[1-2], SnTe is proposed as a dopant or superlattice material to increase switching speed and reduce switching power owing to the weaker bond strength of Sn–Te (359.8 kJ mol−1) compared to the Ge–Te (397 kJmol−1).[3] Relatively weak bond strength in phase change material could significantly increase the crystallization speed. Also, the resistivity in an amorphous state can be decreased with increasing Sn content.[5] Precursors of $[(CH_3)_2N]_4Sn$ and $(Me_3Si)_2Te$ were adapted for SnTe deposition. The process was studied in detail to verify the ALD behavior of SnTe film. Figure 1 shows that the growth of SnTe film was saturated at around 30 $ng{\cdot}cm^{-2}cy^{-1}$. Sn:Te ratio of the film was also saturated at the slightly Te-rich condition. $Ge_xSn_yTe_z$ ternary deposition was performed using $GeTe_2$ to confirm the doping possibility of Sn. $GeTe_2$ was deposited with $Ge(Oet)_4$ and $(Me_3Si)_2Te$ precursors for Ge and Te.[6] Figure 2 shows the $Ge_xSn_yTe_z$ ternary deposition results through the alternating deposition sequences of the $GeTe_2$ and SnTe layers. Apart from the initial conjecture, the film composition lye on $GeTe_2$-$SnTe_2$ tie line rather than $GeTe_2$-SnTe tie line, suggesting that the complicated chemical interaction is involved in the ternary film growth. Detailed discussions on the growth behavior will be made in the presentation.

AA-MoP-15 Atomic-Layer-Deposited LiAlO Protective Layer for Li Metal Anode in Li-ion Secondary Batteries

H Lee, ***Dae Woong Kim,*** *T Park,* Hanyang University, Republic of Korea

Li metal anode for Li-ion secondary batteries has been recently developed to enhance the battery performances. However, the physicochemical instability of Li causes a dendrite formation at the electrode surface by electrochemical reaction with electrolyte during charging/discharging cycle. Even though several protective layers were suggested, most of them have common problems of conformality and low conductivity. To address this problem, we suggest atomic-layer-deposited (ALD) Li-Al-O protective layer which is free from physicochemical degradation by lithiation during charging/discharging cycle. The addition of Li ions to metal oxides such as Al_2O_3 tends to increase the ionic conductivity.[1] ALD Li-Al-O thin films with various compositions were grown by repeated sub-cycle of ALD LiOH and Al_2O_3, and thickness was measured by spectroscopic ellipsometry (Fig. 1). The process temperature was controlled below 100°C for avoiding degradation of Li metal during ALD. The composition of thin films was estimated by X-ray photoelectron spectroscopy. The ionic conductivity of thin films was measured by electrochemical impedance spectroscopy. The experimental results will be presented in detail.

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AA-MoP-16 Effect of Growth Temperature on the Structural and Electrical Properties of i-ZnO by Atomic Layer Deposition Method

***Yeonbae Shin**, V Arepalii, J Kim,* Cheongju University, Republic of Korea

Highly resistive i-ZnO can play a critical role to prevent leakage current paths from CIGS thin film solar cells. In this work, we demonstrated the effect of growth temperature on the structural and electrical properties of i-ZnO using atomic layer deposition (ALD) method on to both Si (100) and soda lime glass (SLG). The deposited films were characterized by performing scanning electron microscopy (SEM), X-ray diffraction, UV-Visible spectroscopy, and four-point probe measurements. The four-point probe measurement revealed that samples grown at 80 showed higher resistivity of 10^6 Ω.cm whereas sample grown at 180 showed low resistivity of 10^{-3} Ω.cm. We will further discuss the device characteristics of CIGS solar cells with using both highly resistive and low resistive ZnO.

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Keywords: ZnO, ALD method, solar cells, growth temperature

AA-MoP-17 Atomic Layer Deposition of GeSe Films with Discrete Feeding Method for Ovonic Threshold Switch

***Woo Hyun Kim**, C Hwang,* Seoul National University, Republic of Korea

Phase-change Random Access Memory (PcRAM) is a strong candidate for the next-generation memory with characteristics of non-volatility, fast operating speed, and low power consumption. To overcome the existing limitations in the memory density of the PcRAM in 2D structure, the 3D-stackable memory of the crossbar array has been proposed as a promising solution. Despite the advances in 3D structural designs to scale down the memory, sneak current that frustrates accurate reading/writing of data in each cell remained a critical issue. The selector devices such as a P-N junction diode, metal-insulator-metal diodes, Ovonic Threshold Switch (OTS) have been devised to minimize these errors in operation.

Among the options for the selector device, OTS based on the volatile voltage snapback effect of amorphous chalcogenides possesses several desirable characteristics: bidirectional switching, processability for 3D structure and controllable threshold voltage. Among the materials that can be used as OTS, GeSe has strong glass forming ability (T_{cry}~340 ºC) compared to GeTe (T_{cry}~150 ºC) with a simple binary composition. Here, a new method for depositing GeSe films by Atomic Layer Deposition (ALD) was described in which $HGeCl_3$, $[(CH_3)_3Si]_2Se$ were used as Ge-, Se-precursor, respectively. The precursors formed the films through a ligand exchange reaction at a low substrate temperature of 70-150 °C . However, the pseudo-saturation behavior of the ALD, which takes a long time to achieve the saturation growth rate, was observed due to the physisorbed precursor and byproduct molecules on the reaction sites. To overcome slow saturation and excessive use of the Ge-precursor, we applied Discrete Feeding Method (DFM) where $HGeCl_3$ was supplied multiple times consecutively with subdivided pulse times. The ALD without DFM refers to a conventional ALD process where Ge and Se pulse and purge were injected alternatively. The ALD with DFM, by comparison, divides the total Ge pulse and purge times into several shorter times. DFM led to saturation of GeSe growth rate at a much shorter total injection time of Ge precursor and improved the morphological/chemical qualities and electrical performance of the film. Also, these GeSe films exhibit short switching time of ~40 ns, ON/OFF ratio of ~10^7, the selectivity of ~10^4, and the OTS behavior consistent with the modified Poole-Frenkel (PF) mechanism in the OFF state. The ALD method of GeSe films will contribute to the fabrication of 3D integration memory as selector device for preventing sneak current.

AA-MoP-18 Low-temperature Atomic Layer Deposition of Hafnium Oxides using NH_3 as the Catalyst.

***Nak-Kwan Chung**, Y Kang, S Kim, J Yun, J Kim,* Korea Research Institute of Standard and Science (KRISS), Republic of Korea

We have presented low-temperature preparation of hafnium oxides (HfO_2) by atomic layer deposition (ALD). The hafnium oxide thin films were deposited from tetrakis ethylmethylamino hafnium (TEMAHf) as the Hf precursor, ozone (O_3) as the reactant, and NH_3 as the catalyst on 200 mm silicon wafers at substrate temperatures from 50 to 300°C. The properties of HfO_2 films were investigated by scanning electrom microscopy, X-ray photoelectron spectroscopy, and X-ray deflection. The quality of the films formed at low temperature of 50°C using the combination of O_3 and NH_3 compares well with deposition at higher temperatures (350°C) using O_3 only.

AA-MoP-19 Electrical Properties of Al-doped $SrTiO_3$ Films Grown by Atomic Layer Deposition on Ru Electrodes

***Sang Hyeon Kim**, C An, D Kwon, S Cho, S Cha, C Hwang,* Seoul National University, Republic of Korea

Atomic layer deposition (ALD) of Al-doped $SrTiO_3$ (STO) dielectric thin films were investigated in metal-insulator-metal capacitors for the dynamic random access memory application. STO thin films exhibit much higher dielectric constant compared with currently used ZrO_2-based films, but the leakage current density is higher due to their low band-gap energy. To decrease the leakage current density, several cycles of ALD-Al_2O_3 were inserted at the bottom portion of the STO film. Leakage current was increased with increasing insertion amount of Al_2O_3 for 2 ~ 5 cycles, and STO (110) peak on XRD was broadened as the Al_2O_3 layer was inserted. This is due to the deteriorated crystallization of the STO film during the ALD, which required higher post-deposition annealing (PDA) temperature. The higher PDA temperature induced nano-cracking of the STO film, which caused the leakage current increase. Therefore, only one cycle of the Al_2O_3 layer was adopted. The STO ALD was performed using $Sr(^iPr_3Cp)_2$ and $Cp^*Ti(OMe)_3$ [$Cp^* = C_5(CH_3)_5$] as the Sr- and Ti-precursors, using H_2O and O_3 as the oxygen source of the SrO and TiO_2 sub-layer growth, respectively, at a substrate temperature of 370^{o}C, according to the previous report. [1] $Al(CH_3)_3$ and O_3 were used for the Al_2O_3 ALD.

The investigation of the Al_2O_3 cycle insertion position from the bottom of the film to the top of the film showed that top insertion exhibited the leakage current reduction effect while maintaining the crystallinity of the entire STO thin film. As a result, the leakage current of the STO thin film with a thickness of 9nm decreased from 10^{-6} A/cm^2 to 10^{-8} A/cm^2 at 0.8V. The achieved minimum attainable equivalent oxide thickness (EOT) of the (top) RuO_2/STO/Ru (bottom) capacitor was ~0.7 - 0.8nm, with an acceptable leakage current density (~2.7 X 10^{-8}A/cm^2), which was possible in the films with thicknesses > ~12nm without the Al-doping. Compared with the Al-doping effect in TiO_2 [2], the same process induced a much more obvious degradation in the crystallinity of the STO, when the Al_2O_3 layer was inserted within the bulk STO layer. Further examination results of the physical and chemical properties of the Al-doped STO film will be presented.

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AA-MoP-20 Temperature Effect on Thermally Grown AlN Films by Atomic Layer Deposition

***Yong Kim**, M Kim, H Yun, W Jeong, B Choi,* Seoul National University of Science and Technology, Republic of Korea

Studies of resistive random access memory (RRAM) have been vigorously conducted due to advantages, such as low operating voltage, high reliability, and simple structure. Until now, most of the switching materials used in RRAM are oxide materials owing to its stability and abundance in nature. However, nitride materials, such as AlN, GaN, TaN_x as well as Si_3N_4 have been also confirmed to show resistive switching characteristics. Among them, AlN-based switching materials showed resistive switching phenomena with low energy and high speed by formation of Al-rich conducting channel owing to the generation of nitrogen vacancies. Moreover, AlN has a large band gap (~6.2eV), high thermal conductivity and dielectric constant. Therefore, AlN can be applied for high-k gate dielectric material, various functional layer and resistive switching layer for RRAM applications.

In this study, AlN thin film is deposited by thermal atomic layer deposition (ALD) that is self-limiting deposition technique through the ligand exchange of the precursor molecules and surface functional groups. This process uses the Trimethylaluminum (TMA) and NH_3 as a metal precursor and reaction gas, respectively. The growth rates according to growth temperatures are shown in Fig. 1(a), at the wafer temperature of 265, 274, 287, 307, and 335°C. The inset of Fig. 1(a) shows Arrhenius plot (1000/T) of the growth rate. Through the slope of this fitting line, the reaction activation energy of AlN (~55 kJ/mol) can be obtained. Physical and chemical properties of AlN films grown at the different temperatures are investigated by X-ray diffraction (XRD), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Fig. 1(b) shows the average concentration of each element in the AlN thin film. Decrease of oxygen and increase of nitrogen concentration can be observed as the deposition temperature increases. Also, the electrical properties of AlN films having the Al/AlN/Pt structure are studied. The DC I-V and J-E curve of the device are measured at room temperature. As a result, the conduction mechanism for the device is well fit into the Poole-Frenkel emission, where trap site can be attributed to the point defect, such as O_N and V_{Al} according to the trap depth energy.

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AA-MoP-21 Ultrathin ALD Ru Film Deposition using Discrete Feeding Method (DFM) and Electric Field Assisted ALD (EA-ALD)*, **Hyun Soo Jin**, T Park,* Hanyang University, Republic of Korea

Ruthenium (Ru) has been considered as a promising electrode material for next generation semiconductor devices due to its low resistivity (~ 7 μΩ · cm), high oxidation resistance, and existence of conductive oxide phase, RuO_2 (~ 30 μΩ·cm). **[1]** As a complicated 3-dimensional integration scheme has been developed recently for improving the degree of device integration, ultrathin (< 5 nm) and uniform Ru metal electrode is required. Even though atomic layer deposition (ALD) of Ru film was employed, it is difficult to achieve ultrathin and continuous thin film due to its island growth nature at the initial stage of growth. **[2]**

In this work, we demonstrate efficient Ru film growth using discrete feeding method (DFM) and electric field-assisted ALD (EA-ALD) technique, which enabled to reduce the critical thickness of continuous metal thin film by improving chemical adsorption efficiency and surface coverage at the initial stage of thin film growth. DFM eliminates the physisorbed precursor molecules on the chemisorbed screening the active sites for the following precursor molecules by using cut-in purging during a metal precursor pulse, which increased the density of Ru nuclei at the initial growth stage resulting in a lower resistivity. **(Fig.1)** EA-ALD enhances the nucleation of Ru by attracting the precursor molecules onto a substrate with the help of electric field applied to the substrate during precursor pulse. As a result, layer density of the Ru film increased, and thus the resistivity significantly decreased. **(Fig.2)**

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AA-MoP-22 Formation of Antireflection Structures on Silicon Substrates in Near-infrared Region using AlO_x/TiO_x Bilayer Grown by Atomic Layer Deposition*, **Yong Tae Kim**, J Heo,* Chonnam National University, Republic of Korea

Antireflection (AR) layers on Si were investigated for potential application in optical communication in the wavelength range of 1270–1330 nm. Essential Macleod program was used to find the optimal thickness of the AR structures using AlO_x/TiO_x bilayer schemes. Achievement of the reflectance less than 0.5% was simulated using AlO_x/TiO_x AR structures. For experimental demonstration, atomic layer deposition (ALD) was used for the growth of AlO_x and TiO_x. Average reflectance of 0.2% was achieved in the wavelength ranging from 1270–1330 nm using ALD-AlO_x/TiO_x on Si. Despite the low reflectance of 0.2%, transmittance of ~88%, which is slightly lower than expected, was obtained. Additional air annealing at 300 ^{o}C for 2 hr enabled the crystallization of amorphous TiO_x into anatase phase and it led to the improvement in transmittance up to ~99%. X-ray photoelectron spectroscopy analysis revealed that the oxidation state of Ti in TiO_x influences the absorption in the near-IR region.

AA-MoP-23 Optimization of RuO_2 Thin Films on NiO Nanostructures by Atomic Layer Deposition for Hybrid Capacitor*, **Chang-Min Kim**, S Kwon, S Lee,* Pusan National University, Republic of Korea

Developments of high-performance electrochemical energy storage device is a vital issue in world wide. Electrochemical supercapacitors are one of the most promising energy storage devices in comparison to lithium-ion batteries because it can provide a higher power density, faster charge/discharge rate, and longer working lifetime. In this regard, intense effort has been focused on the fabrication of electrical double layer supercapacitors (EDLC) based on porous carbonaceous materials for commercialization, but this storage system limits the specific capacitance relative to their theoretical value. However, faradic pseudocapacitors based transition metal oxides or mixed oxides provide much higher specific capacitance than EDLC due to superior redox process for charge storage at the surface as well as near the surface of the active electrode. However, nanostructured NiO on Ni foam has been considered as a one of the promising pseudocapacitor materials. Unfortunately, it suffers from stability of the nanostructures during charge and discharge resulting the lower cycle life. Anyhow, ability to control the issue atomic scale thin layer coating of other metal oxides or nobel metal oxides on the surface of NiO is an efficient approach. In this respect, one of the most powerful technique for atomic scale coating is atomic layer deposition (ALD). Herein, we demonstrate the use of ALD for ultrathin RuO_2 coating on surface of three dimensional NiO nanostructure for supercapacitor application . The optimum coating thickness (~ 20 nm) of RuO_2 provide improved electrochemical performance with enhanced cycling stability. We demonstrate that RuO_2 not only prevents the nanostructures of NiO during charge and discharge process but also facilates charge transport and electrolyte diffusion. The sample shows an ultrahigh specific capacitance 1060F/g.

AA-MoP-24 Screening of ALD Barrier Materials Towards use in LED Lightning*, R Ritasalo, T Suni, **Tero Pilvi**,* Picosun Oy, Finland*; S Taeger, E Hörner,* OSRAM Opto Semiconductors GmbH, Germany

Atomic layer deposition (ALD) technique has traditionally been used for controlled deposition of high quality thin films for the semiconductor industry. One of the fields benefiting from ALD technology that has been growing very rapidly recently is optoelectronics, including LEDs. Yole development has forecasted that the market of packaged LEDs will exceed 20 B$ by year 2020 [1].

Fabrication of high performance LEDs requires the use of sensitive materials that can limit the operating lifetime of the device due to insufficient passivation from the environment. Before the materials can be implemented to commercial products, these materials need to be protected from damage caused by environment or next process steps. Conformal, uniform and pin-hole free ALD thin film can give a perfect solution for achieving this when properly designed.

SiO_2 and SiNx by PECVD and Al_2O_3 by ALD are the most common inorganic barrier materials used in microelectronics and in LED-technology. SiO_2 is a rather poor barrier against moisture and can only be used for insensitive devices or in combination with other layers. SiNx is absorbing in the blue / UV wavelength regime and therefore limited in its use for optical devices. Al_2O_3 is a good barrier, but because of its refractive index right between silicon and GaN, it is not optimal for this purpose. In addition its chemical instability limits its use within the process flow of LED manufacturing. Currently there is no barrier film or stack available that fulfills all requirements for LED manufacturing in an ideal way. In the literature different kinds of thin film materials are described that have promising properties, but there is no systematic study that covers all relevant materials and all important properties.

In our work we have made material screening and process development in order to choose the best solutions for LED applications. The PICOSUN™ R-200 Advanced ALD system was used for the depositions. The selected materials included Al_2O_3, Ta_2O_5, SiO_2, Nb_2O_5, TiO_2, HfO_2, ZrO_2, and Y_2O_3. Deposition temperature varied from 100°C to 250°C. The film properties such as morphology, crystallinity, porosity, refractive index, absorption, transmittance, WVTR, composition, breakdown field strength, leakage current and WER were studied to evaluate material compatibility for LED lighting.

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AA-MoP-25 Investigation of Band Structure on Amorphous Zinc Tin Oxide Thin Films Grown by Atomic Layer Deposition for Cd-free $CuGaSe_2$ Solar Cells*, **Sunyoung Lee**,* Konkuk University, Republic of Korea*; A Jeong, J Jeong,* Korea Institute of Science and Technology, Republic of Korea*; Y Min,* Konkuk University, Republic of Korea

Thin film photovoltaic cells require a buffer layer in a window layer stack to prevent unfavourable conduction band line-up which causes interface recombination. Zinc tin oxide (ZTO) has recently attracted great attention as an alternative buffer layer, since this material exhibits some advantages over the existing CdS. However, their work function which is an essential parameter for band alignment at equilibrium has not been characterized in detail. Here, we investigated compositional, structural and optical characteristics of ZTO thin films to construct the band diagram for films with different Sn contents.[1] The relationship between the different Sn contents of ZTO films and the performance of $CuGaSe_2$ (CGS) solar cells are also examined. ZTO films were grown at 150 °C by atomic layer deposition (ALD) using tetrakis(dimethylamido)tin(IV), diethylzinc, and water. The ZTO films were amorphous and exhibited wider optical bandgaps of 2.95–3.07

eV than that (2.45 eV) of CdS. Chemical structure and work function analysis were performed by X-ray photoelectron spectroscopy and Kelvin probe force microscopy, respectively. It indicated that the incorporation of Sn into ZnO strongly influenced the content of oxygen vacancies and work function which is related to carrier concentration. In addition, we found an optimal composition for high solar cell conversion efficiency. The band diagram of the ALD-ZTO films will be useful to understand the band alignment of a photovoltaic cell with a buffer layer of ZTO film.

AA-MoP-26 Optical and Electronic Properties of ALD-grown TiO_2 Films on a Thin Glass Substrate for Applications in Photocatalysis*, Yoon Sang Lee, O Kwon, Y Kim,* Ajou University, Republic of Korea

Anatase TiO_2 films were grown on thin glass substrates using titanium tetraisopropoxide (TTIP) and H_2O as precursors. The as-grown TiO_2 films on the glass substrates were transparent up to the thickness of about 100 nm and found to exhibit anatase phase with a good crystallinity. For a potential application in photocatalysis with a maximum use of visible light, the films were subject to post-nitridation processes under the flow of ammonia at elevated temperatures up to about 600°C. Under the process condition, the films were found to undergo nitridation toward titanium oxynitrides with a varying degree of N content and the enhanced visible absorption. The optical abaorption properties were systematically measured to exhibit enhanced aborption in the visible region depending on the degree of nitridation. The bonding structure and and detailed distribution of nitrogen in the films were further evaluated by x-ray photoelectron spectroscopy. The results confirmed the existence of substitutional and interstitial nitrogen species in the film and their relative concentrations were found to be strongly dependent on the process condition. Depth distribution of these N species was further analyzed and used to explain the changes in the optical properties of the films. Finally, photodegradation efficiency of the films under the visible light was also evaluated.

AA-MoP-27 Atomic Layer Deposition as a Tool to Influence the Sintering of Ni Nanoparticles Supported in the Mesopores of SBA-15*, Piyush Ingale, C Guan, R Naumann d'Alnoncourt, A Thomas,* Technische Universität Berlin, Germany*; F Rosowski,* BASF SE, Germany

Nickel-based catalysts are typically used for the production of synthesis gas by reforming reaction[1]. Dry reforming of methane is an attractive reaction for production of synthesis gas by reduction of carbon dioxide. However, Ni nanoparticles (NPs) used in DRM reaction suffer from severe coking and sintering at high temperature which leads to decreased activity of the catalyst[2,3]. The challenge is to synthesize a catalyst with a high Ni loading and dispersion that is stable under reaction conditions. A high internal surface area makes SBA-15, a material based on uniform hexagonal pores with narrow pore size distribution, a well-suited support material for highly dispersed metal catalysts. By the addition of fluoride ions and variation of ageing time during synthesis, SBA-15 with large mesopores and a reduced fraction of micropores is accessible[4]. Large mesopores allow modification of the catalyst via ALD. Our goal is to investigate the influence of thin alumina layers deposited via ALD of TMA/H_2O on the sintering behaviour of Ni NPs supported in the mesopores of SBA-15.

ALD was carried out in a thermal magnetic suspension balance and a fixed bed reactor[5]. Different catalysts were prepared via ALD of TMA/H_2O on Ni/SBA-15 catalysts as shown in figure 1. The thin alumina layers were deposited either before impregnation of the support with NiO NPs or after impregnation of SBA-15 with NiO NPs. The high temperature applied for NiO reduction and during catalytic testing introduces porosity into the deposited alumina layer, due to shrinking and cracking, making Ni accessible for the gas phase. Strategy C (see Fig.1) aims at producing Ni NPs inside of porous alumina cavities.

The catalysts were tested for activity and stability during dry reforming of methane at different temperatures (500°C-800°C). Sintering of Ni NPs was investigated using XRD and TEM before and after catalysis, and after thermal treatment in different gas atmospheres.

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AA-MoP-28 Metal-doped HfO_2 for Ferroelectric Tunneling Junction Applications using Atomic Layer Deposition*, Chi Thang Nguyen,* Incheon National University, Korea

Conventional non-volatile memories have separate storage of information and transmission of signals. Therefore, there are many difficulties in improving the fabrication steps and operation speed of the devices. In order to overcome these technical limitations, recently, studies on ferroelectric memory devices have been actively conducted. Typically, a metal/ferroelectric layer/metal (MFM) structure has been used for ferroelectric tunnel junction (FTJ) and in addition, a semiconductor bottom layer is used to improve on/off ratio by formation of a Schottky barrier across the ferroelectric-semiconductor junction. However, the on/off ratio of the metal/ferroelectric/semiconductor (MFS) structure is still insufficient to be used for a non-volatile memory device. Recently, in a report, ferroelectric-antiferroelectric properties were switched by controlling doping ratio in a thin HfO_2 layer with specific elements. In this work, atomic layer deposition (ALD) method is used to precisely control specific metal dopants during the HfO_2 deposition cycles, and the electric properties of the metal-doped HfO_2 are investigated in different doping conditions. To understand the results, microstructure and chemical composition of the metal-doped HfO_2 are correlated with theoretical calculation results by density functional theory (DFT).

AA-MoP-29 Atomic Layer Deposition of Al- and Ga-doped HfO_x Films for Resistive Switching Layer*, Sungyeon Ryu, S Oh,* Seoul National University of Science and Technology, Republic of Korea*; W Park, S Kim,* SK Hynix, Republic of Korea*; B Choi,* Seoul National University of Science and Technology, Republic of Korea

Bipolar type resistive switching random access memories (RRAMs) utilized by TaO_x and HfO_x as switching materials, have been demonstrated superior to unipolar type RRAMs owing to the low switching current and better reliability. Likewise TaO_x switching layer, bias-polarity-dependent valence change mechanism in HfO_x is attributed to the repeated generation and rupture of conducting filaments (CF), which could be the clusters of oxygen vacancies (V_o). It has been reported that crystalline HfO_2 film could not create enough oxygen vacancies for resistive switching.1) Crystalline HfO_2 RRAM may cause higher forming voltage, which in turn, device variability could be worse or even catastrophic breakdown could be happen. To change the structure of the film, defect engineering by doping has been deliberately investigated by using various methods, such as, co-sputtering, implantation, thermal and photo-assisted diffusion, etc.

In this study, Al- and Ga-doped HfO_x films are grown by using atomic layer deposition (ALD) to change the structural and chemical properties of HfO_2 film. Tetrakis(ethylmethylamino) hafnium (TEMAH), trimethyl aluminum (TMA), and cyclic dimethylamide gallium ($Ga(NMe_2)_3$) are used as Hf, Al, and Ga precursors, respectively, and H_2O as oxidant gas. Al-doped HfO_2 film was deposited at 250℃, while Ga-doped HfO_2 film was deposited at 200℃ to protect thermal decomposition of Ga source. XRD, SEM, EDS, AES, and XPS are used to examine the structural and chemical properties of the film. The device having TiN contact-plug with 50 to 2000-nm-diamenter formed in SiO_2 inter-layer is fabricated. Electrical property is measured by semiconductor parameter analyzer (HP-4155) and function generator (AFG-3102) for DC and AC measurements. Dopant concentration and location are controlled by the ALD cycle ratio and sequence. Through Al doping, pristine resistance and forming voltage of the device are increased with increasing Al cycle ratio as shown in Fig 1(a) and (b). On the other hand, Ga-doped HfO_2 device shows forming-free and reverse switching polarity as shown in Fig. 1(c). The resistive switching characteristics caused by internal structure of Al- and Ga-doped-HfO_2 films will be presented in detail.

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AA-MoP-30 Synthesis of Well-Defined PO_x/V_2O_5 Powder Catalysts *via* Atomic Layer Deposition*, Kristian Knemeyer,* Technische Universität Berlin, Germany*; V Strempel,* BASF SE, Process Research and Chemical Engineering*; C Schulz, J Xie, R Naumann d'Alnoncourt,* Technische Universität Berlin, Germany*; M Driess,* Institut für Chemie, Germany*; F Rosowski,* BASF SE, Germany

The selective oxidation of n-butane to maleic anhydride (MAN) is an industrial process with a world capacity of over 1 Mt/year. In this highly complex reaction the catalyst plays an essential role for the conversion of butane and selectivity towards MAN. Suitable catalysts for this reaction consist of vanadium, oxygen, and phosphorous, such as vanadyl pyrophosphate $(VO)_2P_2O_7$. Vanadium oxides without phosphorous are total oxidation catalysts with minor selectivity towards MAN.

This paper focusses on the modification of V_2O_5 by depositing various amounts of PO_x via ALD. Subsequent catalytic testing in selective oxidation of n-butane was applied to investigate the influence of P on catalytic performance. The ALD process was carried out in a magnetic suspension balance (MSB)[1][2] to determine ideal ALD conditions and to prove self-limiting growth. Samples with varying amounts of PO_x on V_2O_5 were prepared by performing different ALD cycle numbers with subsequent calcination at 450°C in synthetic air. The as prepared samples were characterized and tested in an automated parallel reactor set-up. ICP-OES analysis show a steady increase of P amount with ALD cycle number but the growth per cycle decreases. No significant loss of P was obtained during calcination or during the reaction, which is in contrast to wet impregnated and subsequent calcined PO_x/V_2O_5 catalysts.[3] Catalytic testing shows a huge influence of P on the selectivity towards MAN. Pure V_2O_5 is a total oxidation catalysts with a selectivity <5 % to MAN at low conversion and temperatures, whereas adding P leads to a high increase of selectivity. Conversion is barely influenced by adding phosphorous.

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AA-MoP-31 Use of New Cyclopentadienyl Tris(dimethylamino) Based Zirconium Precursors for the Leakage Current Reduction of Atomic Layer Deposited ZrO_2- Thin Films

Baek Su Kim, Seoul National University, Republic of Korea*; H Kim, S Hyun, Y Lee, K Kim, T Moon, H Park, Y Lee, J Noh,* Seoul National University and Inter-University Semiconductor Research Center, Republic of Korea*; C Hwang,* Seoul National University, Republic of Korea

ZrO_2 materials have attracted a great deal of attention as they are widely used in the $ZrO_2/Al_2O_3/ZrO_2$ (ZAZ) structure of DRAM capacitors and their mixture with HfO_2 exhibit promising ferroelectric properties. Decreasing the off-state leakage characteristics of DRAM capacitors with ZrO_2 materials is critically important for further scaling, which can be aggravated by subsequent high-temperature annealing for crystallization. Hence, reduction of the leakage current can be expected if the thermal budget is lowered by inducing in-situ crystallization during a high-temperature atomic layer deposition (ALD) process followed by low-temperature post-deposition annealing (PDA). Recently developed New Cyclopentadienyl Tris(dimethylamino) based Zirconium (PCp -Zr) is used as a Zr precursor since it has higher thermal stability compared with the conventional Cp-Zr or amide-based precursors. O_3 was used as an oxygen source and, ALD was performed at 300°C and 350°C on the sputtered TiN substrates, which were relatively higher than the conventional ALD temperatures between 250°C and 280°C. Capacitance-voltage (C-V) characteristics were measured at the as-deposited state and after the PDA at different temperatures of 450°C, 500°C, and the dielectric constant was obtained from the slopes of the equivalent oxide thickness vs. physical oxide thickness plots. For the ALD temperature of 300°C, the achieved dielectric constant for the as-deposited film, and after the PDA at 450°C, 500°C was 27.3, 28.9, and 29.1, respectively. The corresponding values of the film grown at 350 °C were 41.3, 22.9, and 29.1, respectively, suggesting that the increasing ALD temperature was not as efficient as expected initially. The leakage characteristics were confirmed by current-voltage measurements at thicknesses between 5.7 nm and 9.8 nm under the specified annealing conditions. As a result, the leakage current density of 10^{-7} A/cm^2, which is a necessary condition of DRAM capacitors, was obtained for all of the conditions at 0.8 V. Further research will be necessary to fully explore the potential of this newly developed precursor.

AA-MoP-32 Control of Refractive Index by Atomic Layer Deposition on Various Textile Surfaces

Woo Hyeok Kwon, M Khan, H Kim, H Lee, Incheon National University, Republic of Korea

Attempts to integrate various electronic systems and sensors into textiles have been made for future wearable electronics. Conducting textile which is a key component for these wearable electronics is usually called electronic textiles (e-textiles). Since most of conventional textiles are electrically insulator, conducting materials, such as metals, should be added to textiles during or after synthesis processes of textile. In the aesthetic point of view, however, the addition of metal for fabrication of e-textiles has a big disadvantage that is grey and black color of textile from the reflection and scattering of metal components. In addition, the conventional dying technology could not be applied to the e-textile systems after addition of metals due to lack of surface chemical species which are bonded to dye molecules. In our recent paper, we reported that conventional cotton textiles were successfully changed to e-textiles by Pt coating by atomic layer deposition (ALD), and we have produced color coated e-textiles by depositing oxide multilayer thin films. In order for color coated electronic fibers to be used in real life, however, they must have physical and chemical stabilities, in addition, wide compatibility on various textiles. In this work, we fabricated color coated electronic fiber by depositing Al_2O_3/TiO_2 on various electronic fibers to confirm not only the mechanical environment such as tensile, shrinkage and friction which can be exposed in daily life but also the chemical stability due to acid base exposure. By ensuring the mechanical and chemical stability of color coated electronic filaments, it is expected that electronic filaments can be applied to a wider range of applications in the near future.

AA-MoP-33 Zinc Tin Oxide Thin Films Grown by Atomic Layer Deposition for Charge-Trap Flash Memory

Jun Shik Kim, E Hwang, S Lee, Y Jang, S Jeon, C Hwang, Seoul National University, Republic of Korea

As the further scale down of the 2-D planar memory device is challenged by various technical limits including cell-to-cell interference, 3-D memory devices such as vertical-NAND (V-NAND) flash [1, 2, 3] have been proposed as the new effective way of memory density increase. Concerning the transistors in these V-NAND devices, however, the single crystal Si transistors in 2D planar devices was replaced with poorly crystallized poly-Si. However, the low carrier mobility of this poly-Si channel imposes a fundamental limitation to further increase in the integration density. In this regard, the amorphous oxide semiconductor (AOS) grown by atomic layer deposition (ALD) has been proposed as one of the most promising alternative techniques owing to its high mobility, excellent step coverage and low-temperature growth characteristics. [4, 5]

In this work, therefore, n-type zinc tin oxide (ZnSnO) thin films were prepared via ALD with the various film thickness and the atomic ratio of zinc to tin to achieve higher carrier mobility and stable transistor operation. ZnSnO ALD was performed by the alternation of ZnO (with DEZn) and SnO_2 (with TDMASn) ALD cycles in proper ratio utilizing O_3 as the oxygen source. The electrical performance of ZnSnO films was estimated by fabricating bottom-gated thin film transistors where the heavily-doped p-Si was the gate, and thermally growth 100nm-thick SiO_2 was the gate oxide, as shown below. Finally, the charge-trap memory devices were fabricated using ALD ZnSnO film as the channel layer, and low-pressure chemical vapor deposited Si_3N_4 as the charge trap layer. The program/erase characteristics of the fabricated devices were analyzed.

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AA-MoP-34 Protective Layer TiO_2/Pt/C Catalyst for Excellent Durability deposited by Fluidizing Bed Reactor Atomic Layer Deposition

Woo-Jae Lee, T Kim, S Kwon, Pusan National University, Republic of Korea

Proton Exchange Membrane Fuel Cell (PEMFC) is one of the most promising power sources ranging from portable electronic devices to automobile industry because of its advantages such as low operating temperature, fast start-up and sustained operation at high current density. In PEMFC, the challenges for the commercialization are to resolve the high cost and low durability of Pt catalyst which currently is used. As common synthesis for Pt catalyst, Wet process such as electrodeposition, Electroless can make thresholds due to the long process term, pre-treatment and, un-uniform Pt size and distribution leading to decrease of Pt/C utilization. To resolve these problems, dry based-technique for Pt catalyst must be developed. Among dry based-methods, ALD (Atomic Layer Deposition) is the prominent method due to the excellent uniformity, accurate thickness control and island -shaped growth of noble metal at the initial stage. In addition, fluidizing bed reactor can be introduced to the atomic layer deposition for more excellent uniform Pt/C and mass production.

In this work, to improve the cost and durability, protective layer/Pt/C structure was deposited and optimized in situ process by using fluidizing bed reactor ALD. TiO_2/Pt (30wt%) on carbon black powder was successfully deposited using TTIP, H_2O for TiO-$_2$ and $MeCpPtMe_3$ precursor and O_2 reactant for Pt by using the fluidizing bed reactor ALD. ALD cycle is changed from 0 cycle to 10cycle to optimize the thickness. Loading, particle size and distribution were investigated by TGA, STEM measurement. With increasing the TiO-$_2$ ALD cycle on Pt/C, overall TiO_2/Pt loading increased regularly and particle size have no big change due to the ultra TiO--$_2$ thin film. From TEM-EDS, TiO_2 was selectively positioned around Pt, making the TiO_2 shell/Pt core. After 1000 Cycle ADT(Accelerated degradation test), TiO_2(10cycle)/Pt/C prepared by ALD shows good and stable durability.

AA-MoP-35 Atomic Layer Deposition of Si-doped HfO_2 Thin Film by using $HfCl_4$, $SiCl_4$ and H_2O for FeRAM Device Application

***Se-Won Lee**, M Kim,* Versum Materials Korea, Republic of Korea*; M MacDonald, X Lei,* Versum Materials, Inc.*; Z Zhu, A Yoon,* Lam Research Corp*; H Yoo, D Suh, Y Choi,* SK Hynix Inc

Recently, next-generation memory devices such as PRAM, ReRAM and FeRAM have been widely studied to replace conventional DRAM and NAND flash devices. Especially, FeRAM has high potential that it can achieve fast write/erase speed, compatible integration (3-D stack architecture) and low power consumption. There are a number of materials that demonstrate ferroelectric properties, among which silicon doped hafnium oxide (Si:HfO_2) is one of promising ferroelectric materials because it operates at very thin thickness (about 5~10 nm) without losing its functional properties and has excellent compatibility [1].

In this study, we have investigated thermal ALD of Si:HfO_2 using $HfCl_4$ and $SiCl_4$ precursors with H_2O as an oxygen source at deposition temperatures 250°C and 300°C, and also studied ferroelectric characteristics of MFM FeRAM device structure with various Si doping concentrations (about 2, 4 and 6 mol % Si). To control mol % Si in the HfO_2 films, we used a 3-step Si precursor pulsing method including sub-cycle and main-cycle such as [(HfO_2 x m sub-cycle/ SiO_2 x 1 sub-cycle /HfO_2 x m sub-cycle) x n main(super)-cycle] (see the Fig.1 below). For example, (HfO_2 x 9 cy /SiO_2 x 1 cy /HfO_2 x 9 cy) x 5 cy at 250°C resulted in ~4 mol% Si. SiO_2 sub-cycle number was fixed at 1 cycle for all films. XPS was used to measure contents of Si, Hf and impurities of resulting Si:HfO_2 films. No Cl and C impurities were found in the film, and O content was ~65 at%. FE properties were measured after rapid thermal process (RTP) at 600°C for 20 sec or 800°C for 1 sec.

With samples deposited at 300°C, good FE characteristics were achieved. Wake-up property remained after RTP at 600°C for 20 sec and it disappeared after RTP of 800°C for 1 sec conditions. Remnant polarization (P_r) value of 16 $\mu C/cm^2$ and coercive electric field (E_c) of 1.1 MV/cm was achieved with the 2.5 mol % Si sample after 800°C annealing process. 600°C annealing temperature is not enough to activate 5.6 mol% Si sample and it showed anti-FE characteristics at 800°C annealing temperature. However, in the 250°C deposited samples, poor FE characteristics were obtained. With RTP condition of 600°C for 20 sec, all samples were not activated enough to show FE characteristics. Over annealing temperature of 800°C, 4.0 mol% Si samples showed FE properties, but also showed high leakage current (see Fig.2 below).

In summary, we have demonstrated that the 2.5 mol % Si in Si:HfO_2 samples deposited using $HfCl_4$, $SiCl_4$, and H_2O are the most effectual FE material, because the FE characteristics is superior to those of other samples.

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AA-MoP-36 Combining ALD with Pulse Current Electroplating of Gold to Deposit on the Wall of High Aspect Ratio Silicon Grating

***Tae Eun Song**, H Han,* National NanoFab Center (NNFC), Republic of Korea*; S Jung, S Kim,* Yeungnam University, Republic of Korea*; C Ahn,* National NanoFab Center (NNFC), Republic of Korea

Deposition on the wall of high aspect ratio silicon grating with gold is a frequent requirement in the fabrication of X-ray phase contrast imaging technique as well as micro-electronic components and other fabrication processes[12]. Utilizing Silicon grating etched by deep reactive ion etching have been fabricated in silicon wafers. Electroplating of gold in silicon grating with a high aspect ratio greater than 40 over a grating area of 10 cm * 10 cm require conductive supports which were created by uniformly depositing Ru on the silicon by Atomic Layer Deposition (ALD). Moreover pulse current electroplating led to uniformly deposit gold on the wall of silicon grating for such structures[345].

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AA-MoP-37 Atomic Layer Deposition of Ru Metal Thin Film with Substrate-Dependent Growth Behavior on Ta_2O_5 Substrate

Cheol Hyun An, Seoul National University, Republic of Korea*; W Lee,* Northwestern University*; S Kim, D Kwon, S Cha, S Cho, C Hwang,* Seoul National University, Republic of Korea

The growth of Ru noble metal has been studied for several purposes such as catalyst, an oxygen diffusion barrier layer or electrode materials due to its electrical properties and chemical stability. Especially, Ru metal is also nominated for an electrode of the capacitor in DRAM due to its high work function which could reduce the leakage current of the capacitor. For applying Ru electrode on capacitor under 20nm, atomic layer deposition (ALD) of Ru film is inevitable since its precise thickness controllability and high conformality. The ALD growth of Ru metal has been progressed using various Ru precursors, most of those are metal-organic (MO) precursor which have carbon containing ligands. Also, the ALD methods with MO precursors have difficulties on the nucleation of Ru metal on a substrate and show long incubation time which induces less conformal film surface.

In this study, the RuO_4 and N_2/H_2 gas were used in ALD process of Ru metal thin film as a precursor and reactant gas, respectively. The RuO_4 precursor, which has small molecular size and high volatility, is adaptable for depositing Ru metal on the narrow and complex structure. Moreover, the Ru film deposited by RuO_4 precursor could have low carbon impurity since any carbon atom is contained in the precursor and oxygen atoms are only ligand atoms. The ALD growth of Ru film with RuO_4 has been reported before, but it was examined mainly on Si substrate. However, the growth behavior of the Ru film on transition metal oxides needs to be examined for the DRAM capacitor application. Therefore, growth behavior of Ru film on the Ta_2O_5 substrate was confirmed in this study. The self-limited growth was observed with RuO_4 precursor feeding time as conventional ALD method, while 2-step saturation behavior was observed versus N_2/H_2 reactant gas feeding time. Moreover, the growth per cycle of Ru films were higher than conventional ALD studies. Since this unideal growth behavior was not observed on inert Au substrate under the same deposition conditions, the growth mechanism was further examined by X-ray analysis and secondary ion mass spectroscopy. Apart from the general assumption of the inactive role of stable bottom Ta_2O_5 layer, it showed catalytic properties for precursor absorption and film formation. During N_2/H_2 reactant gas exposure, the Ta_2O_5 film was reduced to Ta metal phase which migrated towards the growing Ru surface. The catalytic activity of Ta atoms on the chemical adsorption of multiple layer of RuO_4 molecules was considered to be the plausible mechanism of the unideal growth behavior. Nonetheless, the abnormal growth did not influence the electrical properties and physical properties.

AA-MoP-38 Forming of Conformal Multilayer on Periodic Microstructures for Solar Selective Absorption

***Makoto Shimizu,** H Akutsu, S Tsuda, M Kumano, H Yugami,* Tohoku University, Japan

Solar absorbers are a key component in solar thermal utilization systems such as concentrated solar power generation (CSP) and solar thermal chemical conversion systems. For using solar energy effectively, the enthalpy of sunlight should be utilized up to the maximum extent possible. The operating temperature of solar thermal systems such as CSP systems is increasing. Regarding high-temperature usage, to create microstructures on-top of metal surfaces is a promising technology.

Typically, these materials are able to possess spectrally selective absorption properties for high-temperature usage. However, this technique is typically not well-suited because deep microstructures should be required to attain high spectrally selective absorption properties. In this study, we investigated high spectrally selective absorption properties; i.e., broad and high-absorptance in a short wavelength range and low emittance in a long wavelength range, with shallow honeycomb array cylindrical-microcavities coated by metal-dielectric multi-layers.

Honeycomb array cylindrical microcavities were fabricated on tungsten substrate with interference lithography and multi-layers consisting of platinum nano-film sandwiched by Al_2O_3 layers were created for a uniform coating via atomic layer deposition. Due to high conformal multilayer on the cylindrical microcavity thanks to characteristics of ALD method, absorptance spectrum is well consistent with the simulated result. A solar absorptance value of 0.92 and a hemi-spherical total emittance value of 0.18 at 700^{o}C was determined from the fabricated solar selective absorber. Additionally, thermal stability of up to 700^{o}Cwas confirmed in vacuum a pressure range of 1 Pa.

AA-MoP-39 Ti-doped ZnO Films Grown by Atomic Layer Deposition for Solar Cell Applications, ***Ji Hye Kim**, C Kim, H Park, Z Urrehman,* ISAC Research Inc., Republic of Korea

Transparent conductive oxides(TCOs) are widely used in various industry such as displays, solar cells, thin-film-transistors. Zinc oxide(ZnO) based semiconductors has been extensively studied due to their high optical transmission and electrical conductivity and lower material cost. Furthermore, for flexible optoelectronics in future, it is desired to prepare TCOs as low temperature as possible. Among various deposition techniques, doped ZnO thin films were deposited by atomic layer deposition (ALD) due to low temperature growth, excellent step coverage, good conformality.

In this work, we investigated the electrical, structural and optical properties of Ti doped ZnO thin films prepared by thermal ALD and plasma enhanced ALD.

AA-MoP-40 Crystal Structure and Electrical Properties Modulation of Al-doped $HfZrO_2$ Thin Films by ALD, ***Seung-Won Lee**, J Ahn, J Choi, C Hyeon,* Korea Maritime and Ocean University, Republic of Korea; *M Ahn, S Jeon,* Korea University, Republic of Korea

As the size of semiconductor device is scaled down, electronic components such as gate oxide, DRAM capacitor are more important for high-k materials. Among the various high-k materials, the oxide thin films based on Zr and Hf can be realized by deposition conditions or by phase stabilizer doping such as monoclinic, tetragonal, cubic. Especially, when having tetragonal phase, it is known to have high dielectric constant about 40. In addition, it has relatively wide bandgap and it is highly compatible with Si integration technology. So, it is applied to high-k device. Recently, $HfZrO_2$ thin films have ferroelectric and anti-ferroelectric properties by Zr content. So, many studies are underway to utilize them for ferroelectric devices. On the other hand, the study on the electrical characteristics of phase transition through thin film doping based on ZrO_2 and HfO_2 has been done. However, the study on change of dielectric constant by doping binary oxide film based $HfZrO_2$ have been deficient compared to applicability.

Therefore, we investigated the sturcture and electric properties of $HfZrO_2$ thin films doped by controlling Al contents. In the process of depositing $HfZrO_2$ thin film using PEALD, the Al dopant was doped by two methods : supercycle and sequential cycle. Then, the characteristics of Al doped $HfZrO_2$ films were observed for ellipsometer, XRD, XPS and semiconductor parameter analyzer.

AA-MoP-41 In situ Capping of VO_x using PEALD of V_2O_5 and/or VN, ***Rémy Gassilloud**, M Fraccaroli, C Charpin,* CEA-Leti, France; *C Vallée,* CNRS-LTM, France

Resistive memories composed of Ta_2O_5/TaO_X dielectrics sandwiched between a TaN cathode and noble-based anode have good potential for use as nonvolatile switch in large-scale integrated circuits [1]. Another group 5 element that shows a pretty good compatibility with standard Si technology and more sustainable than Ta, is Vanadium. Thermal ALD deposition of VO_2 has already been achieved using Tetrakis(EthylMethyl)Amino Vanadium (Air Liquid TEMAV) [2][3]. Many reports discuss on the growth of this material and the required post deposition anneal under O_2 ambient to reach the well-known MIT VO_2(M) monoclinic phases. The required partial pressure of oxygen must be so precise that it restrains its integration in devices [4]. Another solution is to keep VO_2 in its as-deposited amorphous state and use it as oxygen reservoir in a ReRAM based configuration VO_2/V_2O_5, with V_2O_5 as switchable insulator, i.e. through filament vacancies formation. In the meantime, Vanadium nitride has also been developed using the same TEMAV molecule and NH_3 plasma. Resistivity as low as 200 µOhm.cm were obtained for as-deposited VN which is in the range of resistivity values obtained with TaN or even TiN. In this work, we will review and present our results on the ALD deposition of VO_2 amorphous and monoclinicphase using TEMAV and water on 300mm Si. We will extend the work on V_2O_5 deposition using O_2 plasma and show results on in-situ bilayer deposition. We will finally go further on the VN electrode deposition with VO_2/V_2O_5/VN tri-stack fully in-situ deposited.

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AA-MoP-42 PE-ALD for Deposition of TiN as a Refractory Plasmonic Material, *G Dogan, U Sanli,* Max Planck Institute for Intelligent Systems, Germany; *H Karl,* University of Augsburg, Germany; *G Schütz, **Kahraman Keskinbora**,* Max Planck Institute for Intelligent Systems, Germany

Titanium nitride (TiN) was recently proposed as an alternative to gold for high-temperature plasmonic applications such as concentrated solar thermal power generation. The refractory plasmonics material TiN was shown to be more stable than Au after intense laser irradiation.[1] Conformality aspect of atomic layer deposition (ALD) is recently being exploited for fabricating high-quality dielectric nanostructures for applications in optics.[2,3] Therefore, ALD processing of plasmonic materials with a low electrical resistivity and high crystalline quality is a very interesting prospect.

In this work, we have studied the influence of growth conditions on the physical properties of TiN films by analytical techniques including *in-situ* and *ex-situ* spectroscopic ellipsometry (SE), X-ray reflectivity (XRR) and diffraction (XRD), X-ray photoelectron emission spectroscopy (XPS), and four-point probe (FPP) measurements. The TiN thin films were deposited on single crystal silicon substrates at 350°C by plasma-enhanced atomic layer deposition (PE-ALD) using $TiCl_4$ and N_2-H_2 plasma as the precursor and the co-reactant, respectively. *In-situ* SE confirmed ALD type growth and the deposition rate was found to vary between 0.024 to 0.032 nm/cycle depending on the plasma ratio N_2-H_2 and plasma exposure time. The XRD results exhibit a strong (002) texture in the deposited films. The electrical resistivity of the films can be tuned between 1200 to 290 µohm.cm by varying the process parameters. Low resistivity correlates with low chlorine content and large TiN grain size, obtained for films deposited with a plasma-ratio of 7.5 and plasma exposure time of 4 s. We will further discuss how these results can be utilized as a precursor for integration of TiN into nanostructured materials for optical applications.

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AA-MoP-43 Physical Characaterization of Transition Metal Dichalcogenide MoS_2Thin Films Synthesized by Atomic Layer Deposition, ***Hongguo Zhang**, M Zeng, C McCleese, C Kolodziej, P Lin, K Zhang, C Burda, Q Li, H Baumgart,* Old Dominion University

Transition metal dichalcogenides (TMDC s), such as MoS_2, WSe_2 and $MoSe_2$, exhibit layered structures in which are in-plane covalent bonds are strong and interplane van der Waals forces are relatively weak. This bond structure demonstrates extraordinary in plane thermal, mechanical, electrical, optical properties. The monolayers exfoliated from bulk counterparts, commonly called as two-dimensional (2D) materials, are paid significant attentions due to their unique and tunable material properties: (1) indirect to direct band gap transition when the bulk material is exfoliated to a single layer, making them become ideal quantum well. (2) higher carrier mobility with 100cm^2/Vs. (3) enhanced spin orbit coupling used in spin based electronic devices. These unique properties of 2D TMDCs are promising to be applied in sensors, filed effect transistors, photodetectors, piezoelectric devices and solar cells.

To date, many techniques have been developed for the synthesis of mono and few-layer TMDC films on different substrates, such as pulsed laser deposition (PLD), chemical vapor deposition (CVD). However, very little is known about atomic layer deposition (ALD) synthesis of MoS_2 films there are very only few references. ALD technique exhibits self-limiting atomic layer reactions in each introduced ALD cycle. It can accurately control film layer thickness stoichiometry, composition, uniformity, and sharp interface. Furthermore, ALD also can be used to deposit conformal film onto very complex structures.

Here we report on synthesis of MoS_2 films on Silicon substrates by ALD system. Molybdenum hexacarbonyl ($Mo(CO)_6$) and dimethyldisulfide (CH_3SSCH_3, DMDS) are employed as the chemical ALD precursors for Molybdenum and Sulfur, respectively. Generally, 20 sccm N_2 was used as a carrier gas for the precursors. The growth temperature was set at 200, 230 and 250^{o}C. The crystallinity of as-deposited MoS_2 thin film could be improved by post-annealing under saturated sulfur vapor. The Raman spectroscopy analysis show the MoS2 thin films demonstrate the characteristic of E12g and A1g Raman modes. The decay processes and valence band splitting are in accord with the known energy scheme for MoS_2 thin films. A band gap of about 1.8 eV of MoS_2 thin film is in the range of 1.1 eV (bulk MoS_2) to 1.9 eV (monolayer MoS_2). The band gap of ALD MoS_2 thin films is much closer to the monolayer limit than to the bulk limit.

AA-MoP-44 Synthesis of ALD Iridium Thin Films on 3-D Fabricated Monel K-500 Steel Samples*, P Oelslager,* ***Helmut Baumgart,*** Old Dominion University

Iridium (Ir) thin films have been extensively investigated for a variety of applications. Ir is a potential optical material for Fresnel zone X-ray microchannel plates, inductive grid filters, and potential electrode materials. It is also a noble metal making it well suited to corrosion resistance in harsh environments

Atomic Layer Deposition (ALD) is considered a modification of chemical vapor deposition (CVD), where two different chemical precursors are pulsed separately into a reactor chamber one at a time, requiring two self-limiting surface chemical reactions to occur on the substrate. It is possible for ALD technology to synthesize high quality materials over large areas at low temperature. ALD technology has numerous advantages over conventional thin film deposition techniques. ALD can precisely control film layer thickness, stoichiometry, composition, and uniformity, and produce sharp interfaces in nanolaminate structures. ALD can also be used to deposit conformal films onto very complex surface morphology structures

In this work, iridium metal films were deposited on silicon (Si) and Monel K-500 alloy substrates by ALD using Iridium (III) acetylacetonate known as Ir(acac) or $[CH_3COCH=C(O-)CH_3]_3Ir$ as precursor, and industrial grade O_2 as oxidizing reactant. The solid Ir precursor was heated to 150°C, and the substrate temperature was varied to establish an optimum growth window. The lowest temperature in which Ir growth was is 200°C, and the thin film growth rate increased as a function of temperature up to 250°C. Higher temperatures have not yet been attempted due to equipment constraints. The Monel K-500 steel alloy flat discs were cut from commercially available Monel K-500 bars of ~1 inch diameter.

In this study we report on the successful synthesis of Ir metal films on both Si and Monel K-500 substrates by ALD system with $Ir(acac)_3$ and Oxygen between 200 and 250^{o}C. Detailed characterization has been performed using X-ray diffraction (XRD), atomic force microscopy (AFM), and field emission scanning electron microscopy (FE-SEM) of samples which have been notched with focused ion beam (FIB) techniques for cross-sectional film thickness measurements. The XRD and FE-SEM results reveal that the ALD Iridium thin film are polycrystalline at deposition temperatures based on Volmer–Weber island growth mode. Heterogeneous nucleation on Si and Monel K-500 alloy surfaces and yielded excellent surface coverage and does not require special surface treatments.

AA-MoP-45 Precursor Dependent Optical Properties of ALD TiO_2*,* ***Ritwik Bhatia,*** Veeco-CNT

There has been increased interest in the use of atomic layer deposition for optical applications due to the ability of ALD to uniformly coat curved substrates and ease of scale up of ALD to large batches and/or large substrates. Many optical designs require alternating layers materials with low and high refractive index. TiO_2 is a material of interest in optical coatings due to its high refractive index (~ 2.4) and transparency across most of the visible spectrum (band gap ~ 3eV). However, TiO_2 can be absorbing in the visible region (sub-band gap) absorption, typically attributed to oxygen vacancies.

In this work we discuss the optical properties of TiO_2 and how they depend on deposition parameters like precursor type, deposition temperature and precursor exposure. We have found that TiO_2 deposited with tetrakis(dimethylamino)titanium (TDMATi) and water is absorbing across the visible spectrum, while TiO_2 from titanium chloride ($TiCl_4$) and water is transparent across the visible region - only showing the expected band edge absorption ~ 400nm. Further, we investigate the processing parameters required to make TiO_2 from TDMATi less absorbing.

AA-MoP-46 Accurate Modeling of the Gate Leakage Currents in Metal-Insulator-Semiconductor (MIS) Devices using Ultra-thin High-k Oxides*,* ***Hector Uribe-Vargas****, J Molina-Reyes,* National Institute of Astrophysics, Optics and Electronics

Ultra-thin high-k oxides are widely used in advanced CMOS technology in order to continue scalability and to increase performance. Nevertheless, as the devices reach the nanometer regime, accurate predictions ensuring long-term operation of these devices is now more complicated due to several physical and electronic considerations: 1) precise atomic control of the high-k material in the ultra-thin regime (thickness, stoichiometry, dielectric constant, etc), 2) excessively large gate leakage current levels, 3) appearance of several conduction mechanisms able to degrade the performance and reliability of the devices, 4) interfacial defects at the high-k/silicon interface and 5) low thermodynamic stability of the high-k materials after being exposed to the inherent thermal treatments during several Front-End-Of-Line (FEOL) or Back-End-Of-Line (BEOL) stages.

In order to contribute to better predictions of electrical performance and reliability characteristics, this work carefully reviews the conduction mechanisms in Metal-Insulator-Semiconductor (MIS) devices fabricated using ultra-thin Al_2O_3, and TiO_2 (less than 10 nm in thickness for each dielectric) deposited by atomic-layer deposition (ALD). This deposition technique has excellent conformality, outstanding control (to atomic level) on the thickness and stoichiometry, interface quality with the semiconductor substrate, and low deposition temperature ($T \leq 250°C$) for these metal oxides, assuring high reproducibility for each device.

After fabrication, MIS devices were electrically characterized using standard Ig-Vg, C-V, Ig-Vg-temperature measurement conditions in order to determine the precise carrier conduction mechanism for each dielectric under different conditions of substrate passivation (by using a chemical oxide SiO_x) and post-metallization annealing (PMA). The experimental measurements were compared with semi-empirical tunneling models like direct tunneling (DT), Ohmic conduction (OC), Poole-Frenkel emission (PF), Trap-Assisted Tunneling (TAT), Schottky Emission (SE) and Fowler-Nordheim tunneling (FN). Physical parameters such as effective mass, barrier height (SE and FN), and trap energy level were extracted and then compared with simulations using MATLAB and SILVACO software. All values were compared with those found in literature, having excellent agreement. The accurate identification of self-consistent conduction models for the gate leakage current in MIS devices allows for better performance/reliability predictions before degradation or failure of these devices and this is possible due to the high quality of the ultra-thin high-dielectric constant materials enabled by thermal ALD.

AA-MoP-47 Optimization of Microwave Generated Surfatron for Wafer-scale Plasma Enhanced ALD System*, J Kim,* ISAC Research Inc., Republic of Korea*; A Poruba,* SVCS Process Innovation s.r.o., Czech Republic*; M Cada,* Institute of Physics of the Czech Academy of Sciences, Czech Republic*;* ***Hyung Sang Park,*** ISAC Research Inc., Republic of Korea*; J Dolak,* SVCS Process Innovation s.r.o., Czech Republic

With the continued down scaling of devices and structure changed to 3-dimensional, new ALD processes are in great demand. Microwave surfatron plasma is considered new plasma source because it enables very low-temperature deposition and good film quality due to its low electron temperature and higher plasma density. For adopting surfatron plasma source to new ALD system, it is essential to understand the physical properties of generated plasma with the varying gas atmosphere. Also we are requested to achieve acceptable homogeneity on wafer-level area. Thus, in this work, we investigated plasma parameters with various gas, pressure, flow and various distances from the plasma outlet with optimized design of plasma nozzle. Furthermore, we will present the preliminary results of TiOx layers achieved with this tool.

AA-MoP-48 Grow of GaN Thin Films over a Si/Al_2O_3 Stack by Thermal and Plasma Enhanced Atomic Layer Deposition as MOS Structure*,* ***Joaquin Alvarado,*** University of Puebla, Mexico*; M Chavez,* CINVESTAV-IPN, Mexico*; D Cortes,* University of Puebla, Mexico*; S Gallardo,* CINVESTAV-IPN, Mexico*; L Martinez, S Alcantara,* University of Puebla, Mexico

Atomic layer deposition (ALD) is a promising technique because highly uniform films can be obtained and allows an excellent growth control [1,2]. Oxides (eg. Al_2O_3) and III nitrides (InN, AlN and GaN) can be obtained with ALD technique . These features make ALD technique a candidate for manufacture high-electron-mobility-transistors (MIS- HEMTs) and metal-oxide-semiconductor high-electron- mobility-transistors (MOS-HEMTs) [3]. Metal-insulator-semiconductor (MIS) structure using Al_2O_3 and GaN as a dielectric and semiconductor respectively obtained by Atomic layer deposition has received much attention because the Al2O3/GaN structure provides low leakage current, whereas GaN layer offers higher mobility than Metal Oxides layers.

Experimental

GaN and Al_2O_3/ GaN layers were carried out at 400°C using both Thermal and Plasma Enhanced Atomic Layer Deposition (PEALD). First, 50 cycles of Al_2O_3 were deposited at 150°C, thermal ALD Al_2O_3 cycle consist of (a) pulse of Trimethyl Aluminium (TMA), (2) Ar purge, (3) H_2O pulse and (4) Ar purge. Furthermore, 1000 cycles of GaN were deposited with PEALD, where each cycle consist of (1) pulse of Trimethylgalium (TMG), (2) Ar purge, (3) N_2 plasma and (4) Ar purge. Base pressure was 150 mTorr. Two structures were obtained Si/GaN and Si/Al_2O_3/GaN and Ohmic contacts of Ti/Al/Ti/Al/Ti/Au (50/30/50/30/60) metals were deposited through evaporation.

Results.

Fig. 1 shows the XRD pattern of GaN and Al_2O_3/GaN films, the peak located at 34.5° (002) confirms the hexagonal phase of Gallium Nitride [4], whereas no peaks of Al_2O_3 are present, which indicates that Al_2O_3 is amorphous.

Fig. 2 shows the results of X-ray reflectivity (XRR) for (a) Si/GaN (b) si/AL_2O_3/ GaN, XRR data indicate the thickness of GaN and GaN/Al_2O_3 layers are 40 nm and 60 nm respectively. The inset figure shows the critical angle (c_a), where the precise position was determined by the minimum of the first derivative. Also the mass density obtained was 6.04 g cm^{-3}. Atomic Force Microscopy, Scanning Electron Microscopy as well as Transmittance and Absorbance characteristics of these films grown at different temperatures will be included.

On the other hand, Fig. 3 shows the C-V and G-V characteristics of Si/Al_2O_3/GaN stack at three different frequencies; thanks to this figure it will be possible to evaluate the insulator-semiconductor interface.

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AA-MoP-49 Reduction of Hysteresis in p-Type Atomic Layer Deposited SnO Thin Film Transistors by Adopting Interfacial Layers, *Younjin Jang*, *J Kim, E Hwang, S Lee, S Jeon,* Seoul National University, Republic of Korea*; J Han,* Seoul National University of Science and Technology, Republic of Korea*; C Hwang,* Seoul National University, Republic of Korea

Oxide thin film transistors (TFTs) have made impressive progress using n-type oxides such as a-IGZO, ZnO, and SnO. However, realizing the complementary metal oxide semiconductor circuit using all oxide TFTs was retarded by lack of high-performance p-type oxide semiconductors. Recently, tin monoxide (SnO) was suggested as a promising p-type material for high hole mobility due to its valence band structure [1]. To date, the SnO thin films were mainly deposited by magnetron sputtering method, but a recent study showed a possibility of fabricating a p-type SnO thin film using atomic layer deposition (ALD) method. Although it showed superior TFT performances compared to the previous results, electrical properties of ALD SnO TFTs have not been sufficiently analyzed yet [2]. In this work, the interfacial layer effects on the hysteresis of p-type SnO TFT were investigated.

p-Type SnO thin films were grown by the atomic layer deposition (ALD) using Sn(dmamp)$_2$ (bis(1-dimethylamino-2-methyl-2- propoxy) tin(II)) and H_2O as the Sn and O sources at 200 °C on SiO_2/p^{++}-Si substrate. To investigate the interfacial effects on hysteresis behaviors, and the Al_2O_3 interfacial layer (IL) grown by ALD (thickness from 2.5 to 5 nm) was inserted between the SnO active layer and the SiO_2 gate oxide layer. Various heat treatments on ILs by rapid thermal annealing (RTA) were carried out.

By optimizing the gas atmosphere of RTA process, a significant decrease in the hysteresis was observed (from 4 V at no IL to 2 V at 2.5 nm-thick IL). It seems that oxygen treated IL reduced the defects close to the channel, which contributed to the reduction of hysteresis. Also, it was confirmed that the hysteresis characteristics were further improved by increasing IL thickness from 2.5 nm to 5 nm. Possible origin of hysteresis would be related to Si diffusion to the SnO layer during the deposition process, but more detailed investigation of hysteresis mechanism is necessary.

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AA-MoP-50 The Impact of ALD ZrO_2 Gate Insulators on Indium Tin Zinc Oxide (ITZO) Thin Film Transistor Applications, *Wan-Ho Choi*, *H Jung, J Sheng, J Lee, J Park,* Hanyang University, Republic of Korea

High-k dielectric materials have been extensively studied in the memory semiconductor and display industries. Especially in the field of displays, high-k materials should be studied for low-voltage operation. Especially, the solution process has been mainly studied for the high-k material for the low voltage drive transistor. However, due to the leakage current of the solution process and limitations of the device behavior, it is necessary to study the high-k dielectric layer using atomic layer deposition (ALD) to obtain excellent insulating layer characteristics. In this study, ZrO_2 films were deposited at various temperatures by ALD. The MIM and MIS structures were fabricated using the deposited ZrO_2 thin films to investigate the dielectric properties of the films. In order to measure the performance of the device, a thin film transistor(TFT) of back-channel-etching (BCE) structure using In-Sn-Zn-O (ITZO), which is a high mobility oxide semiconductor, was fabricated. The ZrO_2 thin films used in each structure were deposited at 100 nm and their thicknesses were measured by spectroscopic-ellipsometry (SE). Leakage current density of 200,250 and 300°C is 7.5´10^{-8}, 2.9´10^{-8} and 3.6´10^{-8} and k value is 17.4, 21,4 and 23.0, respectively . TFT with ZrO_2 showed mobility of 23.4, 7.0, and 4.16 at 200, 250, and 300 °C and hysteresis of 0.13, 0.02, and 0.04 with subthreshold swing of 0.19, 0.15, and 0.16, respectively. And the constant current stress (CCS) test was conducted to confirm the suitability as a driving transistor. The higher the deposition temperature of ZrO_2, the better the reliability. XRD analysis was carried out to examine the crystallinity of the ZrO_2 thin film. XPS analysis of the ZrO_2 surface was also performed to study the origin of the performance difference of the device depending on the deposition temperature. Comparing the surface composition through XPS, the ZrO_2 thin film deposited at 200°C showed more than two times higher composition of Carbon than the other temperature set. Due to this impurity, defect-assist leakage mode is dominent and that increase the leakage current density. The XPS O1s spectra show that the O-deficient peak associated with Vo is the highest in the thin film deposited at 200°C, indicating that the mobility of the device is high and the reliability is poor. We confirmed the suitability of ZrO_2 as a dielectric layer of TFT deposited at over 250°C.

AA-MoP-51 Templated Carbon Nanotube Growth from Reduced NiO Atomic Layer Deposition, *Erin Cleveland*, *K Perkins, P Campbell, A Friedman,* U.S. Naval Research Laboratory

Carbon nanotubes (CNTs) have drawn great attention due to their exceptional thermal, electrical, and mechanical properties. Owing to their unique mechanical properties, CNTs are promising as reinforcement for nanocomposite materials. CNTs have been widely studied using a variety of different growth techniques, including catalytic CVD. In CVD, metal catalytic nanoparticles deposited on substrates from solution or spontaneously formed through nucleation of films formed by physical vapor deposition (PVD) techniques such as sputtering or evaporation are exposed to a gaseous carbon precursor at elevated temperatures. The catalytic particles decompose the precursor, giving rise to surface C and H atoms, with subsequent growth of CNTs from the particle surface.

In general, the size of the catalyst particle rules the diameter and type of carbon nanotube. Large catalyst particles typically result in multi-walled CNTs, which may be relevant to applications benefiting from their mechanical properties. However, a key requirement for growing single walled CNTs is that the catalyst particles be extremely small, typically only a few nanometers in diameter. Uniform and reproducible deposition of such small particles requires careful process control. More importantly, due to PVDs' line-of-sight constraint, these techniques struggle to conformally deposit material on 3D architectures.

A potential solution to these challenges is the use of atomic layer deposition (ALD) for catalyst preparation. ALD uses self-limiting chemistries to deposit thin films in a layer-by-layer fashion with atomic level thickness control and unprecedented uniformity and conformality. A high temperature H_2 anneal step that is part of the CNT synthesis process can subsequently be used to reduce a metal-oxide film into a catalytic metal. In contrast to physical deposition techniques, ALD is capable of coating complex 3D structures with atomic level precision.

In this paper we investigated the use of NiO ALD reduced to metallic Ni for the catalytic growth of CNTs within the confines of a high aspect ratio nanoporous template. Thin films of NiO were deposited using Ni(amd) and

H_2O and reduced in a post-deposition low temperature H_2 anneal. After reduction, films became very granular with increased surface roughness of ~1.6 nm RMS. CNTs grown with ethylene within 5 µm dia. pores exhibited small diameters, well below the pore size. Since grain size of the catalytic metal has a direct effect on the diameter and type of the subsequent CNT growth, different reduction methods were investigated, such as reduction temperature, time and the use of an in-situ H_2 plasma during the ALD deposition.

AA-MoP-53 Atomic Layer Deposition of Titanium Oxide using Heteroleptic Titanium Precursors with a Linked Ligand*, **Seongyoon Kim**, J Kim, J Gu, H Kim, H Jung,* Sejong University, Republic of Korea*; M Park, J Park,* Hansol Chemical, Republic of Korea*; W Lee,* Sejong University, Republic of Korea

Titanium oxide and Ti-based perovskites have been continuously studied for application to DRAM capacitors as high-permittivity materials. ALD technology has replaced PVD and CVD to provide excellent step coverage, accurate film thickness control, and highstoichiometry film quality. The most popular titanium precursors are tetrakis(dimethylamino)titanium (TDMAT) and titanium tetraisopropoxide (TTIP), and the ALD TiO_2 films using those precursors showed narrow ALD temperature window with the maximum ALD temperature of approximately 200°C. In general, higher deposition temperature improves the physical and electrical characteristics of the dielectric film, such as film density, stoichiometry, and purity. However, the ALD precursors decompose at higher temperatures, resulting in poor step coverage and high impurity concentration. Therefore, we need titanium precursors with excellent thermal stability together with high reactivity and sufficient volatility. It was reported that thermal stability of TDMAT is improved by replacing an alkylamine group with a cyclopentadienyl to form tris(dimethylamino)cyclopentadienyl titanium [1]. In the present study, we investigated the ALD of titanium oxide using heteroleptic titanium precursors with a linked ligand. A heteroleptic precursor with alkylamino groups was compared with alkoxy groups. Saturation dose and the ALD temperature window were determined by measuring growth rate with different precursor feeding times, oxidizing agent feeding times, and the process temperatures. The reaction mechanism was studied by using in-situ Fourier transform infrared spectroscopy and quadrupole mass spectroscopy. The physical and electrical properties of the deposited films were also characterized.

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AA-MoP-54 *Ex-Situ* Grown Low-Temperature SiN_x on GaN with Crystalline Interfacial Layer using Hollow Cathode PEALD*, **Xin Meng**, J Lee, A Ravichandran, Y Byun, J Lee, A Lucero, S Kim,* The University of Texas at Dallas*; M Ha,* Myongji University, Republic of Korea*; C Young,* The University of Texas at Dallas*; B Hwang,* Dow Chemicals*; J Kim,* The University of Texas at Dallas

In this work, we report *ex-situ* grown low-temperature SiN_x on GaN with ~1.5 nm crystalline interfacial layer (CIL). The 2.8-2.9 Å d-spacing indicates that the CIL is β-phase Si_3N_4. The SiN_x was grown by hollow cathode plasma-enhanced atomic layer deposition (PEALD) [1]. Tris(dimethylamino)silane (3DMAS) and a remote N_2 plasma were used as the silicon precursor and the nitrogen co-reactant, respectively. Though the growth temperature was as low as 300°C, we obtained excellent film properties comparable to those of high-quality thermal SiN_x films grown at a temperature above 700°C. Owing to the effective passivation of dangling bonds and nitrogen vacancies by the crystalline interfacial layer, GaN MIS-HEMTs with PEALD SiN_x gate dielectric shows excellent threshold voltage (V_{th}) stability (ΔV_{th}<0.3 V) under positive/negative bias stress.

We also compared with other devices using different ALD-grown gate insulators (15 nm), including (a) SiN_x using pentachlorodisilane (PCDS) and N_2/NH_3 plasma, (b) SiN_x using hexachlorodisilane (HCDS) and N_2/NH_3 plasma, and (c) Al_2O_3 using trimethylaluminum (TMA) and H_2O. Of all the devices, PCDS-SiN_x/GaN MISHEMTs exhibited both a highest on/off ratio (~10^{10}) and a negligible V_{th} instability (ΔV_{th}<0.1 V) under a large gate bias stress of 7 V. The extraordinary results suggest an excellent interface of the gate dielectric stacks, as well as negligible bulk traps inside the PEALD SiN_x layer.

The authors would like to acknowledge Dr. Scott Butcher (Meaglow Ltd.) for the technical discussions on the use of hollow cathode plasma source.

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AA-MoP-55 Composition Adjustment of Zn(O, S) Buffer Layer on CIGS Solar Cell by Atomic Layer Deposition*, **Yu-Hsuan Yu**, N Koothan,* Instrument Technology Research Center, Republic of China*; W Xu,* National Tsing Hua University, Republic of China*; C Kei, M Shiao,* Instrument Technology Research Center, Republic of China*; C Lai,* National Tsing Hua University, Republic of China

Depositing Zn(O, S) thin film as the Cd-free buffer layer is an important topic in CIGS solar cells since it offer the potential enhancements for either low cost and good for environment. The band gap and the optical properties, which is crucial to the buffer layer, is controlled by the element composition of Zn(O, S) thin film. In this study, In this study, we deposited ZnO and ZnS thin films by atomic layer deposition(ALD). We deposited ZnO thin film by using diethyl Zinc((C_2H_5)2Zn, DEZ) and H_2O and the ZnS film was deposited by using DEZ and H_2S. And the Zn(O, S) buffer layer was fabricated y alternately depositing ZnO and ZnS thin films. We can control the oxygen/sulfide composition in the Zn(O, S) thin film by changing the cycle ratio of ZnS and ZnO. The properties of Zn(O, S) films were measured by ellipsometry, SEM, XRD and XPS. We also deposited Zn(O, S) films with different O/S composition on CIGS absorber. The device performance were measured by current-voltage measurement.

AA-MoP-56 Effect on Low Plasma Damage by ALD Deposition of Silicon Heterojunction Solar Cell*, **Hyeongsik Park**,* Sungkyunkwan University (SKKU), Republic of Korea*; H Kim,* Incheon National University, Republic of Korea*; Y Kim,* Sungkyunkwan University (SKKU), Republic of Korea*; K Lim,* JUSUNG Engineering, Republic of Korea*; J Kim,* Incheon National University, Republic of Korea*; J Yi,* Sungkyunkwan University (SKKU), Republic of Korea

We report regarding ZnO back reflector by atomic layer deposition (ALD) on a silicon heterojunction solar cell with the rear-emitter structure. ALD ZnO can reduce a plasma damage on silicon heterojunction after an ITO deposition and be leading to maintaining the open circuit voltage. The current density has different around 1 mA/cm^2 led to the cell efficiency depending on a ZnO back reflector. We achieved the efficiency of 22.4% having a ZnO back reflector without a change of open circuit voltage (V_{OC}: 723 mV) and fill factor (FF: 76.8%) as compared the reference specimen (V_{OC}: 723 mV, FF: 76.4%).

AA-MoP-57 A Study on the Mechanical and Electrical Properties of Atomic and Molecular Layer Deposited ZnO – Zincone Alloy Thin Films with change of Molecular Backbone Structures.*, **Seung Hak Song**, S Hwang, B Choi,* Korea University, Republic of Korea

The interposition of zincone thin films into ZnO thin films can improve the properties of structures. Zincones are fabricated by the reactions between zinc reactants and organic precursors. Zincones have a different backbone structures depending on organic precursors, for example, zincone thin films which deposited by the reactions between diethylzinc (DEZn) and ethylene glycol (EG) precursors have a –O-CH2-CH2-O- backbone structures. The reactions between DEZn and hydroquinone (HQ) fabricate zincone thin films that have aromatic backbone structures. The rigid and conjugated structure of HQ is expected to produce durable and electrically conductive materials. In this study, the differences of mechanical and electrical properties between ZnO – zincone (EG) and ZnO-zincone (HQ) alloy thin films were measured. The critical tensile strain and elastic modulus of the thin films were measured using micro tensile tests. Electrical conductivity and sheet resistances were also measured. The structure and growth rates of thin films were investigated using x-ray diffraction and ion mass spectrometry methods.

AA-MoP-58 ALD and Nanocellulose Based Sensors for Ultra-low Power, Room Temperature Ozone Gas Monitoring for Respiratory Ailments and Wellness Management*, A Tanneeru, T Flewwellin, A Young, M Daniele, V Misra, **Bongmook Lee**,* North Carolina State University

Ultra low-powered gas sensors for environment and breath monitoring, can help us tackle health conditions like asthma, emphysema, chronic bronchitis by monitoring for permissible levels of gases like ozone in the atmosphere. The sensitivity of these sensors should be in the 50-100ppb concentration range to detect ozone in the atmosphere so as to avoid exacerbating these chronic conditions. Traditional sensing methods of high temperature heating of the substrate (200^0C-450^0C), consume high-power and are therefore not compatible with wearable technology for long-term gas monitoring. We have demonstrated highly sensitive, selective sensors with low power consumption and room-temperature operation, by depositing nanoscale thick metal oxide layers ALD technique on Si/SiO_2 substrate. Nanocellulose is a material has several advantages such as bio-compatibility, high mechanical ruggedness, high surface area, thermal stability and flexibility. It also has a conformal adherence to epidermal surfaces without adhesives via Vanderwaals forces and is less susceptible to degradation due to mechanical stress. In this work we report ultra-low power room temperature sensing of ozone gas, by atomic layer deposited (ALD) tin oxide sensing layer on a nanocellulose substrate. The sensor fabrication started with a nanocellulose substrate produced by oven drying cultured bacteria over glass slides. A 6nm sensing layer of SnO_2 was deposited by atomic layer deposition with Tetrakis (dimethylamino tin (IV) – $Sn[N(CH_3)_2]_4$) precursor at 200^{o}C, with a 20nm ALD Al_2O_3 interlayer to ensure electrical isolation with substrate. Titanium (20nm)/Gold (250nm) electrodes were deposited by e-beam evaporation. The sensors were tested for response to ozone in 25 to 100 ppb concentration range in a humidity and temperature controlled testing chamber. UV LED with a 5-10% duty cycle was used to reset the resistance to the baseline value keeping the total power consumption under 200uW. The flexible ozone sensor shows highly sensitive and selective responses from 25 parts per billions (ppb) to 100 ppb. This ultra-low power, highly selective and sensitive nano-scale thick ALD deposited ozone sensor can be integrated with a highly bio-functional nanocellulose substrate in the flexible system. Combined with the body powered, battery-free and wearable health monitoring systems as developed at NSF-ASSIST center, this has a potential to play a key role in management of respiratory ailments

AA-MoP-59 Plasma-enhanced Atomic Layer Deposition of Ruthenium Thin Film using (p-cymene)(dimethyl-hexadiene)Ruthenium*, J Choi,* UP Chemical Co., Ltd., Republic of Korea*; S Kim,* Sejong University, Republic of Korea*; B Yoo, W Han,* ***Wonyong Koh****,* UP Chemical Co., Ltd., Republic of Korea*; W Lee,* Sejong University, Republic of Korea

The resistivity of copper interconnect increases rapidly as the linewidth decreases beyond 30 nm due to the sidewall scattering of electrons. The resistance of copper interconnect increases even further because it is hard to scale the thickness of barrier and cladding layers. In addition, the maximum allowable current density in high-performance logic devices will be limited by the electromigration failure of scaled copper interconnects. These problems can be solved by replacing copper by an alternative metal. Ruthenium and cobalt are attracting attention as candidate conductor materials because they have shorter mean free paths of electrons and higher melting point compared with copper. They can also improve the resistivity by reducing the barrier thickness because they do not attack the lower layer. Atomic layer deposition (ALD) is a promising method for gapfilling of damascene pattern or the conformal deposition of a seed layer for electroplating. The most popular co-reactant in ALD ruthenium is O_2. However, the drawback of O_2 is the formation of the insulating layer by oxidation the underlying layers, resulting in high resistance. In the present work, therefore, we studied the plasma-enhanced ALD (PEALD) of ruthenium thin film using (p-cymene)(dimethyl-hexadiene)ruthenium and non-oxidizing co-reactants, the mixtures of N_2 and H_2 or NH_3. Ruthenium thin films were grown in a showerhead-type cold-wall PEALD reactor. The growth rate, composition, and resistivity of the deposited films were investigated with varying co-reactant and plasma condition.

AA-MoP-60 Low Temperature Plasma Enhanced Atomic Layer Deposition of SiO_x Films using New Divalent Si Precursor for Thin Film Encapsulation*,* ***Jung-Hoon Lee****, J Lee, W Choi,* Hanyang University, Republic of Korea*; J Park,* Hansol Chemical, Republic of Korea*; J Park,* Hanyang University, Republic of Korea

Silicon dioxide (SiO_2) is a well-known dielectric material, which have been used for semiconductor industries such as gate dielectric, gate spacer and deep shallow trench.

Besides, SiO_2 attract its attention as a promising material for thin film encapsulation (TFE), organic devices such as light emitting diode, photoelectric device need encapsulation layer to prevent degradation of organic materials caused from oxygen and water vapor. Conventionally, SiO_2 films are deposited by chemical vapor deposition (CVD), sputtering and thermal evaporation. The above methods have some problem for TFE such as high growth temperature, poor step coverage, point defect. Plasma enhanced atomic layer deposition (PEALD) method is popular that can achieve high quality SiO_2 without defect at relatively low temperature.

In our study, SiO_x thin film was deposited by PEALD method using N,N'-tert-butyl-1,1-dimethylethylenediamine silylene as a precursor, oxygen plasma as a reactant. PEALD processes show surface limit reaction behavior as increase precursor dose with constant purge time 10s during processes. Also, it exhibited significant process window in the temperature range of 80-200^{o}C with negligible ble carbon, nitrogen impurity concentration. Film thickness, refractive index of SiO_x thin films are investigated using spectroscopic ellipsometry (SE) and films have about 1.45-1.5 refractive index value which is correspond to SiO_2' refractive index although we used divalent precursor. Due to low temperature process, SiO_x thin films are deposited on polymer substrate under 120^{o}C and Water vapor transmission rate (WVTR) is measured by Ca-test method. As a result, we can compare the WVTR properties of SiO_x depending commercial precursor and new divalent precursor.

AA-MoP-61 Atomic Layer Deposited Tungsten (W) Thin Films using Fluorine-free W Precursors*, S Kim,* ***Min Young Lee****, T Kim,* Yeungnam University, Republic of Korea

The tungsten films have good properties such as relatively low resistivity (bulk resistivity: 5.6μΩ·cm), low reactivity with oxygen, and good step coverage deposited by chemical vapor deposition method. So, it has widely investigated in semiconductor device technologies including the word lines and bit lines of memory devices. However, with the continuous shrinkage and novel 3D structure with high aspect ratio of device, a conformal deposition technique on a high aspect-ratio trench and hole structure with excellent uniformity of thickness and process controllability is essential. In these respects, atomic layer deposition (ALD) for these materials have been drawn much attention because ALD uses a self-limiting film growth mode by surface-saturated reaction, which enables atomic scale control of the film thickness with excellent step coverage. The WF_6 precursor was commonly used as a precursor for atomic layer deposition but this process using WF_6 precursor has some problems. It has long incubation time and additional pretreatment carried out. Furthermore, fluorine remaining in the tungsten film made critical damage on underlying substrate. To solve these problems, we report the plasma-enhanced ALD (PEALD)-W and thermal ALD-W processes using two kinds of fluorine-free precursor, an inorganic WCl_5, and a novel tungsten metalorganic precursor with various reactants. For example, tungsten thin films using WCl_5 precursor were deposited by using showerhead type ALD reactor (ALD, Lucida-M100, NCD technology) with H_2 plasma as a reactant. The deposition temperature's range is from 200 to 350°C. We check the grazing incidence angle (q = 3°) XRD patterns of the typical PEALD-W film deposited on SiO_2 substrate. Five peaks from primitive cubic-structured beta tungsten were clearly shown. T he properties of PEALD-W and thermal ALD-W films with deposition conditions have been evaluated by using various tools; resistivity by 4-point probe and XRR(or X-SEM), step coverage by XTEM, phase using XRD, composition by SIMS, and chemical bonding by XPS.

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AA-MoP-62 Low Temperature Atomic Layer Deposited MoN_x as an Efficient Cu-diffusion Barrier*, S Kim,* ***Tae Hyun Kim****, D Nandi,* Yeungnam University, Republic of Korea

A deposition technique with extremely precise control over film thickness, the low deposition temperature and non-corrosive by products (like acids) during deposition are the essential criteria for an efficient barrier layer. To address all of these issues, molybdenum nitride (MoN_x) is deposited at a relatively low temperature (175-300^{o}C) by atomic layer deposition (ALD) using molybdenum hexacarbonyl [$Mo(CO)_6$] as a novel precursor for Mo and ammonia gas (NH_3) as reactant. The as-grown MoN_x are mostly amorphous, however poor nano-crystalline *h*-MoN phase formation is evident from the deposition temperature of 250^{o}C and beyond. The lowest resistivity less than 6000 μΩ-cm for as-deposited film reflects the suitable properties of these MoN_x films to be used as barrier material. Nevertheless, X-ray diffraction (XRD) analysis also reveals that the crystallinity could be enhanced by post-annealing from 500^{o}C to 700^{o}C that converts the film into cubic-Mo_2N phase as well. Corresponding with this, the film resistivity was decreased to ~4000 μΩ-cm. The properties of as-deposited and annealed films are further well-characterized by secondary-ion mass spectroscopy (SIMS), X-ray photo electron spectroscopy (XPS), Rutherford back-scattered spectroscopy (RBS) etc. Two set of ALD-MoN_x films (~4 nm) grown at 225 and 275^{o}C are tested as a diffusion layer against Cu. It is observed that the film deposited at higher temperature acts better for this purpose. The possible reason for this might be the higher density of the ALD-MoN_x films grown at 275^{o}C compared to the films deposited at 225^{o}C.

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AA-MoP-64 State Key Laboratory of Digital of Manufacturing Equipment and Technology, School of Mechanical Science and Engineering,Huazhong University of Science and Technology, ***Qinyong Xiang****, B Zhou, K Cao, B Shan, R Chen,* Huazhong University of Science and Technology, China

$CsPbX_3$ (X=Cl, Br, I) lead halide perovskite quantum dots (LHPs) have attracted great attention due to their excellent optical properties, such as tunable wavelength, narrow emission, and high photoluminescence quantum efficiency [1]. However, When LHPs are exposed to external environment (humanity, heat and light), the degradation of LHPs occurs and leads to the photoluminescence quenching [2-3]. In this work, alumina shell is deposited by atomic layer deposition to stabilize $CsPbBr_3$ QDs-silica nano luminescent sphere. The $CsPbBr_3$ QDs are coated with nanoscale Al_2O_3 layers with excellent uniformity and the aggregation of QDs are also avoided during ALD process. The as prepared $CsPbBr_3$ QDs-silica nano luminescent spheres not only retain the high photo luminescent quantum yields, but also exhibit excellent stability in water and heat. Further characterizations results show that Al_2O_3 coating effectively avoids the destruction of QDs' crystalline structure in water and thus enhance the stability. This method is potentially applicable to the stabilization of other QDs such as CdSe, InP and PbS and backlight devices.

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AA-MoP-66 Research on Properties of Protective Film Deposited on Silver Hat with Large and Complex Morphology at Low Temperature, ***Yang Liang****, L Lina,* Kaili University, China

Sulphides and oxides formed on the surface of silver hat will degrade the appearance seriously.To solve the problem,Al2O3 protecting film was deposited on silver hat for anti-tarnishing by thermal atomic layer deposition technique with $Al(CH_3)_3$ and H_2O as precursors at low substrate temperature. The film with thickness uniformity less than 6.8% has been successfully prepared on both the internal and external surfaces of silver hat by designing and using a dispersal device to make the gas flow uniform. Some small particles appearing on the surface of the film disappear by optimizing process parameters. The x-ray diffraction test shows that the film is amorphous at 120℃. The x-ray photoemission spectroscopy and scanning electron microscopy-energy dispersive spectrometer test show that the atomic ratio and weight percent of oxygen to aluminium for the Al_2O_3 film are 1.52 and 0.86 respectively. The accelerated corrosion experiment, diffuse reflection test and color difference calculation show that the protecting film with thickness of 30nm has a satisfactory anti-tarnishing effect and produces no effect on the appearance of silver ornament.

AA-MoP-68 Fabrication of Microchannel Plate (MCP) using 3D Printing and ALD Coatings, ***Anil Mane****, L Xia, J Xie, R Wagner, H Nicholson, M Pellin, J Elam,* Argonne National Laboratory

Microchannel plates (MCPs) are 2D-electron amplifiers with high gain (10^3-10^5) used in a variety of commercial applications including night vision and particle detection. Traditional MCPs are made with lead glass capillary arrays with millions of pores of size from a few to tens of microns diameter [1]. A pair of MCPs sealed in a package under ultra-high vacuum with a photocathode window is the basis for photodetectors that provide picosecond time resolution and sub-millimeter spatial resolution. Recently, MCPs have been fabricated using non-lead micro capillary array (MCA) glass substrates functionalized by ALD coatings with dramatically larger area and improved properties compared to lead glass MCPs [2]. 3D printing may provide a more flexible and cost effective route for producing micro capillary array substrates. To explore this approach, we used a 3D printer based on 2-photon polymerization with ~50 nm spatial resolution to fabricate capillary arrays ~1 cm^2 in area. We functionalized these 3D printed substrates with ALD resistive coatings composed of a W-Al_2O_3 nanocomposite, and MgO secondary electron emission layers [2, 3]. These 3D printed MPCs show gain and spatial uniformity comparable to the MCA glass MCPs. Here we will discuss the synthesis, characterization, and testing of MCPs using 3D printed structures and ALD functionalization. 3D printed MCP substrates offer the possibility of significant cost savings in materials and labor compared to MCA glass. More importantly, 3D printing can easily create tailored structures not possible using conventional techniques, and this will facilitate new applications for MCP technology.

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AA-MoP-69 Zn-doped TiO_2 Hollow Fibers Fabricated by ALD Nanolamination for Photocatalysis, ***Li-Chen Wang****,* National Tsing Hua University, Taiwan, Republic of China*; W Liu, C Su, T Perng,* National Tsing Hua University

Recently, one-dimensional (1D) materials such as SnO_2, ZnO, and TiO_2 nanowires or nanotubes have attracted immense attention due to their unique and tunable optical, magnetic, electrical, and chemical properties. Tremendous attempts, therefore, have been made to refine these properties by incorporating various ions into the 1D nanomaterials for application in photocatalysis. In this study, we demonstrated a controllable synthesis of Zn-doped TiO_2 (Zn-TiO_2) hollow fibers as a photocatalyst by atomic layer deposition (ALD) via nanolamination for hydrogen evolution and continuous-flow dye degradation. Herein, diethyl zinc (DEZ), titanium tetrachloride ($TiCl_4$) and H_2O were utilized as precursors of Zn, Ti, and O in the ALD reaction, respectively, to fabricate laminated layers of ZnO and TiO_2 on hollow polysulfone fibers (PSFs). The laminated composite was then annealed to remove the PSF and get a uniform doping of Zn in TiO_2. It was revealed that the photocatalytic efficiency of the Zn-TiO_2 hollow fibers could be affected by the concentration of Zn (X_z) and the film thickness of Zn-TiO_2. The X_z could be precisely controlled by the cycle numbers of DEZ/H_2O (N_z) and $TiCl_4$/H_2Ocycles (N_T) in a supercycle (N_z+N_T), and the film thickness of Zn-TiO_2 could be determined by the number of supercycles (n(N_z+N_T)). More importantly, this dry process to deposit Zn-TiO_2 thin film with perfect conformality on the porous PSF template offers a large surface area for the novel nanostructured photocatalyst. The structure of interconnected Zn-TiO_2 nanotubes inside the fiber wall benefits efficient trapping of the reflected photons within the hollow fibers, further improving the photocatalytic efficiency of hydrogen evolution and continuous-flow dye degradation.

AA-MoP-70 Co Decorated Ni/Al_2O_3 Catalysts Fabricated via Atomic Layer Deposition with Coking and Sintering Resistance Towards Dry Reforming of Methane, ***Kun Cao****, M Gong, J Yang, J Cai, B Shan, R Chen,* Huazhong University of Science and Technology, China

The advances in natural gas recovery have drawn much attention to dry reforming of methane (DRM) with carbon dioxide.[1] Nickel is an effective component for the reforming of methane in terms of the catalytic activity and cost, while Ni is plagued by deactivation due to sintering and heavy coking in the catalytic environment.[2] It is necessary to tune the catalytic structure and add the properties of high resistance to sintering, hot spot formation, and coke deposition, to the Ni catalysts. In this work, a mesh-like cobalt oxide coating structure is prepared on Ni nanoparticles via atomic layer deposition. The CoO /Ni catalysts demonstrate both good coking eliminable and sintering resistance ability compared with supported Ni nanoparticles catalysts and CoO /Ni catalysts prepared by incipient wetness method. Co oxide layer is deposited on Ni nanoparticles with discontinuous structure. The mesh-like coating layer could inhibit continuous carbon nanotubes formation, meanwhile CoO deposited on Ni surface partly passivates the coking sites also eliminate carbon formation. In addition, the coating layers provide physical barriers that anchor Ni nanoparticles and improve the sintering resistance.

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AA-MoP-71 Atomic Layer Deposition of Y:ZrO_2 on Nanoporous Silver for Thermally Stable Solid Oxide Fuel Cell Metal Cathodes, ***Hyung Jong Choi****, K Bae,* Korea University, Republic of Korea*; D Jang,* Korea university, Republic of Korea*; G Han, J Koo, J Shim,* Korea University, Republic of Korea

Solid oxide fuel cells (SOFCs), which produce electricity by converting chemicals directly into electrical energy, are attracting much attention due to their high efficiency and fuel flexibility. Since low-temperature SOFC (LT-SOFC) has a short start-up time and a wide selection of SOFC materials, studies are under way to lower the SOFC operating temperature (<500°C). However, by reducing the operating temperature, the oxygen reduction reaction (ORR) kinetics on the cathode sharply diminishes and degrades the overall electrochemical performance of the LT-SOFC. Therefore, for a high-performance LT-SOFC, it is essential to develop a cathode having high ORR activity.

Metal-based materials can be considered as LT-SOFC cathodes. For example, platinum (Pt) is the representative fuel cell cathode material because it has the excellent ORR activity when comparing to others. However, the cost of Pt is very high due to low reserves which hinders the widespread use of Pt. Silver (Ag) can be a potential alternative cathode material because it is much cheaper than Pt and has high oxygen solubility and diffusivity. However, Ag can be thermally agglomerated at the operating temperature of LT-SOFC due to the rapid reduction of AgO_x to Ag and the low melting point. Thermal agglomeration of Ag can destroy the overall microstructure of the cathode and reduces the three-phase boundary of Ag, the active site for ORR. As consequence, the long-term performance of LT-SOFC using Ag cannot be guaranteed.

In this study, we propose a method to fabricate a thermally stable metal cathode by coating a nanoscale $Y:ZrO_2$ (YSZ) thin film on Ag surface using atomic layer deposition (ALD). ALD allows precise control of thickness in atomic-scale while enabling uniform YSZ coatings on nanoporous Ag structures. Electrochemical performance experiments showed that a surface treated Ag cathode showed a power density comparable to a porous Pt cathode. Also, during long-term testing, the Ag coated with ALD-YSZ exhibited a stable current, but a bare Ag cathode showed abrupt deterioration. Through scanning electron microscopy, we found that the bare Ag cathode agglomerated severely while the surface-coated Ag could retain its nanoporous structure after the test. Thus, we can conclude that the electrochemical performance of Ag can be enhanced by ALD-YSZ capping on the surface that can preserve the nanoporous structure of the cathode at LT-SOFC operating temperatures.

AA-MoP-72 Plasma Enhanced Atomic Layer Deposition of Co-C Thin Film as Hydrogen Evolution Electrocatalysts, ***Qi Peng Fan**, Z Liu, Q Chen, Z Wang, L Sang,* Beijing Institute of Graphic Communication, China

In recent years, transition metal carbides (TMCs) have attracted increasing interest in the fields of mechanics, biomedicine and nanomagnetism due to their scientific and industrial importance. Among these transition carbides, cobalt carbide is one of important TMCs because of its excellent magnetic properties, which is identified as an alternate to rare earth magnets. Beside this, cobalt carbide was also studied as a promising catalysis for the dehydrogenation of ethanol to acetaldehyde, the production of lower olefins from syngas and low temperature water-gas shift. The present study reports the deposition of cobalt carbide films by the technique of plasma enhanced atomic layer deposition (PEALD). Bis(N,N-diisopropylacetamidinato)-cobalt（Ⅱ）($Co(^{ipr2}AMD)_2$) was used as cobalt and carbon precursor, and hydrogen plasma as reactive agent. The PEALD process is able to produce smooth, pure, and low resistivity Co-C thin films with an ideal selflimiting ALD growth fashion. Co-C thin films with a uniform thickness can be found throughout the entire trench with an aspect ratio as high as 20:1.The influences of the precursor pulse time, deposition temperature and input power on the growth rate of Co-C thin films were investigated. When the deposition temperature is 80℃ and the input power is 60 W, the saturated growth rates of the films are 0.065 nm/cycle . XRD and XPS measurements suggest that these films are composed of the amorphous phase. The ALD-synthesized Co-C/carbon cloth catalyst acted as efficient electrocatalyst for HER at low overpotential ($\eta_{10\ mA\ cm-2}$=182 mV) with long-term stability (keeping the activity at least 48 h) in 1 M KOH.

AA-MoP-73 TiO_2 Layer by Low Temperature Atom Layer Deposition for Perovskite Solar Cells, *Q Chen, **Yumeng Wang**, D Wang,* Beijing Institute Of Graphic Communication, China

In PSCs, the n-type electron transport layer (ETL) plays an important role in extracting photo-induced free electrons and suppressing front-surface.The simplification of perovskite solar cells (PSCs) which replaces the mesoporous electron selective layer (ESL) with a planar one is advantageous for large-scale manufacturing and greater selection of flexible substrates.Toward this end, we utilize thermal atomic layer deposition (T-ALD) to deposit ultra-thin (20nm) compact TiO_2 underlayers at 140℃ low-temperature as an eletron transporting layer in planar halide perovskite solar cells.Herein we regulate the electron transport layer energy level by plasma treatment to maintain good carrier extraction.When replacing Sol-gel method with thermal atomic layer deposition,the fabrication of our perovskite solar cells was conducted at low temperatures, which should simplify manufacturing of large-area perovskite devices that are inexpensive and perform at high levels.

AA-MoP-74 Oxides Encapsulation for Surface Passivation of Aluminum Nanoparticles via Atomic Layer Deposition, ***Jiawei Li**, K Qu, J Zhang, X Liu, R Chen,* Huazhong University of Science and Technology, China

Aluminum nanoparticles have attracted great attention for energy storage applications such as solid fuels, aerospace propulsion etc.[1,2] However, Al nanoparticles are easy to be oxidized by moisture and oxygen in ambient condition, which leads to the decrease of energetic metallic Al component. The surface passivation is necessary to enhance the stability of Al nanoparticles for practical applications. This work develops an oxide-encapsulation method for Al nanoparticles via atomic layer deposition to enhance their stability. Different types of oxides are encapsulated on Al nanoparticles. It is found that Al nanoparticles coated by ZrO_2 exhibit excellent corrosion resistance ability against hot water-bath compared with Al_2O_3 coating. The failure mechanisms of Al_2O_3 coating are studied. The generated hydrated oxide such as AlOOH reacts with active Al are responsible for the perforation of Al_2O_3 thin film. For ZrO_2 coating, denser ZrO_2 thin films and the generated interfaces between native Al layers enhance the stability of Al nanoparticles significantly.

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AA-MoP-75 Atomic Layer Deposition of Titanium Oxide-based Electrocatalysts for Li-O Battery, ***Yongliang Li**,* Shenzhen University, China

$Li-O_2$ batteries have been attracted worldwide research interests and considered to be the potential alternatives for the next-generation devices. Nitrogen doped carbon nanofibers (N-CNFs) prepared by electrospinning are used as flexible substrate and the TiO_2-based layers are coated by atomic layer deposition (ALD) and are employed as electrocatalysts for $Li-O_2$ batteries. The TiO_2-based electrocatalysts deliver a high specific capacity, improved round-trip efficiency and good cycling ability. The superior electrochemical performance can be attributed to the superior catalytic activity of TiO_2-based electrocatalysts toward oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) during the discharge/charge processes. This work paves a way to develop the catalyst materials for the future development of high-performance $Li-O_2$ batteries.

AA-MoP-76 Fabrication of Pt Nanoparticles on VN@TaC Porous Structure by Forced-Flow ALD for Proton Exchange Membrane Full Cell, ***Li-Chuan Tsai**, T Chin, T Perng,* National Tsing Hua University

Proton exchange membrane fuel cell (PEMFC) is considered as a promising clean energy because it can convert hydrogen and oxygen into electricity and the only byproduct is water which does not pollute the earth. In PEMFC, Pt is commonly used as the catalyst. In order to maximize the Pt catalytic activity, extensive studies have been made on uniform deposition of nano-sized Pt particles on the catalyst support. Herein, we report a controllable fabrication of Pt nanoparticles on our homemade VN@TaC porous structure by a forced-flow atomic layer deposition (ALD) process for PEMFC. TaC porous structure was first synthesized by a salt flux method, and it showed good electric conductivity, large surface area, and high stability which are the three indispensable requirements for the PEMFC catalyst support. It was then deposited with VO_x by a sol-gel method, followed by reduction in an ammonia atmosphere to form VN@TaC. Here, VN can act as not only a catalyst support but also a cocatalyst for PEMFC, which can enhance the performance of PEMFC with less Pt. For the forced-flow ALD process, the sample powder of VN@TaC was dropped on a glass microfiber filter which was then placed on a stainless steel mesh in the reaction chamber. The precursors, $MeCpPtMe_3$ and O_2, were forced to flow perpendicularly through the filter so that the Pt particles could be more uniformly deposited on VN@TaC than by conventional horizontal flow ALD. The Pt particles were semispherical and 3-6 nm in diameter. For comparison, Pt was also deposited by forced-flow ALD on TaC and VN. All of the three samples, i.e., Pt@TaC, Pt@VN, and Pt@VN@TaC, loaded with approximately 5% Pt, demonstrated higher specific power density than commercial electrode (20% Pt loading on carbon black). More importantly, Pt@VN@TaC showed better performance than Pt@TaC and Pt@VN, that is attributed to the synergistic effect between TaC and VN.

AA-MoP-77 Atomic Layer Deposition of TiO_2 Thin Films on Aluminium Foil: Material Properties and Application as Protective Layer for Food Packaging*, V Dias,* Universidade do Vale do Paraíba, Brasil*; **Rodrigo Pessoa**, A Lobo, F Marciano,* Universidade Brasil, Brasil*; H Maciel,* Instituto Tecnológico de Aeronáutica

Several types of coatings have been used for corrosion protection of food packaging [1]. The CO_2-containing beverages such as beer and carbonated drinks have acidity and chlorides in the composition and, when packed in Al cans, can promote the corrosion process by encountering the Al material. To prevent this, commercial Al cans are coated internally by synthetic resins that aims to protect the Al surface from direct contact with the beverage. However, when the resin is not applied correctly or when the Al can undergo mechanical impact or elevated temperatures, the occurrence of localized corrosion is verified due to the presence of pinholes, cracks or grains boundaries in the coatings [2]. In food packaging, the application of ALD technique has already been discussed for the protection and increase of shelf life of products such as paperboard used in food packaging with Al_2O_3 and TiO_2 coatings. However, the synthesis of protective thin films using the ALD process in the field of aluminum cans for carbonated beverages have not yet been reported. The aim of this work was to investigate the TiO_2-covered Al foil properties and evaluate its electrochemical behavior using as electrolyte a commercial beer. The samples were separated into three groups: (i) Al foil, (ii) commercial resin coated Al foil and (iii) Al foil coated with TiO_2 film obtained from ALD process using Beneq TFS-200 equipment. $TiCl_4$ and H_2O were used as precursors at 100ºC, while the reaction cycle number ranged from 500 to 2000. The corrosion resistance was carried out in a potentiostat / galvanostat AUTOLAB302N (Metrohm). The commercial beer was used as electrolyte. RBS, FT-IR and SEM were performed in TiO_2/substrates to investigate the GPC, elemental composition, chemical bonding and surface morphology. The electrochemical impedance spectroscopy (EIS) tests were performed on open circuit potential during 1h. From the potentiodynamic polarization, the corrosion and passivation potential of each sample were measured. To analyze the film strength, the protection efficiency was calculated for each sample. SEM images show that the films tend to follow the substrate surface roughness, even at high film thickness. The EIS results demonstrate an increase of up to five times in the corrosion resistance of aluminum when coated with TiO_2, when compared with bare aluminum foil. The EIS analyses focus on understanding the kinetics of the corrosion process and correlate with film properties.

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AA-MoP-78 Atomic Layer Deposition of Nitrogen-incorporated MoO_x Films: Electrical and Electrochemical Properties*, **Arpan Kumar Dhara**, D Saha, S Sarkar,* Indian Institute of Technology Bombay, India

Oxynitrides or nitrogen incorporated oxides of transition metals are rapidly gaining attention in materials research because of their tunable electrical and optical properties. They offer usage in variety of applications like photocatalysis, phosphors, electrochemical energy storage, magnetic materials etc. Primary changes in the material properties after incorporation of nitrogen occur due to the difference in electronegativity, electronic charge and polarizability between oxygen and nitrogen atoms. However, effective and homogeneous doping in the host material is a major practical issue till date. Constructive ways to increase the conductivity without significantly altering the material's chemical properties after doping are still a challenge. Usually nitrogen incorporation is carried out by annealing oxides under NH_3 or N_2/H_2 gas environment. In such circumstances the metal ions are sensitive to reduction which results in the formation of undesirable phases in the doped materials. Also the possibility of dopant inhomogeneity is a major drawback towards obtaining good quality doped materials.

Here we report, amorphous nitrogen-incorporated molybdenum oxide (MoO_x:N) thin films synthesized by atomic layer deposition (ALD) at relatively lower temperature of 170ºC. One ALD cycle of molybdenum nitride (MoN_x) is sandwiched for nitrogen incorporation between two MoO_x layers. The concentration of nitrogen is controlled by varying the ratio of MoO_x/MoN_x layers. Quartz crystal microbalance (QCM) measurement is carried out to study the mass change after every single precursor dosed into the reactor. Secondary Ion Mass Spectra **(**SIMS) shows the presence of nitrogen throughout the deposited films. Hence uniform inclusion of N-atom is adequately achieved at the reaction temperature. It is observed that conductivity of MoO_x films increase with increase in nitrogen concentration. Room temperature and low temperature electrical properties of different films are also studied in detail to understand the transport mechanism with and without nitrogen incorporation.

Both pristine and N-incorporated MoO_x are deposited on high surface area MWCNTs and applied as anode material in lithium ion batteries. As expected, addition of nitrogen helps to improve the electrochemical performance because of the increased ionic and electronic conductivity.

AA-MoP-79 Deposition of Multi-Component Amorphous Oxide Semiconductor for the Oxide Thin-Film Transistors*, **Jong Beom Ko**, S Lee, S Park,* Korea Advanced Institute of Science and Technology, Republic of Korea

Amorphous oxide semiconductor (AOS) thin films are appropriate candidate for the driving devices of the high-end display due to their several important advantages. Mostly, to obtain amorphous phase of oxide semiconductors, two or more cations with different atomic sizes and ionic charges are mixed, and various kinds of AOS materials with multi-component system are reported including IZO, ZTO and ITZO. The most of multi-component of AOS materials are deposited by physical vapor deposition, especially sputter. However, it may cause non-uniformity of electrical characteristics in large area due to heterogeneous distribution of O_2 plasma. In contrast, the atomic layer deposition (ALD) is superior method to deposit films with good uniformity.

In here, the IZO and ITZO films were deposited with plasma-enhanced ALD (PEALD) by feeding metal precursors and oxidize with O_2 plasma. We successfully deposited different composition of IZO and ITZO for the semiconductor and applied to the TFTs. To control the composition of AOS films, the feeding dose of indium precursor was modified while fix the dose amount of another precursor.

From the XRD pattern, we confirm that the phase of the IZO and ITZO films deposited by PEALD was amorphous which appropriate to the active layer due to good electrical characteristics. The composition of the IZO and ITZO films also investigated by means of XPS. As the dose of the indium precursor increase, the indium composition in IZO and ITZO also increase. The different composition of the IZO and ITZO films were applied to the BGBC TFTs as the active layer, and their electrical characteristics were investigated. The linear mobility of the TFTs with IZO was about $18cm^2/Vs$ and the mobility value was increased as the indium composition of IZO increased. The turn-on voltage (V_{on}) of the IZO TFTs was -1V and it shift to the negative direction as the indium composition increase. For the TFTs with ITZO, the field effect mobility and V_{on} were about $30cm^2/Vs$ and -1V, respectively. For the measurement of stability at the bias and temperature stress condition, the devices were biased with +20V and -20V at 60^oC condition during the 10000 sec. The transfer curve of IZO TFTs were barely shifted during the stress, however, the transfer curve of the ITZO TFTs were shifted about 0.5 and -1V after positive and negative bias, respectively. From the research, we found the feasibility of applying the PEALD process for the multi-component AOS for the oxide TFTs. The composition of the AOS films was easily controlled and showed different electrical properties depending on the composition.

AA-MoP-80 Identification and Improvement of Reliabilities on Oxide Semiconductor TFTs with Al_2O_3 Gate Insulator Layer Deposited by Various Atomic Layer Deposition Process*, **Kyoungwoo Park**, G Jeon, S Lee, J Ko, S Park,* Korea Advanced Institute of Science and Technology, Republic of Korea

Among the backplanes for the next generation display, the oxide semiconductor TFTs is receiving the most attention because of its characteristics such as high mobility, high stability, scalability, low process temperature and high transparency. However, due to the intrinsic problem of oxide semiconductors caused by oxygen and hydrogen species, it is hard to control reliabilities under various stress conditions. One of the most effective ways to improve this reliability is defect passivation by hydrogen. However, previous studies have shown that hydrogen can act positive or negative roles in oxide TFTs.

In order to overcome these issues, we investigated the causes of degradation of oxide TFTs by applying Al_2O_3 gate insulator layer (GI) deposited by various atomic layer deposition (ALD) methods using trimethylaluminum (TMA). ALD method was used to determine the factors affecting the positive bias temperature stress (PBTS) and negative bias illumination stress (NBIS) reliabilities by varying the reactants such as H_2O and O_2 plasma in Al_2O_3 GI deposition. In case of TFT with Al_2O_3 deposited by using H_2O reactant, it shows very stable characteristics under PBTS due to hydrogen passivation, however, NBIS has shown unstable results. On the contrary, TFT with Al_2O_3 deposited by using O_2 plasma reactant, it exhibited stable NBIS characteristics but exhibited very unstable PBTS due to plasma-related defects. From the above results, we have confirmed that the hydrogen may passivate the defects at the shallow level, and may also generate the new defects at the deep level in oxide semiconductors. And the influence of hydrogen on the characteristics of oxide TFTs was confirmed by controlling the amount of hydrogen by varying the deposition temperature of Al_2O_3 GI. As a result of measuring the electrical properties of these TFTs with the various deposition temperature of Al_2O_3 GI, there was no significant difference between the devices. However, it was confirmed that the hydrogen contents decreased as the deposition temperature of Al_2O_3 increased, and the NBIS instability was improved from -4.36V to -2.48V. In addition, photoluminescence (PL) analysis results of Al_2O_3 thin films with the various deposition temperature shown that as the number of hydrogen increases, new peaks are generated at the deep level. From the above results, we have confirmed that excessive hydrogens influx can generate new defects at the deep level, which can degrade NBIS reliability.

Based on these results, we will propose the way to improve reliabilities of oxide semiconductor TFTs via GI process optimization.

Atomic Layer Etching
Room Premier Ballroom - Session ALE-MoP

Atomic Layer Etching Poster Session

ALE-MoP-1 A Reliable Atomic Layer Etching Approach in Angstrom-level Flatness Control for Uniform CVD Grown TMDs Preparation*, **Chao-An Jong**,* National Nano Device Laboratories, Republic of China*; P Chiu,* NARL, Republic of China*; C Wang, M Lee,* National Taiwan Normal University, Republic of China*; P Chen,* Minghsin University of Science & Technology, Republic of China*; C Lin, C Hsiao,* NARL, Republic of China

Transition metal dichalcogenides (TMDs) has attracted considerable attention because of their tunable electrical and optical properties which is sensitive to their thickness. It is well known that the bandgap transited from direct to indirect when thickness increased [1-3]. The TMDs films usually obtained by exfoliated and CVD process are widely explored for different electronics and optoelectronic device fabrication. Although CVD process is announced for the large scale and continuous film preparation, it is still challenging to control the layer uniformity during the randomly nucleation and growth process. (Fig. 1)

A modified CVD process, which deposit precursor film on desired substrate and followed by the chemical reaction with chalcogens, is promising not only its potential for wafer scale synthesis but also the capability of a continuous, selective area synthesis and uniform layered TMDs formation. Lots of experimental data announced for the controllability between the precursor thickness and the numbers of TMDs layers [4-5]. However, it is very challenging for bottom-up growing film in angstrom level thickness and flatness control.

In this study, we propose a prospective application of atomic layer etch (ALE) process [6] in precursor film thickness and flatness control for uniform CVD grown TMDs preparation (Fig. 2). An ionic plasma source is equipped for thinning down. The ions were supplied from ionized Ar gas (99.9995%) with corresponding 380 W RF power, 300 V grid voltage, and 300 mA current. A set of radio frequency neutralizer (RFN) was used to prevent charge build-up on the substrate surface. By adjusting the RF power and the grid current/voltage, the thickness and flatness of precursor film can be well controlled.

The flatness of studied films are characterized by atomic force microscope (AFM). 10nm WO_3 film is prepared for etching. Followed by the sulphurization process, layered WS_2 films were also characterized by Raman and photoluminescence (PL) measurement. The root mean square (rms) roughness of as-deposited WO_3 film, etched WO_3 film and WS_2 film were taken. The rms data of etched WO_3 films are around 5A ± 0.5A within 80mm x 80mm scanned area (Fig. 3). The rms data for WS_2 film formed by sulfurizing etched WO_3 film are 4A ± 0.5A. The layer number of WS_2 film can be well identified by calculating Raman frequency difference between the in-plane (E^1_{2g}) and out-of-plane (A_{1g}) modes (Fig. 4). Compare to the PL spectrum, a specific number layer of high quality TMDs can be precisely synthesized. The approach is promising for wafer-scale, continuous and uniform TMDs film and stacking heterojunction p-n TMDs-based device fabrication.

ALE-MoP-2 Surface Cleaning of SiO_2 Layers by Atomic Layer Etching with Low Global Warming Potential Gases*, **Yongjae Kim**, T Cha, S Lee, Y Cho, H Chae,* Sungkyunkwan University (SKKU), Republic of Korea

When determining the yield and performance of semiconductor devices, controlling impurities and particles is important. Etching process generates many contaminants for instance native oxide, organic materials and inorganic materials. Among them, native oxide is considered critical one because it causes higher contact resistance. It can create higher contact resistance, which makes the IC inoperable. Other disadvantages of native oxide involve leakage current on gate oxide and inadequate formation of silicide in devices. [1] Typically wet cleaning processes are mainly applied to remove native oxide, but the processes are reaching the limits in high aspect ratio patterns in nanoscale and highly integrated devices. [2] Recently new dry-cleaning technology are being studied to overcome these problems of wet cleaning processes. [3] Many perfluorocarbon (PFC) such as CF_4, CHF_3, and C_4F_8 gases are widely used in semiconductor processes for etching and cleaning processes. PFCs are global warming gases and the have long lifetime. [4]

In this work, cyclic plasma process was studied for SiO_2 (native oxide) removal with surface modification in an inductively coupled plasma (ICP) reactor with $C_3F_7OCH_3$, Ar, O_2 chemistries. The process consists of two steps of surface modification and removal step. In the first step, SiO_2 surface is modified with fluorocarbon polymers generated with $C_3F_7OCH_3$ having low global warming potential. In the second step the fluorinated oxide is removed with ions or radicals generated from Ar or O_2 plasma. Formation of fluorocarbon polymer layer on SiO_2 surface was confirmed by SEM and XPS analysis. Cleaning rate was investigated by varying bias voltage and ion density by monitoring the processes with a VI probe and an ion probe. It is also confirmed that the removal rate showed self-limited characteristics as the processing time increases. Removal rate were compared at various conditions of reaction gases and plasma power and the rate could be controlled under 10 Å/cycle.

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ALE-MoP-3 Electrical and Residual Gas Diagnostics of Pulsed Plasma Atomic Layer Etching in Silicon*, G Kwon, **Hee Tae Kwon**, W Kim, G Shin, H Lee,* Kwangwoon University, Republic of Korea

As the plasma etching process requires atomic-scale fidelity,ALE(Atomicl Layer Etching) is now emerging. This is because conventional plasma etching causes various types of problems,for example, ARDE(Aspect Ratio Dependent Etch), and the feature size fabricated in the manufactures shrinks rapidly in nanoscale.

ALE has two kinds of method.The first is called as ALE,which is opposite to ALD. The second is called Quasi-ALE. This Quasi-ALE consists of several types,such as chemistry reaction,energy control,and flux control.With these two kinds of ALE method,ALE is steadily developing. By the way,there are not many diagnostics of ALE yet.

Therefore, we did plasma diagnostics qualitatively with introducing Quasi-ALE with energy control. Pulsed Plasma was used for tailoring plasma parameters, in order to achieve atomic layer etching of silicon in CCP (Capacitively Coupled Plasma) reactor. Both chlorine gas and argon gas were injected into the reactor for adsorption and desorption. For plasma diagnostics of ALE in silicon qualitatively, we used electrical probe to figure out low temperature (T_e). Also, RGA (Residual Gas Analyzer) was used to check by-products. All experiments were set with proper environment such as adequate pulse frequency and pressure, and so on.

ALE-MoP-4 Spontaneous Etching Behavior of Oxide and Sulfide Underlayers during Atomic Layer Deposition of $Cu_{2-x}S$ using $Cu(dmamb)_2$ and H_2S*, J Han,* Seoul National University of Science and Technology, Republic of Korea*; **Raphael Agbenyeke**,* University of Science and Technology, Republic of Korea

The rapid diffusivity of Cu^+ ions in the hexagonal-close-packed crystal structure of $Cu_{2-x}S$ is a trigger for many interesting and sometimes unexpected observations made during the growth of $Cu_{2-x}S$ films. In this study, we present the etching of oxide and sulfide thin film underlayers during the atomic layer deposition (ALD) of $Cu_{2-x}S$, which is driven by the high diffusivity of the Cu^+ ions. Although the infiltration of the underlayers by Cu^+ ions plays an essential role in the etching process, it is suspected that the eventual etching behavior of the underlayer are strongly dependent on the lattice or bond dissociation energy of the underlayer materials. In the experiments, thin films of ZnS, ZnO, SnS, and SnO were etched to different degrees during ALD of $Cu_{2-x}S$. In contrast, SnO_2 exhibited a high resistance to etching. Interestingly, a selective removal of Zn^{2+} was observed when a ternary $Zn_{1-x}Sn_xO$ film was used as underlayer. Based on X-ray spectroscopy results, and the results from other supplementary experiments, we proposed a possible reaction mechanism for the etching process. Finally, the etching phenomenon was extended to the synthesis of $Cu_{2-x}S$ nanowires, which have the potential of being used as absorber materials for photovoltaic cells.

ALE-MoP-5 The Phenomenon of Reduction on the Austenitic Stainless Steel Affected Hydrogen Species into the Screen Plasma Technology*,* *Jongdae Shin,* Korea Institute of Industrial Technology(KITECH) and Inha University, Republic of Korea*; S Kim,* Korea Institute of Industrial Technology(KITECH), Republic of Korea

Although austenitic stainless steel has excellent corrosion resistance, it has low applicability due to low hardness. Therefore, various surface hardening treatments have been developed. Especially, plasma nitriding process has been under various researches due to its environment and easy applicability. However, if the oxide film of the material cannot be uniformly removed, it is difficult to secure a uniform nitride layer during the nitriding process. There were discussions about the role of high-energy hydrogen species to understand the principle of oxide film removal which arising form laser ablation, microwave assisted non-thermal hydrogen plasma, and ion implantation technology. Generally, Hα (656.28nm, 1.89eV), which is a hydrogen species generated by glow discharge, is characterized by the fact that the surface reduction of the Austenitic stainless steel becomes very uneven due to its reaction energy. On the other hand, in the case of the plasma by the screen plasma technology, high-energy and high-density hydrogen species can be generated by adjusting the degree of vacuum, current, and gas mixture . Through this, it was judged that intense physical-chemical reaction and a uniform reduction reaction occurs inside the chamber. Hydrogen species due to high energy generation are predicted to be about Hβ (486.1 nm, 2.55 eV), Hγ (434.1 nm, 2.86 eV), which occurs depending on the parameters in the screen plasma apparatus. The state of the hydrogen active species was observed through OES (Optical Emission Spectroscopy). At this time, the state of the energy and the ion density were analyzed through the Langmuir probe to closely diagnose the plasma state. After that, the relevant facts was studied by analysis using contact angle measurement, Auger Electron Spectroscopy, and Glow Discharge-Optical Emission Spectroscopy of the oxidation-reduction on the surface.

ALE-MoP-6 Fabrication of GaSb Mesa Structures by Atomic Layer Etching using Trisdimethylaminoantimony*,* *Katsuhiro Uesugi*, *H Fukuda,* Muroran Institute of Technology, Japan

We investigate atomic layer etching (ALE) of GaSb dot structures using trisdimethylaminoantimony (TDMASb) precursor to fabricate GaSb mesa structures. Self-assembled GaSb dots have been grown on GaAs(001) substrates at the temperature of 480-520°C by using metal-organic molecular beam epitaxy (MOMBE). At 480°C, GaSb quantum dots (QDs) with 8 nm-height and 70 nm-width were grown in Stranski Krastanow mode. Then the GaSb QD surfaces were etched by the reaction with TDMASb at the substrate temperature of 480°C. At the initial stage of GaSb QD etching, the dot diameter has not been changed. However, the height reduction of dots was observed with increasing of TDMASb supply. The GaSb QDs after 90 s etching showed the truncated pyramidal shape and the average height and width of them were 4 nm and 70 nm, respectively. All GaSb QDs were etched by the TDMASb supply for 140 s, and the surfaces was changed to atomically flat (1x3) surfaces. This result indicates that the ALE process of GaSb QDs using TDMASb primarily causes the decrease in dot height. The etching reaction was promoted at the top (001) facet in comparison with the other facets of dot side.

The submicron-sized GaSb dots were also grown at 520°C. The height and width of GaSb submicron dots (SDs) were 100 nm and 350 nm, respectively. Self-size-limiting phenomenon of dome-shaped GaSb SDs depend on temperature was clearly observed. After ALE of GaSb SDs, GaSb mesa structures were fabricated by the TDMASb supply for 30 s at 450°C. The GaSb mesa structures were found to be laterally surrounded by (111) and (110) facets together with circular (100) facet at a convex curved region. The diameter of circular (100) facet was 120 nm. These results suggest that the size and facets of GaSb mesa structures can be controlled by using ALE technique with TDMASb.

ALE-MoP-7 Interaction of Hexafluoroacetylacetone (HFAC) Molecules with Nickel or Nickel Oxide Film Surfaces for Atomic Layer Etching (ALE) Applications*,* *Abdulrahman Basher,* *M Isobe, T Ito, K Karahashi, S Hamaguchi,* Osaka University, Japan

Magnetic Random Access Memories (MRAMs) are one of the most promising nonvolatile memories. Manufacturing MRAM devices with nano-scale dimensions is still a challenge due to the difficulties in nano-scale patterning of magnetic tunnel junction (MTJ) stacks which are used in MRAMs to store data [1]. An MTJ stack consists of two ferromagnetic layers separated by a dielectric barrier layer. Therefore, the development of controllable etching processes in the range of nanometer scales is required with high anisotropy and low damage for magnetic materials. Organic etchants may be used to establish low-damage and highly controlled etching processes [2]. Hexafluoroacetylacetone (hfac) has proved its efficiency for the use in dry etching of several materials such as semiconductors, minerals, as well as magnetic materials [1-4]. It has been found experimentally that nickel hexafluoroacetylacetonate $Ni(hfac)_2$ can be formed when gas-phase hfac is exposed to a pre-oxidized nickel (Ni) surface and the surface temperature is increased, which suggests the etching of Ni takes place under such conditions. On the other hand, when a clean Ni metal surface is exposed to hfac, hfac tends to break down and no Ni atom seems to desorb from the surface. The goal of this study is therefore to understand the interaction of an hfac molecule with a Ni or nickel oxide (NiO) surface and to evaluate the feasibility of hfac dry etching processes for metallic Ni and NiO films. In this study, quantum mechanical (QM) numerical simulation analysis is performed with Gaussian 09 to evaluate chemical reactions of hfac with Ni metal and NiO. It has been found that a decomposition of an hfac molecule can be energetically preferred when an hfac molecule is placed on a metalic Ni surface whereas an hfac molecule can be stably adsorbed on a NiO surface.

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ALE-MoP-8 Cost Effective Plasma Generation with High Efficiency and Reliability for Remote Plasma Removal Process: Magnetic Induction Plasma Source*,* *Tae Seung Cho*, *S Park, D Lubomirsky,* Applied Materials

Remote plasma removal process is playing an importance role in material removal with high selectivity in 3D structures of semiconductor. In remote plasma removal process system, the wafer process regime is completely isolated from plasma source by perforated metal plate such as showhead. The charged particles as well as radicals are generated by electrical discharge and only the radicals could pass through the perforated metal plate. In the wafer process regime, certain radical species reacts only with the material to be removed from the wafer while there's no reactions with any materials on the wafer. Since the charged particles are screened by the plate, the damages by energetic charged particles can drastically be reduced. Therefore, efficient radical generation with higher dissociation rate and less charged particle leakage to wafer process region could dramatically promote the performance of remote plasma removal process.

Magnetic induction plasma concept is being used for lighting bulbs as well as Tokamak fusion reactor for several decades (Fig.1). Especially, the magnetic induction lighting and its driving electronics is being optimized for many years. Since the magnetic induction lighting doesn't have any electrode inside the bulb there's no particles from the electrode sputtered by energetic ions. In addition, magnetic induction plasma source as an inductively coupled plasma has higher dissociation rate compared to typical capacitively coupled plasma. Thus, introducing the magnetic induction lighting and its driving technologies to remote plasma removal process would make removal process more efficient and reliable with reduced cost of ownership.

Prototype chamber for magnetic induction plasma source for remote plasma removal process has been simply assembled with standard KF flanges of elbows and crosses that could be brought off the shelf (Fig.2). The commercial electronic ballast for magnetic induction lighting bulb has been used to generate the plasma inside the chamber. The control circuit to make the plasma stable by modulating the power and frequency (0-400Wmax and 200-400kHz) has been added to the ballast. For preliminary study, Ar+N_2 plasma has been successfully generated in the chamber by using the ballast with wide operating pressure ranges from 50mTorr to 200Torr (Fig.3). Based on OES study, it has been confirmed that emission intensity from argon increases with increasing power from 47W to 120W (Fig.4) and will be further confirmed that remote plasma removals of material increases with power.

ALE-MoP-9 A Study of InGaAs Nanowire Fabrication by Atomic Layer Etching*, **Doo San Kim**, J Park, W Lee, G Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

Atomic layer etching (ALE) is a next generation etching technique consisting of cyclic removal of monolayer by repeating adsorption and desorption, and it is suitable for nanoscale semiconductor device fabrication due to the layer-by-layer control and minimizing the surface damage of the materials. So far, the ALE methods have been studied by many researchers on various semiconductor materials. Among these materials, III-V semiconductor compounds such as indium gallium arsenide (InGaAs) can be applied to 3-demiensional structure nanodevices such as nanowire field effect transistors due to a great electrical characteristics than silicon-based devices.

In this study, InGaAs nanowire was fabricated with a 50 nm-line patterned polystyrene (PS) as a etch mask which was formed using a nano-imprint lithography (NIL) technique. For InGaAs ALE, chlorine was used as the adsorption gas and, for desorption, a low-energy Ar^+ ion beam was used to remove the chlorine chemisorbed InGaAs on the surface. Using an optimized ALE conditions, the InGaAs was etched and the PS mask remained on the InGaAs surface was removed by oxygen-ICP plasmas, and the fabricated InGaAs nanowires were observed by Field emission-secondary electron microscope (FE-SEM). After the fabrication of InGaAs nanowires, the properties of InGaAs nanowires were investigated and compared with those fabricated with conventional reactive ion etching methods.

ALE-MoP-10 Chrome Atomic Layer Etching*, **Jin Woo Park**, D Kim, W Lee, G Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

The uniformity of the critical dimension (CD) of the photomask is important for the nanoscale high-intergraded circuits (ICs) for the fabrication of next-generation semiconductor devices. The photomask is generally consisted of quartz, chrome (Cr), and molybdenum silicon oxynitride (MoSi). Depending on the type of photomasks such as standard chrome on glass (COG), opaque MoSi on glass (OMOG), and phase-shifting mask (PSM), Cr is dry-etched and the Cr is used as a hard mask to fabricate the photomask due to the low-etch selectivity between MoSi and quartz. Thus, the dry etch procss of Cr with a low surface damage (such as low LER and low LWR) and high-uniformity plays an important role in determining the CD of the photomask.

Atomic layer etching (ALE) technology can be used as a exquisite process at the atomic level with a high-uniformity and low-defect density of surface regardless of plasma uniformity during the semiconductor manufacturing process, and is attracting attention as an etching technique for next-generation semiconductor fabrication of nanoscale. In this study, the ALE characteristics of Cr have been investigated using O_2 or Cl_2/O_2 for adsorption and Cl_2 or Ar ion beam for desorption, respectively, during the etch cycle to control the etch depth precisely and to minimize the surface damages of Cr. Also, the monolayer removel mechanism of Cr was investigated by X-ray Photoelectron Spectroscopy (XPS). By using ALE, the controlled Cr etch depth per cycle and very high-etch selectivity of Cr over various Si-based materials such as silicon, silicon dioxide, and silicon nitride etc. in addition to minimized surface damage could be obtained.

ALE-MoP-11 MoS_2 Lateral-Heterojunction Device Using Atomic Layer Etching*, **Ki Seok Kim**, Y Ji, K Kim, G Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

Molybdenum disulfide (MoS_2) has been intensively investigated because of its unique properties in various electronic and optoelectronic applications. More specifically, as the layer is reduced from bulk to bilayer and monolayer, the band structure changes from indirect to direct at the K point of the Brillouin zone, and the band-gap also changes from 1.2 to 1.9 eV. Accordingly, the technology involved in controlling the MoS_2 layers is very important in various nano-device applications. To control the MoS_2 layers, atomic layer etching (ALE) (1st step: radical adsorption / 2nd step: reacted compound desorption) can be a highly effective and precise technique while avoiding damage and contamination that can occur during the etching. In this study, for the MoS_2 ALE, the Cl radical is used as the adsorption species and a low-energy Ar^+ ion is used as the desorption species. In addition, mono-/bi-layer lateral-heterojunction device was fabricated using ALE technique after PR patterning of bilayer MoS_2. The results showed that the photocurrent was increased in heterojunction regions due to the difference in work function and electron affinity between mono-/bi-layer MoS_2. The photocurrent is increased because the exciton generated in the monolayer MoS_2 is thermally diffused into the bilayer MoS_2 region and the additional carrier is generated. Therefore, the lateral-heterojunction 2D device fabricated using ALE technique can be a very important device that can be applicable to next-generation nano-sensor devices.

ALE-MoP-12 Study of Atomic Layer Etching (ALE) of SiO_2 Using Inductively Coupled Plasma (ICP) Etch Chambers with Multi-chamber or Multi-step Approach*, **Shuang Meng**, S Ma,* Mattson Technology, Inc.

Atomic layer etching (ALE) of SiO_2 has been traditionally done with a fluorocarbon deposition followed by Ar and/or O_2 plasma activation per etch cycle. However, the resultant etch per cycle (EPC) and across-wafer uniformity are strongly affected by CFx deposition condition, and to a lesser degree, the plasma activation condition. In this report we studied the impact of CFx gas species (CF_4 vs. CHF_3), gas composition (Ar/N_2/Forming gas), adsorption kinetics (thermal vs. radical), adsorption pressure and temperature, as well as plasma activation conditions (Ar vs. O_2) on ALE etch characteristics and across-wafer uniformity using Mattson's 300mm Aspen III platform. This platform includes two ICP chambers with vacuum transfer capability in-between, one chamber being a ICP plasma asher which can be used for CFx deposition at relatively high temperature and high pressure, and the other one being a low-temperature low-pressure etcher that performs radical and ion bombardment. Alternatively, the CFx deposition can also be performed in the etcher at low temperature and low pressure followed by *in-situ* plasma activation. This system allows independent controls of CFx deposition conditions and the subsequent plasma activation conditions.

Our results show that SiO_2 removal rate and across-wafer uniformity are largely affected by CFx adsorption temperature and pressure as well as mixing gas species, and less dependent on CFx molecule type. Adsorption of CFx at higher temperature and higher pressure gives lower EPC compared to adsorption at low temperature and low pressure. In addition, Ar plasma activation results in higher EPC than O_2 plasma activation which has additional effect of removing residue carbon from the oxide surface. Across-wafer uniformity can be effectively tuned by controlling the amount of Ar injected during the CFx deposition steps.

ALE-MoP-13 Tuning Etching Characteristics of Plasma-Assisted ALE of SiO_2 via Hydrocarbon Precursors*, **Ryan Gasvoda**,* Colorado School of Mines*; S Wang, E Hudson,* Lam Research Corp.*; S Agarwal,* Colorado School of Mines

Due to ever decreasing device dimensions and the introduction of 3D device architectures, it is challenging to operate within a narrow processing window using conventional plasma etching. One method to address the demands of the next-generation of devices is atomic layer etching (ALE) which provides high fidelity, selectivity, directionality, and layer-by-layer removal. Plasma-assisted ALE has been extensively studied for a variety of materials, including Al_2O_3, HfO_2, Si, and Si–based dielectrics. Plasma-assisted ALE of SiO_2 typically uses two sequential steps in a cyclic fashion: CF_x deposition from a C_4F_8/Ar plasma followed by an Ar plasma activation step. ALE of SiO_2 has been demonstrated to remove ~4 Å per cycle. It is proposed that broader control of the surface reactions and etching characteristics can be achieved by introducing an additional reactant.

In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy and *in situ* four-wavelength ellipsometry during ALE to monitor the surface reactions, film composition, as well as the net film thickness. To controllably alter the EPC, we introduce a hydrocarbon precursor into the reactor prior to the CF_x deposition step. This precursor reacts with the surface Si–OH groups leaving a SiO_2 surface terminated with hydrocarbons. An infrared spectrum of the surface shows that the hydrocarbon precursor is resistant to the C_4F_8/Ar plasma. After the Ar plasma activation step, a broad increase from ~1230 – 1800 cm^{-1}

indicates that a graphitic hydrofluorocarbon film accumulates on the surface. This graphitic hydrofluorocarbon film prevents the complete activation of the CF$_x$ film during the Ar plasma step, thus resulting in a lower EPC than the baseline ALE process. This modulation of etch properties may have applications for controlling etch selectivity.

The hydrocarbon precursor consists of two different groups: the hydrocarbon backbone and reactive head group. Changing the reactive head group leads to different surface coverage on the Si–OH terminated SiO$_2$ film and thus a different EPC. In this poster, two different classes of hydrocarbon precursors (aminosilanes and acid chlorides) are screened for surface coverage, EPC reduction, and surface composition after the Ar plasma activation step. The length and structure of the hydrocarbon chain are also discussed.

ALE-MoP-14 Modeling and Simulation of *in-situ* Cleaning Sequence Using NF$_3$/NH$_3$ Remote Plasma, ***Romel Hidayat***, *T Mayangsari, J Gu, H Kim,* Sejong University, Republic of Korea; *Y Kwon,* Kyung Hee University, Republic of Korea; *J Jung, W Lee,* Sejong University, Republic of Korea

In semiconductor manufacturing processing, the removal of native oxide on the silicon surface is one of the critical issues to obtain low contact resistance. Although wet cleaning process using a dilute HF solution is the most widely used method for oxide removal, it cannot completely prevent the formation of native oxides because the wafer is exposed to air before being loaded into the selective epitaxial growth chamber or metal deposition system. Siconi^{TM} cleaning process based on NF$_3$/NH$_3$ remote plasma was successfully employed as pre-Ni Silicide cleaning at 65 nm and showed lower junction leakage [1]. This process is composed of two steps, the fluorination of silicon oxide by a remote plasma of NH$_3$/NF$_3$ at near room temperature and the sublimation of fluorinated layer by annealing at 180°C. Understanding the detailed reaction mechanism underlying the cleaning process will lay a foundation for developing new atomic layer cleaning processes. The reaction mechanism was proposed [1], however, more experimental evidences are needed, and more detailed mechanisms have not yet been elucidated. In this study, we modeled and simulated the Siconi^{TM} process by density functional theory (DFT) and molecular dynamics (MD) calculations. The fluorination of oxide was simulated by introducing HF and NH$_4$F on OH- or F-terminated SiO$_2$ surfaces by DFT, and the sublimation process was simulated by MD-annealing. We found the fluorination process is limited by forming the SiF$_6$(NH$_4$)$_2$ salt on the surface, showing that NH$_4$F is the key molecule for the *in-situ* cleaning process.

Keyword: *simulation, remote plasma, siconi, density functional theory, molecular dynamic*

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ALE-MoP-15 Biological Characteristics and Antibacterial Performance of Tantalum Oxide and Zinc Oxide Thin Films, ***Yin-Yu Chang,*** National Formosa University, Republic of China; *H Huang,* China Medical University, Republic of China; *M Tsai,* Hungkuang University, Republic of China; *Y Lin,* National Formosa University, Republic of China

The surface modification of biomaterials with better biocompatibility and antibacterial feature has been a challenge for many years. Tantalum oxide (Ta$_{1-x}$O$_x$) and zinc oxide (ZnO) thin films have been used as the material of orthodontic and dental implants due to their impressive biocompatibility, corrosive resistance, and antibacterial activity on the microorganisms. Among the surface engineering techniques, atomic layer etching (ALE) and plasma electrolytic oxidation (PEO) are rising technologies which can produce unique surface for cell adhesion and improve the biocompatibility for further implantation. In previous studies, thin films of Ta$_2$O$_5$ and ZnO have been found to show both the antibacterial ability and biocompatibility in vitro. In this study, a pre-treatment of surface modification on titanium (Ti) substrates has been made by ALE and PEO. Porous oxide layers formed, and a series of Ta, ZnO, and Ta$_2$O$_5$ and ZnO films were then deposited onto the porous surface of Ti substrates by using a twin-gun high power impulse magnetron sputtering system. The surface morphology, crystal structure, and bonding state of the films were identified by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). To evaluate the antibacterial ability, Staphylococcus aureus (S. a., Gram-positive bacteria) and Actinobacillus actinomycetemcomitans (A. a., Gram-negative bacteria) were tested. S. a. and A. a. were the main origins of infection mostly occurred in clinical orthopedic/oral implants, and both of these two types of bacteria were tested by a fluorescence staining method (Syto9) and bacterial viability agar tests. The in vitro cytotoxicity was tested followed by the standard of ISO 10995-5:2009. Cell viability and proliferation of human osteosarcoma cell line (MG-63) and human skin fibroblast (SKF) cells cultured on these films were also determined by using the MTT assay. The result showed that an appropriate ALE/PEO pre-treated Ti with Ta$_2$O$_5$ and ZnO thin films improved both the antibacterial ability to *A. a.* and *S. a. bacteria* and biocompatibility to *SKF* and *MG-63* cells in vitro.

ALE-MoP-16 *In situ* Quantitative Analysis of Chlorine Adsorption on Ion-irradiated GaN for Atomic Layer Etching, ***Masaki Hasegawa,*** *T Tsutsumi, H Kondo, K Ishikawa, M Hori,* Nagoya University, Japan

Gallium nitride (GaN) is a candidate material for fabrication of the next-generation power electronic devices. To realize the GaN devices, atomic level control of etching of GaN is necessary. Thus, atomic layer etching (ALE) technique of GaN was suggested by cyclic processes of Ar ion exposure and Cl adsorption onto GaN. For precise control, we issues on variations of atomic level removal of GaN-Cl by-products, that is, the ion bombarded GaN surface varies on both Ar ion-energy and Cl-flux for the adsorption. Therefore, we are focusing on Ar and Cl reactions with GaN and have elucidated Cl adsorption on the Ar ion bombarded GaN surface using the beam experiments with *in situ* X-ray photoelectron spectroscopy (XPS), as developed previously.[1,2]

Sample is the GaN grown on sapphire by Hydride Vapor Phase Epitaxy (HVPE) method. After wet cleaning (5% HF), native oxide on GaN surface was removed by Ar ion sputter. Subsequently, Cl radicals generated in Cl$_2$ gas (flow rate 0.5 sccm) plasma by application of RF power of 400 W were exposed to the sample surface with a dosage of 10^{19} cm^{-2}. Sequentially, Ar ions generated in Ar gas (flow rate 1.0 sccm) plasma by application of RF power of 400 W were exposed to the sample surface with accelerating voltage of 200 V and a dosage of 10^{16} cm^{-2}. At each treatment, we observed the sample surface by *in situ* XPS method.

After GaN surface was irradiated by Ar ions with accelerating voltage of 200 V and a dosage of 2×10^{16} cm^{-2}, the surface was formed by a Ga rich layer with a thickness of approximately 0.8 nm stacked on a 0.2-nm-thick amorphous layer (a-GaN). After Cl radicals were exposed with a dosage of the order of 10^{19} cm^{-2}, the Ga rich layer was removed selectively and a mixing layer of Ga-N-Cl was formed with almost similar thickness of 0.8 nm in the a-GaN layer. For the ALE of GaN, parameters such as ion energy, etchant fluxes, and surface reactions play an important role for atomic control of stoichiometric removal of GaN.

Acknowledgement the authors thank to Mr. A. Tanide of the SCREEN holding Co., Ltd. for fruitful discussion.

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ALD Applications

Room 107-109 - Session AA1-TuM

Memory Applications: RRAM & Neuromorphic, MIM Capacitors

Moderators: Shi-Jin Ding, Fudan University, Jaeyoung Ahn, Samsung Electronics

8:00am **AA1-TuM-1 Using ALD to Engineer Metal/Insulator/Metal Devices*, John Conley, Jr.,*** Oregon State University **INVITED**

Simple thin film metal-insulator-metal (MIM) devices find application as capacitors (MIMCAPs) in the back-end-of-line (BEOL) of integrated circuits, as tunnel diodes for optical rectenna based IR energy harvesting, in IR detector arrays, in large area macroelectronics, as building blocks for hot electron transistors, and as selector devices to avoid sneak leakage in resistive memory (RRAM) crossbar arrays. This invited talk will highlight how atomic layer deposition (ALD) insulators, nanolaminates, and metal electrodes can be used to engineer interfaces, materials phases, energy barriers to electron transport, turn-on voltage, and non-linearity and asymmetry of current and capacitance vs. voltage characteristics of MIM and MIIM devices [1-7].

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8:30am **AA1-TuM-3 Impact of Metal Nanocrystal Size and Distribution on Resistive Switching Parameters of Oxide-based Resistive Random Access Memories by Atomic Layer Deposition*, Chang Liu,*** *Y Cao, A Li,* Nanjing University, China

Resistive random access memory (RRAM) devices are promising candidates for nonvolatile-memory (NVM), analog circuits, and neuromorphic applications. The mainstream resistive switching mechanism of RRAM is the formation and rupture of nanoscale conductive filament (CF) inside the insulation layer. However, the random nature of the nucleation and growth of the CFs leads to dispersed resistive switching (RS) parameters, which is a major challenge for oxide-based RRAM applications. The introduction of metal nanocrystals (NCs) has been confirmed to improve electrical uniformity of oxide-based RRAM devices significantly.

In this work, we focused on the impact of metal NCs size and distribution on the RS performances of oxide RRAM by atomic layer deposition (ALD) based on experiment results and theoretical calculation. The dependence of ALD cycles of 50~130 during Pt or $CoPt_x$ NCs growth on the RS parameters of Al_2O_3 memory units has been evaluated systematically. Both memory cells with embedded Pt or $CoPt_x$ NCs show similar trends: with increasing ALD cycles, the forming voltage, set/reset voltage, low resistance state/high resistance state, and resistance ratio firstly decrease and then increase. And in the middle region of about 90 and 100 cycles, the lower RS parameters are obtained with flat change and better RS properties. When ALD cycles exceed a critical value of about 110 to 120, the RS parameters suddenly become large with degraded RS performances due to percolation effect. The impact of metal NCs size and distribution on local electric field strength of RRAM devices has been calculated by using the finite element method. Although all metal NCs with various sizes enhance the electric field strength compared to at the planar region, only metal NCs with proper grain size and areal density (9 nm/$6\sim10\times10^{11}$/cm^2 in this work) can effectively produce stronger localized electric field at the tip of metal NCs, leading to optimal RS behavior.

Keywords: resistive random access memory, metal nanocrystals, atomic layer deposition, electrical uniformity

8:45am **AA1-TuM-4 Epitaxial Electronic Materials by Atomic Layer Deposition*, Peter J. King,*** *M Vehkamäki, M Ritala, M Leskelä,* University of Helsinki, Finland

ALD has already delivered unparalleled thickness, conformality and composition control in thin films - enabling the continued scaling of MOSFET and DRAM devices to feature sizes previously thought impossible. Additionally, ALD is now a feature defining tool, using the self-aligned layer principle to set the tolerance of device dimension into the nanoscale.

More control is available from the technique in films that are single crystal and registered to the substrate. The advantages here are improved materials properties and better-defined interfaces for improved device properties.

This talk will explore epitaxial layers produced by ALD, and the possibility of growing multi-layer products with the rationale of enabling future electronic devices. Oxide conductor/semiconductor epitaxial multi-layers will be discussed and the advantages and limitations of ALD examined in this context.

Figure 1 presents a TEM measurement of a 8.5 nm $LaNiO_3$ layer deposited on $SrTiO_3$ substrate, demonstrating epitaxial registration after annealing. The film forms anti-phase boundaries to alleviate the strain from the slightly different lattice parameters and lattice types of the integrated films ($LaNIO_3$ is a rhombohedral crystal and forms a pseudocubic epitaxial relationship with the substrate). In this pseudocubic arrangement films are limited to <10 nm in alternating layers, above this thickness the epitaxy is lost and a polycrystalline product results.

9:00am **AA1-TuM-5 Scaling Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ for Back -end of Line Integration*, Jaidah Mohan,*** *S Kim,* The University of Texas at Dallas*; S Summerfelt,* Texas Instruments, USA*; J Kim,* The University of Texas at Dallas

Although ferroelectric random access memory (FRAM) is the most energy efficient memory device (which can operate at <2 V), it has currently reached its scalability limit at the 130 nm node because of two primary reasons: (i) ferroelectric properties could not be demonstrated below 70 nm in conventionally used $Pb(Zr,Ti)O_3$ (PZT) and (ii) It was impossible to demonstrate reliable ferroelectric performance in trenched or stacked capacitors [1-3]. Further, all conventional memory devices are fabricated in the front-end of line making fabrication and scaling more tedious. In the recent years, Ferroelectricity in doped HfO_2 has attracted much attention because of its simplicity in fabrication using atomic layer deposition (ALD), silicon compatibility, ability to scale down <10 nm and its 3D integration capability [1]. Also, the Ferroelectric properties can be obtained at a temperature of 400ºC, making it suitable for back-end of line (BEOL) integration.

In this study, the ferroelectric properties of $Hf_{0.5}Zr_{0.5}O_2$ (HZO), deposited using ALD (Cambridge Nanotech Savannah S100) was evaluated, scaling down up to 5 nm. HZO was deposited using TDMA-hafnium ($Hf[N(CH_3)_2]_4$), TDMA-zirconium ($Zr[N(CH_3)_2]_4$), and O_3 as the Hf-precursor, Zr-precursor and oxygen source respectively at 250°C. Blanket TiN (90 nm thick) electrodes were deposited before and after the HZO deposition as it is believed that the stress exhibited by TiN helps HZO to crystallize into a ferroelectric phase [3]. Then, rapid thermal annealing was done at 400ºC in an N_2 atmosphere for 60 s to crystallize the HZO films. A conventional photo-lithography/etching process was used to make capacitors of different diameters. After performing the "wake-up" field cycling, polarization-electric field hysteresis and pulse read/write tests were performed to extract the ferroelectric polarization. 10 nm HZO showed very large polarization ($2P_r \sim 45$ μC/cm^2), saturating at ~1.5 V compared with 7 nm HZO ($2P_r \sim 37$ μC/cm^2 and V_{sat} ~1.2 V) and 5 nm HZO ($2P_r \sim 8$ μC/cm^2 and V_{sat} ~1 V). Nevertheless, scaling HZO and reducing the operating voltage lower than 1 V can benefit the development novel FRAM. It was also seen that further annealing of the 5 nm HZO at 450°C increased the $2P_r$ to ~20 μC/cm^2 while maintaining the low saturation voltage. Hence, 5 nm HZO annealed at a low thermal budget (450ºC)can be a prospective next generation non-volatile ferroelectric memory with back end of line integration capability.

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9:15am **AA1-TuM-6 Atomic Layer Deposition Processes for Logic Device Applications*, Bong Jin Kuh,*** Samsung Electronics **INVITED**

9:45am **AA1-TuM-8 Effect of ZrO_2 Capping-layer on Ferroelectricity of $Hf_xZr_{1-x}O_2$ Thin Films by ALD using Hf/Zr Cocktail Precursor*, Takashi Onaya,*** Meiji University, Japan*; T Nabatame,* National Institute for Materials Science, Japan*; N Sawamoto,* Meiji University, Japan*; A Ohi, N Ikeda, T Chikyow,* National Institute for Materials Science, Japan*; A Ogura,* Meiji University, Japan

Ferroelectric $Hf_xZr_{1-x}O_2$ (HZO) thin films are considered to be promising candidates for future memory device applications such as FeRAM and FeFET, due to its stable ferroelectricity even in extremely thin region (~10 nm) and CMOS compatibility [1]. The HZO films with HfO_2/ZrO_2 nano-laminate structure were typically deposited by the layer-by-layer ALD process [2]. The nano-laminate structure still remains an issue of an ideal ferroelectric HZO film formation. In this study, we investigate the characteristics of the HZO single film deposited by ALD using Hf/Zr cocktail precursor, and discus the effect of a nano-crystallized ALD-ZrO_2 as a capping-layer on the crystallization and ferroelectricity of the HZO films.

The HZO, ZrO_2, and HfO_2 films were deposited on Si/SiO_2 substrates by ALD at 300°C using $(Hf/Zr)[N(C_2H_5)CH_3]_4$ (Hf/Zr = 1/1) cocktail, $(C_5H_5)Zr[N(CH_3)_2]_3$, and $Hf[N(C_2H_5)CH_3]_4$ precursors, respectively, and H_2O gas. The TiN/HZO/ZrO_2/TiN capacitors with a ZrO_2 capping-layer (Cap-ZrO_2) were fabricated as follows: A HZO film was deposited on the TiN bottom-electrode (BE-TiN) by ALD at 300°C. The thickness of the HZO film was varied from 7.5 to 25 nm by changing the number of ALD cycles. Next, a 2-nm-thick ZrO_2 capping-layer was deposited on the HZO film by ALD at 300°C. After that, the annealing was carried out at 600°C for 1 min in a N_2 atmosphere. TiN top-electrodes (TE-TiN) were then fabricated on the ZrO_2 capping-layer by DC sputtering. The TiN/HZO/TiN capacitors (w/o) were also prepared under the same process.

The growth per cycle of the HZO, ZrO_2, and HfO_2 films were estimated to be 0.065, 0.043, and 0.073 nm/cycle, respectively, from the relationship between the number of ALD cycles and the film thickness. The Hf:Zr ratio in the HZO film was estimated by EDS analysis to be 0.43:0.57. Noted that the maximum remanent polarization ($2P_r = P_r^+ - P_r^-$) (23 μC/cm^2) of the Cap-ZrO_2 capacitor with a 10-nm-thick HZO film was approximately 2 times larger than that (12 μC/cm^2) of the w/o capacitor. The $2P_r$ of both capacitors decreased as the HZO thickness increased. Moreover, the ratio of ferroelectric orthorhombic phase of the Cap-ZrO_2 capacitor was significantly larger than that of the w/o capacitor. Therefore, we found that the ZrO_2 capping-layer plays an important role for the HZO formation with ferroelectric orthorhombic phase. Based on these experimental results, a HZO film with superior ferroelectricity can be obtained by using ZrO_2 capping-layer.

[1] M. H. Park et al., Adv. Mater. 27, 1811 (2015).

[2] S. W. Smith et al., Appl. Phys. Lett. 110, 072901 (2017).

ALD Applications
Room 107-109 - Session AA2-TuM
Photo-Chemical Energy

Moderators: Jae Young Hur, Cheonnam National University, Xueliang (Andy) Sun, University of Western Ontario

10:45am **AA2-TuM-12 Efficient Photoelectrochemical H_2 Generation using Molybdenum Disulfide Film on Black Si Photocathode *via* Wafer-scale Atomic Layer Deposition*, Dae Woong Kim,*** *D Kim, T Park,* Hanyang University, Republic of Korea

The hydrogen is an energy source spotlighted as an eco-friendly environmental fuel to replace fossil fuels. Photoelectrochemical (PEC) water splitting is one of the most promising methods for producing such hydrogen. However, high cost of noble metal catalysts such as Pt and low stability of Si photocathode need to be overcome. MoS_2 is an earth-abundant and low-cost electrocatalyst material for hydrogen evolution enabling to substitute for noble metal catalysts. [1] Atomic layer deposition (ALD) is proposed as a reliable and atomic scale-adjustable process for growing MoS_2 directly on Si photocathode with an exact thickness and composition. Furthermore, wafer-scale uniformity of the film even on a complicated nanostructure facilitates a mass production.

In this work, ALD amorphous MoS_2 film was grown on Si photocathode forming a Schottky junction at the interface of MoS_2/Si photocathode, which reduced the overpotential and improved stability of Si photocathode resulting in improved photovoltaic characteristics. Figure 1 shows typical photoelectrochemical current density curves of the PEC cells with MoS_2 layers with various thicknesses. Detailed experimental results will be presented.

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11:00am **AA2-TuM-13 Junction Interface Passivation by ALD in CIGS Solar Cells*, Wei-Lun Xu,*** National Tsing Hua University, Republic of China*; N Koothan,* Instrument Technology Research Center, Republic of China*; J Huang,* Institute of NanoEngineering and MicroSystems*; Y Yu,* Instrument Technology Research Center, Republic of China*; C Ke,* Instrument Technology Research Center*; C Lai,* National Tsing Hua University, Republic of China

Increasing the efficiency of CIGS solar cells is of a crucial topic. One way of increasing the performance of CIGS solar cells is to grow a passivation layer between the CIGS and the buffer layer. The chemical and charge property of passivation layer is used to reduce the recombination between p-type and n-type and helps to increase the efficiency but the layer has to be grown in a certain way that it does not affect the current flow between the absorber layer and buffer layer. Also, the texture of the junction passivation layer has to be maintained to have a better interface. The ALD technique is known for its uniformity and conformal coverage, therefore the junction layer was deposited by ALD without needing any additional patterns. For the first time, we explore the effect of junction interface passivation with different materials including HfO_2 and AlO_x. The mechanism of the passivation effect is discussed in detail. Based on the results, suggestion for the best practice for the passivation is also discussed.

11:15am **AA2-TuM-14 Spatial Atomic Layer Deposition: Up-scalable Route of Metal Oxide Functional Layers for High Efficient and Stable Perovskite Solar Cells and Modules*, Valerio Zardetto,*** TNO/Holst Center, Netherlands*; M Najafi, D Zhang,* ECN, Netherlands*; F Di Giacomo,* TNO/Holst Center*; I Dogan,* TNO/Holst Center, Netherlands*; W Verhees,* ECN, Netherlands*; A Senes, H Lifka, H Fledderus, F van de Bruele,* TNO/Holst Center, Netherlands*; S Veenstra,* ECN, Netherlands*; R Andriessen,* TNO/Holst Center, Netherlands*; P Poodt,* Holst Centre - TNO, Netherlands

Atomic layer deposition (ALD) technique is well acknowledged to fabricate dense, conformal, uniform films over large area with an accurate control of the deposited thickness. ALD has been widely explored in several applications including photovoltaics (PV). In the last 5 years, organometallic halide perovskite solar cells (PSCs) attracts the interest in the PV community, due to the rapid increase in power conversion efficiency (PCE). However, the high performance has been achieved adopting lab scale techniques such as spin coating on small area (< 0.2cm^2).[1] In order to move PSC towards commercialization, large area sheet-to-sheet (S2S) and/or roll-to-roll (R2R) deposition methods are required. Whilst ALD technique has been adopted to deposit several functional metal oxides layers,[2] low deposition rates and the presence of expensive vacuum systems are not desired in the case of a low cost photovoltaic technology based on in-line large area manufacturing processes. Atmospheric pressure spatial atomic layer deposition (s-ALD) can couple the benefits of conventional ALD technique with high deposition rates and the absence of vacuum systems.[3]

In this contribution, we demonstrate the beneficial effect of the introduction of n-type s-ALD layers such as ZnO, TiO_2 and SnO_2 in the perovskite "p-i-n" planar perovskite solar cell. The presence of the s-ALD layer is found crucial to replace the conventional metal top electrode with a semitransparent sputtered ITO, which is required for hybrid tandem PV architectures (i.e., in combination with silicon solar cells). The s-ALD layer prevents sputtering damages during ITO deposition, enabling devices with efficiency up to 17% on small area (0.04 cm^2) and up to 13.5% on an integrated series connected mini-module (4 cm^2). The presence of the s-ALD layer increases the device stability during thermal aging tests. Our standard PSC degrades extremely fast when stressed at 85°C in N_2 environment, losing 90% of the initial performance (PCE_0) after 500hrs. The introduction of s-ALD ZnO enables the device to retain more than the 80% of the PCE_0 after 900hrs. Furthermore, we explored the deposition of s-ALD layers n-type layers in "p-i-n" PSC where the p-type contact and the intrinsic perovskite films have been deposited via S2S slot-die technique. We observe that s-ALD SnO_2 process delivers higher performance (16%

with Al electrode, and 14% with sputtered ITO) with respect to the s-ALD-free PSC (15% with Al contact).

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11:30am **AA2-TuM-15 Applications of Atomic Layer Deposition in Solar Energy Conversion***,* ***Xianglin Li****, Z Wang, H Fan, A Tok,* Nanyang Technological University, Singapore

Atomic layer deposition (ALD) provides a unique tool for the growth of thin films with excellent conformity and thickness control down to atomic levels. The application of ALD in solar energy research has received increasing attention in recent years. The research focus of our work is focused on the fabrication, surface passivation of nanostructured photoelectrodes based on ALD technique. Various of "host & guest" type composite photoanodes have been designed and fabricated for efficient photoelectrochemical (PEC) water splitting based on ALD. In such a design, a highly porous and conductive nanostructures act as the "host" skeleton it provides direct pathways for faster electron transport, while the conformally coated semiconductor layers act as the "guest" absorber layer. For example, 3D FTO/FTO-NR/TiO_2 composite invers opal structure, Nb--SnO_2 nanosheet/TiO_2 and Nb--SnO_2 nanosheet/Fe_2O_3 heterostructures were designed for PEC water splitting application. Also the ALD thin layer surface passivation and ALD ZnSnO, Zn(O, S) Cd-free buffer layers for CIGS solar cells were studied. Challenges and future directions of ALD in the applications of solar conversion will be discussed.

11:45am **AA2-TuM-16 Inorganic Charge Transport Layers Grown via Atomic Layer Deposition for Highly Stable and Efficient Perovskite Solar Cell***,* ***Seongrok Seo****, S Jeong, C Bae, N Park, H Shin,* Sungkyunkwan University, Republic of Korea

Despite the high power conversion efficiency (PCE) of perovskite solar cells (PSCs), poor long-term stability is one of the main obstacles preventing their commercialisation. Several approaches to enhance the stability of PSCs have been proposed. However the accelerating stability test of PSCs at high temperature under the operating conditions in ambient air remains still to be demonstrated. Herein, we show interface engineered stable PSCs with inorganic charge transport layers (*p*-NiO and *n*-Al:ZnO grown *via* atomic layer deposition (ALD)). First of all, NiO has been chosen as hole transporting layers due to its a wide band gap (~3.6 eV) and *p*-type semiconducting porperties. It also has good optical transparency and high chemical stability, and thus has the capability aligning the band edges to the perovskite ($CH_3NH_3PbI_3$) layers with efficient energy transfer. Ultra-thin and un-doped NiO films with much less absorption loss were prepared by ALD with highly precise control over thickness without any pinholes. Thin enough (5–7.5 nm in thickness) NiO films with the thickness of few time the Debye length (L_D = 1–2 nm for NiO) show enough conductivities achieved by overlapping space charge regions. Second, t he highly conductive Al doped ZnO films have been chosen as an efficient electron transporting layers while acting as dense passivation layers. This layer prevents underneath perovskite from moisture contact, evaporation of component, and reaction with a metal electrode. Finally the inverted-type PSCs with inorganic charge transport layers exhibited a PCE of 18.45 % and retained 86.7 % of the initial efficiency for 500 hours under continuous 1-sun illumination at 85 °C in ambient air with electrical biases (at maximum power point tracking).

References

[1] S. Seo, I. J. Park, M. Kim, S. Lee, C. Bae, H. S. Jung, N. G. Park, J. Y. Kim, H. Shin, *Nanoscale* **2016**, *8*, 11403

[2] S. Seo, S. Jeong, C. Bae, N.G. Park, H. Shin, *Adv. Mater.* **2018** (in press)

ALD Fundamentals
Room 116-118 - Session AF1-TuM

Precursor and Process II

Moderators: Mikko Ritala, University of Helsinki, Wonyong Koh, UP Chemical Co., Ltd.

8:00am **AF1-TuM-1 Atomic Layer Deposition of Yttrium Oxide from Bis(Methylcyclopentadienyl) (MethylPentyl Pyrazolato) Yttrium (III)***,* ***Jun Feng****, G Liu, M Fang, C Dezelah, J Woodruff, R Kanjolia,* EMD Performance Materials

Yttrium Oxide (Y_2O_3) is a promising dielectric material due to its relatively wide band gap (~5.5 eV), high permittivity (>10), and high thermal stability. As semiconductor fabrication processes move toward high-aspect-ratio structures, highly conformal deposition methods for Y_2O_3 are required. Herein, we report the atomic layer deposition (ALD) of Y_2O_3 thin films based on a newly developed liquid precursor, Bis(Methylcyclopentadienyl) (MethylPentyl Pyrazolato) Yttrium (III), with ozone or water as co-reactants. The ozone process was tested in the range of 150 - 250^{o}C. The best uniformity and lowest thermal decomposition are achieved at 180 - 225^{o}C substrate temperature window, where the saturated growth rate is ~0.5 Å/cycle and refractive index is 1.69. Using H_2O as the co-reactant tested in the range of 125 - 250^{o}C, the optimum growth window is 135 - 180^{o}C, with a growth rate of 0.5 - 0.6 Å/cycle and refractive index of 1.73. However, due to the reactivity between Y_2O_3 and water to form hydroxides, higher purging gas flow and extra-long purging time are required to obtain dense Y_2O_3 films. For the films deposited under different conditions, we performed XPS study for compositional information, as well as AFM study for surface morphology and roughness. Our Y_2O_3 ALD processes offer the material fundamentals to enable future high-performance electronic devices, especially those with three-dimensional frameworks that require dielectric coatings in high-aspect-ratio structures.

8:15am **AF1-TuM-2 Low-temperature Thermal ALD of SiO_2 – Increasing the Possibilities***, M Mäntymäki, J Kalliomäki, T Sarnet,* Picosun Oy*; T Pilvi,* Picosun Oy, Finland*; Q Demarly,* Air Liquide Electronics*; N Blasco,* Air Liquide Advanced Materials***; Juhana Kostamo****,* Picosun Oy, Finland

Silicon dioxide has great chemical and electrical properties that have made it the sought-after solution in many applications. In addition to the classic microelectronics applications due to its dielectric properties, SiO_2 can also be used to tailor the mechanical properties of films or prevent gas diffusion to protect various materials.

In ALD, SiO_2 has been made by many different processes. The main issues with most of the chemistries, such as the chlorides or chlorosilanes has been the relatively high deposition temperatures (>300°C). Low deposition temperatures are important for both sensitive substrates and to prevent interlayer diffusion at interfaces. In addition, chloride precursors can create particles and chloride impurities in the films. These are unacceptable in many applications. Therefore, the amine precursors have become more popular.

In general, low deposition temperatures have been achieved with the assistance of plasma processing [1]. This is not advantageous, as thermal processing would enable throughputs that are an order of magnitude larger. Moreover, plasma processing gives limitations to aspect ratios of the substrates, as radical lifetimes are limited.

Furthermore, achieving industrially feasible growth rates at low temperatures with thermal processes has been a challenge. For example, with a commonly used process such as bis(diethylamino)silane and ozone, the growth rate at 100°C is only < 0.1Å per cycle [2].

We present a chemistry for reliably depositing SiO_2 at temperatures below 100°C with growth rates in excess of 1Å per cycle. At 100°C, the growth rate has been shown to be 1.4Å per cycle (Figure 1).

The experiments were made with a PICOSUN™ R-200 Advanced hot-wall ALD system, equipped with a Picohot300™ source for low vapor pressure precursors. 200mm Si wafers with native oxide layers were used as substrates. Properties such as growth rates, morphology, crystallinity, refractive index, composition, breakdown field strength and leakage current were studied to evaluate the process and the resulting thin films.

Figure 1: SiO_2 thickness series at 100°C. Nucleation delay of 21 cycles. Refractive index fixed at 1.457.

[1] Won et al., *IEEE Electron Device Lett.***31** 2010

[2] Hirvikorpi et al., *Appl. Surf. Sci.***257** 2010

8:30am **AF1-TuM-3 Non-pyrophoric Aluminum Precursor for Thermal Atomic Layer Deposition of Al_2O_3 Thin Films**, ***Jungwun Hwang***, *K Mun, J Seok, J Park,* Hansol Chemical, Republic of Korea

Al_2O_3 thin films are used for encapsulation layers of displays, passivation layers in solar cells, and gate dielectrics of microelectronics device such as dynamic random access memory (DRAM) and metal-oxide-semiconductor field-effect transistor (MOSFET). Trimethylaluminum (TMA) is a conventional precursor for atomic layer deposition (ALD) of Al_2O_3 because of its excellent step coverage and thickness control.

However, pyrophoric nature of TMA causes safety and handling issues, which has led to active research concerning an alternative to TMA.

In this research, a non-pyrophoric aluminum precursor was designed and characterized in thermal ALD of Al_2O_3 thin films as follows. First, evaporation of the new precursor was found to occur in a single step with low residue (< 1%) at 300°C. Second, comparisons of ALD of the Al_2O_3 thin films from the new precursor and TMA were made using H_2O or O_3 as an oxidant. Self-limiting reaction, growth rates, and growth linearity were investigated. Wide ALD windows of the precursor ranging from 130 to 320°C and from 200 to 300°C were shown using H_2O and O_3, respectively. Finally, properties of the Al_2O_3 films from both the new precursor and TMA were analyzed via XPS, XRR, and TEM. The analysis results confirmed stoichiometric composition of the Al_2O_3 thin films with no appreciable carbon incorporation as well as comparable density and excellent step coverage from both the new precursor and TMA.

8:45am **AF1-TuM-4 Study on ALD Carbide Chemistry Approach for Rhenium**, ***Jani Hämäläinen***, *K Mizohata, K Meinander, P King, M Heikkilä, L Khriachtchev, J Räisänen, M Ritala, M Leskelä,* University of Helsinki, Finland

Rhenium is both a noble metal and a refractory metal. Noble metals have substantial resistance to corrosion and oxidation, and thus are known for their inertness. On the other hand, refractory metals are typified by extremely high melt temperatures and high wear resistance. Rhenium is well known for its reluctance to form carbides, and therefore high pressures and high temperatures are distinctively required for synthesis of stoichiometric rhenium carbides. With that in mind we here examine such ALD chemistry that with other metals typically has resulted in carbide like films.

ALD of metal carbides has not been extensively studied and thus the selection of carbide materials and processes is quite limited. One of the most widely used approaches is to combine a metal halide with trimethyl aluminum (TMA) as recently exemplified by Blakeney and Winter [1]. In the same way, we use in our study $ReCl_5$, which has already been reported for ReS_2, ReN_x, and Re [2, 3], and TMA as a carbon source to deposit thin films at temperatures up to 300°C. The films were successfully grown on 5 x 5 cm^2 native oxide covered silicon (100) substrates in an ASM Microchemistry F-120 ST ALD reactor. The deposited films consisted of up to 70 at.% of carbon while the carbon to metal ratios were up to 4.3 as analyzed by TOF-ERDA. These values are among the highest carbon contents ever reported for thermal ALD. TOF-ERDA, XPS, Raman, EDX, and XRD techniques are used to examine the phase content and composition of these carbon-rich films.

[1] K. J. Blakeney and C. H. Winter, *J. Vac. Sci. Technol. A* 36 (**2018**) 01A104.

[2] J. Hämäläinen, M. Mattinen, K. Mizohata, K. Meinander, M. Vehkamäki, J. Räisänen, M. Ritala, and M. Leskelä, *Adv. Mater.* (**2018**), Early View Online. Https://doi.org/10.1002/adma.201703622

[3] J. Hämäläinen, M. Mattinen, M. Vehkamäki, K. Mizohata, K. Meinander, J. Räisänen, M. Ritala, and M. Leskelä, ALD 2017, Denver, USA, talk.

9:00am **AF1-TuM-5 Development of Advanced Precursors for Deposition of Cobalt Films**, *A Cooper,* ***Sergei Ivanov,*** Versum Materials*; S Lee, M Kim,* Versum Materials Korea, Republic of Korea*; A Derecskei-Kovacs,* Versum Materials

Copper encapsulation with thin cobalt films has 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. One of the most common precursors used for deposition of pure cobalt films, tert-butylacetylene dicobalt hexacarbonyl (CCTBA), suffers from low thermal stability and low vapor pressure. Low-temperature thermal ALD of cobalt oxide films was demonstrated using CCTBA at 68^{o}C but above 80^{o}C saturation is limited by thermal decomposition of CCTBA[2]. Relatively pure cobalt films can also be deposited at 150-170^{o}C by thermal CVD, but further increase in deposition temperature results in carbon contamination due to precursor thermal decomposition. The goal of this study was to identify a more thermally stable cobalt precursor for deposition of pure cobalt films with improved step coverage on patterned substrates.

In this study, Density Functional Theory (DFT) at the BLYP/DNP level was employed to calculate ligand dissociation energies from a series of cobalt acetylene complexes with various substituents on the acetylene ligand. The ligand dissociation energy in general decreased with an increase of the steric bulk of the acetylene ligand. Significant differences in thermal stability and carbon content in the cobalt films were observed depending on the type of substituent on the acetylene ligand. Liquid precursor, CCTNBA, was identified and showed improved thermal stability compare to CCTBA based on DSC and TGA analyses. Thermal CCVD and ALD processes were studied on various substrates. Step coverage of >80 % was demonstrated on patterned substrates. The effect of process conditions on step coverage and cobalt films properties will be presented.

1. Emiko Nakazawa, *et al.,* Advanced Metallization Conference (AMC) 2008, p.19-23, Materials Research Society (2009).

2. Byeol Han, et al., Electrochemical and Solid State Letters, 2012, 15 (2), D14-D1

9:15am **AF1-TuM-6 Diamine Adduct of Cobalt(II) Chloride for ALD of Stoichiometric Cobalt(II) Oxide and Reduction Thereof to Cobalt Metal Thin Films**, ***Katja Väyrynen***, *T Hatanpää, M Mattinen, M Heikkilä, K Mizohata, K Meinander, J Räisänen, M Ritala, M Leskelä,* University of Helsinki, Finland

Thin films of cobalt and its compounds can be utilized in a myriad of applications ranging from microelectronics to emerging energy technologies as well as catalysis and gas sensing [1–3]. For these materials to be adapted in future applications, accurate deposition methods, such as ALD, are required. The development of ALD processes for Co, CoO_x, CoN_x, or $CoSi_2$ has, however, been hindered by the lack of suitable precursors. There is a pressing need for new cobalt precursors that are volatile and thermally stable yet easy to reduce or oxidize depending on the desired material. The precursors should also be inexpensive and easy to synthesize to be applicable on an industrial scale.

In this work, we present a promising new precursor for the ALD of cobalt-based materials. $CoCl_2$(TMEDA) (TMEDA = N,N,N′,N′-tetramethylethylenediamine) is a diamine adduct of cobalt(II) chloride that is extremely easy to synthesize with a practically quantitative yield, and it exhibits the characteristics of an ideal ALD precursor, also from the industry point of view. Furthermore, by changing the ligands, the same approach can be extended to other transition metals, such as nickel, as well.

Herein, we also describe a full ALD study of cobalt(II) oxide thin films deposited using $CoCl_2$(TMEDA) and water at 225–300°C. A saturated growth rate of 0.38 Å/cycle was measured at 275°C. $CoCl_2$(TMEDA) is reactive towards water, whereas most other Co precursors require ligand combustion by ozone or oxygen plasma that inevitably results in the formation of Co_3O_4 instead of CoO [4]. The films deposited using $CoCl_2$(TMEDA) were highly crystalline with a mixture of both hexagonal and cubic phases of CoO. The hexagonal phase is specific to nanomaterials only and is not seen in bulk CoO [5]. A 50 nm film deposited at 275°C exhibited 1:1 Co:O stoichiometry and very low impurity levels below 1.0 at.%.

$CoCl_2$(TMEDA) is a potential candidate also for the ALD of Co metal, provided that it is combined with a suitable reducing agent. In this work, Co metal films were prepared indirectly via reduction of the deposited CoO films. The reduction studies were carried out at an exceptionally low temperature of 250°C in forming gas using TiN substrates. The Co content of the reduced films was as high as 95 at.%, with the rest being oxygen and hydrogen.

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[2] Y. Shao-Horn et al., *Nat. Mater*. **2003**, *2*, 464.

[3] J. Gerken et al., *J. Am. Chem. Soc.* **2011**, *133*, 14431.

[4] J. Kim et al., *Chem. Mater.* **2017**, *29*, 5796.

[5] W. Seo et al., *J. Am. Chem. Soc.* **2005**, *127*, 6188.

9:30am **AF1-TuM-7 Development New Metal Precursors for Atomic Layer Deposition at KRICT**, *G Lee, S Han, E Jung, C Kim, B Park,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; J Han,* Seoul National University of Science and Technology, Republic of Korea*; **Taek-Mo Chung**,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea **INVITED**

We have deeply concentrated our passions to develop a wide variety of new metal precursors for atomic layer deposition (ALD) and chemical vapor deposition (CVD) for a few decades. To synthesize the desired metal precursors, we did our best efforts with the synthetic strategy for the design of organic ligands on the molecular level. From the research works, various new aminoalkoxide type organic ligands such as 1-(dimethylamino)-2-methyl-2-propanol (dmampH), 1-(dimethylamino)-2-methyl-2-butanol (dmambH), and 1-[2-(dimethylamino)ethyl](methyl)amino}-2-methylpropan-2-ol (demampH) have been prepared. With these organic ligands, a lot of novel precursors which exhibit high volatility and thermal stability and are suitable to be applied to thin films deposition by ALD have been successfully developed by the general synthetic methods. They are copper precursors for CuO and Cu_2O, nickel complexes for NiO, and strontium compounds for strontium titanium oxide (STO). Moreover, new metal precursors such as tin, indium, and gallium complexes have been recently developed for transparent conducting oxides (TCO) and applied to deposit their oxide thin films by ALD and CVD. In this talk, we will discuss development and application of metal precursors for ALD at KRICT.

ALD Fundamentals
Room 116-118 - Session AF2-TuM
Mechanism and Surface Science

Moderators: Simon D. Elliott, Schrödinger, Won Seok Yoo, Samsung Electronics

10:45am **AF2-TuM-12 Surface Chemistry during Atomic Layer Deposition of Nickel Sulfide***, **Ran Zhao**,* Peking University, China

Atomic layer deposition (ALD) of metal sulfides has been recently developing very rapidly, and many new metal-sulfide ALD processes have been reported over the past several years. However, the surface chemistry in many sulfide processes remains still yet to be investigated. Our group recently developed a new ALD process of nickel sulfide (NiS) using bis(*N,N'*-di-*tert*-butylacetamidinato)nickel(II) ($Ni(amd)_2$) as the nickel precursor and H_2S gas as the sulfur source (*Chem. Mater.***2016**, *28*, 1155). This process was found to follow a typical layer-by-layer ALD growth mode and was able to produce smooth, pure, and conformal NiS films. However, the film growth rate was relatively low (~0.015 nm/cycle), and therefore the associated surface chemistry deserves further investigation.

In this presentation, we will show our recent mechanism study on the surface chemistry of the ALD of NiS from $Ni(amd)_2$ and H_2S, using combined in-situ techniques of X-ray photoelectron spectroscopy (XPS), low-energy ion scattering (LEIS), quartz crystal microbalance (QCM), and quadrupole mass spectrometry (QMS). The surface chemistry was found to deviate from the conventional ligand-exchange scheme, as the amidinate surface moiety from $Ni(amd)_2$ was not released during the H_2S half-cycle. Further analysis with control experiments revealed that a non-volatile acid-base complex between the acidic surface sulfhydryl and the basic amidine was formed on surface during ALD. Since the precursors used herein are fairly representative for ALD of metal sulfides, the findings should be of important reference for many other sulfide ALD processes.

11:00am **AF2-TuM-13 Exchange Reactions during Atomic Layer Deposition: ZnO Conversion to Al_2O_3 by Trimethylaluminum***, T Myers, A Cano, J Clancey, D Lancaster, **Steven M. George**,* University of Colorado - Boulder

Atomic layer deposition (ALD) is typically described by the self-limiting reaction of precursors with surface species that leads to controlled thin film growth. Missing from this picture is the possibility that the precursors can also undergo exchange reactions and convert the surface of the initial substrate to a new material. These exchange reactions are expected if the conversion produces a more thermodynamically favorable reaction product. These exchange reactions may be common during ALD nucleation.

In this study, the exchange between Zn and Al is explored during the initial reaction of trimethylaluminum (TMA) on ZnO films during Al_2O_3 ALD at temperatures from 100-225°C. The exchange is evident from a variety of experimental measurements. Fourier transform infrared (FTIR) investigations detect absorbance changes consistent with ZnO loss and Al_2O_3 gain after the TMA reaction on ZnO ALD films. Quadrupole mass spectrometry (QMS) measurements also observe $Zn(CH_3)_2$ reaction products as expected from the conversion reaction: $3ZnO + 2Al(CH_3)_3 \rightarrow Al_2O_3 + 3Zn(CH_3)_2$. In addition, studies of the effect of TMA exposures on ZnO nanoparticles with a diameter of ~10 nm measured the conversion of ZnO to Al_2O_3. The conversion produces a large mass loss that is consistent with the formation of an Al_2O_3 surface layer. The ZnO to Al_2O_3 conversion is also self-limiting as a function of TMA exposure.

X-ray photoelectron spectroscopy (XPS) and X-ray reflectivity (XRR) investigations are also consistent with the conversion of the surface of ZnO ALD films to Al_2O_3 after the initial TMA exposure. The XPS and XRR measurements both yield an Al_2O_3 surface layer with a thickness of ~1.0 nm on the ZnO ALD film. In addition, quartz crystal microbalance (QCM) measurements detect a substantial conversion of ZnO to Al_2O_3 after the initial TMA exposure during Al_2O_3 ALD. The QCM studies reveal that the mass losses are much more pronounced for thin ZnO films compared with thick ZnO films. In addition, the mass losses are more for ZnO surfaces terminated with $Zn-CH_3CH_3$ species compared with Zn-OH species.

These studies of the exchange between Zn and Al during the initial reaction of TMA on ZnO illustrate that ALD precursors can convert the surface of the initial substrate to a new material. These exchange reactions must be considered when analyzing ALD nucleation.

11:15am **AF2-TuM-14 Elucidation of the Mechanisms of Nickel (II) and Iron (III) Oxide Films Grown with Ozone by Atomic Layer Deposition***, **Joel Schneider**, J Baker, C MacIsaac, S Bent,* Stanford University

Atomic layer deposition (ALD) offers the capability of depositing materials in conformal films, roughly one atomic layer at a time in a controlled fashion. This ability, however, is highly dependent on the self-limiting nature of the constituent surface reactions. With the development of more sophisticated ALD processes such as ternary and quaternary materials that seek to finely tune materials properties, there is an increasing need to understand the mechanisms by which these materials grow. In this study, nickel (II) and iron (III) oxide thin films, two materials of interest in catalysis and microelectronics, were grown by ALD. Despite the prevalence of both processes in the literature, few studies examine their self-limiting behavior and growth mechanism. Here, the mechanisms of ALD were investigated using a combination of characterization techniques.

Nickel oxide and iron oxide thin films were grown from nickelocene and ozone and t-butyl ferrocene and ozone respectively, and films were characterized using variable angle spectroscopic ellipsometry,both *ex situ* angle-resolved and *in vacuo* x-ray photoelectron spectroscopies, x-ray reflectivity, and atomic force microscopy. It was found that significantly higher precursor doses than generally used in literature were required to reach saturation, resulting in higher saturation growth rates than are typical for ideal ALD; moreover, in the deposited films, the near-surface region was observed to have a different density than the bulk. This near-surface region was revealed to contain an accumulation of super-stoichiometric oxygen, and its thickness and oxygen content were found to correlate strongly with the ozone-to-precursor exposure ratio. Results of these studies suggest that oxygen is taken up into the film from ozone and then diffuses out again to react during subsequent metal precursor pulses.

The morphology of the films was also probed via synchrotron-based grazing incidence wide angle x-ray scattering and by scanning electron microscopy. It was found that the incorporation of surface oxygen correlates with degree of texturing in the films, but higher oxygen incorporation disrupts the film crystallinity entirely and mechanically stresses the film. The studies show that both the nickel (II) and iron (III) oxide processes exhibit significant non-idealities in ALD involving oxygen, and that these behaviors lead to changes in the structure and morphology of the film. This understanding illustrates how the growth and morphological properties of these films can be tuned with ozone exposure, and it has implications for both binary ALD and mixed ALD processes.

11:30am **AF2-TuM-15 Reaction Mechanisms of the Atomic Layer Deposition of Indium Oxide Thin Films Using Ethylcyclopentadienyl Indium***, **Fumikazu Mizutani**, S Higashi,* Kojundo Chemical Laboratory Co.,Ltd., Japan*; M Inoue, T Nabatame,* National Institute for Materials Science, Japan

Previously, we reported the development of a new liquid precursor, ethylcyclopentadienyl indium (EtCpIn), for atomic layer deposition (ALD) of high purity indium oxide films, and demonstrated the deposition of high purity indium oxide films using water and plasma oxygen as oxidizing reactants [1]. In this work, reaction mechanisms of the ALD using the EtCpIn were investigated.

As the EtCpIn molecules have the half-sandwich structure, it is considered that the EtCpIn adsorb to substrate by coordinate bonding between indium of EtCpIn and the surface oxygen. Therefore Si wafers with surface oxide films were used to settle the nucleation problem. To deposit high purity films, water and plasma oxygen were exposed in order as oxidizing reactants in the ALD cycles (WpO). For comparative investigation, other oxidizing reactants, water followed by oxygen (WO), plasma oxygen followed by water (pOW), only plasma oxygen (pO), only oxygen (O), and only water (W), were used instead of WpO.

Varying EtCpIn pulse time, thermal stability of EtCpIn was determined. Constant as the growth rates were at 150 degree C and at 200 degree C, the EtCpIn showed decomposition behavior at 250 degree C. Therefore, substrate temperature of 200 degree C was used for this ALD reaction mechanism study, and self-limited reactions were observed for water pulse time and plasma oxygen pulse time of WpO process at 200 degree C.

Linear growth with no nucleation delay was observed for WpO process, and the growth rate was about 0.09 nm/cycle. Since nucleation delay was not observed for all other processes (WO, pOW, pO, O, and W), it is probable that EtCpIn well adsorbs onto surface oxygen. For WO process, linear growth was also observed, and the growth rate was about 0.11 nm/cycle, significantly larger than that of WpO process. These results support the prospected reactions at oxidation step in WpO process; substitution of hydroxyl groups for ethylcyclopentadienyl ligands by water and subsequent sufficient surface oxidation by plasma oxygen. In WO process, the oxygen without plasma activation does not oxidize surface hydroxyl groups, and the remaining hydroxyl groups cause additional adsorption at the EtCpIn adsorbing step. The additional adsorption increases the growth rate of WO process. For the other processes (pOW, pO, O, and W), the growth rates were markedly small due to incomplete reactions in oxidation step.

Reference

[1] F. Mizutani, S. Higashi, and T. Nabatame, “High purity indium oxide films prepared by modified ALD using liquid ethylcyclopentadienyl indium”, 17th International Conference on Atomic Layer Deposition (2017)

11:45am **AF2-TuM-16 Reaction Mechanisms of Halogenated Silanes on N-rich Surfaces during Atomic Layer Deposition of Silicon Nitride*, Gregory Hartmann,*** University of Texas at Austin*; P Ventzek,* Tokyo Electron America*; T Iwao, K Ishibashi,* Tokyo Electron Technology Solutions Ltd.*; G Hwang,* University of Texas at Austin

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 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 cycle: (1) adsorption and decomposition of silicon-containing precursors and (2) nitridation of the Si-rich surface by active N species emanating from the plasma. Halogenated silanes 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 N-rich SiN surface during PEALD 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 combined with experimental characterization, we have examined and identified a novel mechanism for the adsorption and decomposition of DCS on a N-rich SiN surface. Our study predicts that the DCS adsorption and dissociation can occur by overcoming a moderate barrier (≈0.3 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 also elucidated the principles underlying the reaction mechanism, notably the hypervalent nature of Si which permits the facile reaction of molecularly adsorbed DCS with a primary or secondary amine functional group on the surface, followed by dissociation releasing protons and Cl anions with subsequent HCl formation. We have examined the same mechanism utilizing alternative precursors and the predicted trends are corroborated with the important properties of the system. Understanding these principles allows us to develop guidelines for processing conditions, such as the importance of maintaining the proper surface composition to facilitate 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 surface reactions during ALD.

Atomic Layer Etching
Room 104-106 - Session ALE1-TuM

ALE: Gas-phase and/or Thermal ALE

Moderators: Steven M. George, University of Colorado at Boulder, Venkat Pallem, Air Liquide

8:00am **ALE1-TuM-1 Fluorocarbon-based Atomic Layer Etching of Silicon Dioxide in Conventional Plasma Tools*, Stefano Dallorto,*** Lawrence Berkeley National Laboratory*; A Goodyear, M Cooke,* Oxford Instruments Plasma Technology, UK*; S Dhuey, A Schwartzberg,* Lawrence Berkeley National Laboratory*; C Ward,* Oxford Instruments Plasma Technology*; I Rangelow,* Ilmenau University of Technology, Germany*; S Cabrini,* Lawrence Berkeley National Laboratory

Controlling Ångstrom-thick film etching is essential for further development of sub-10 nanometer semiconductor manufacturing. The atomic scale era requires the use of decreasing film thickness together with stringent surface property control: preventing material damage and controlling over etching directionality and material selectivity.

Single digit nanofabrication requires the ability to achieve atomic scale etching control and material selectivity during pattern transfer. Atomic Layer Etching (ALE) satisfies these needs as critical dimensions continue to shrike. An ALE process consists of two sequential steps: A) surface modification: a thin reactive surface layer with a well-defined thickness is created B) layer removal: the modified layer is more easily removed than the unmodified material.

Here we study a Fluorocarbon(FC)-based ALE process using Ar plasma and CHF_3 gas for controlling the etching of silicon dioxide at the atomic level. During the saturative surface reaction, CHF_3 is injected in the steady state Ar plasma. CHF_3 breaks and forms some fluorocarbon polymer on the SiO_2 surface. CHF_3 is then purged from the chamber and FC polymer is a source of fluorine, which reacts with SiO_2 modifying its surface. For low energy Ar^+ ion bombardment conditions, the physical sputter rate of the substrate vanishes, whereas the modified surface can be etched when FC reactants are present at the surface .

With the goal of achieving high selectivity FC-based ALE, we first investigated the etching per cycle (EPC) using spectroscopic ellipsometer on unpatterned surfaces. Using CHF_3-based ALE for SiO_2 etching, we proved ALE self-limiting behavior with etching rate of 6 Å/cycle. Figure 1 in Supplement shows SiO_2 features varying the ion power during the removing step (which decrease moving left to right) etched using different masks: ZEP and Chromium. Using a Cr mask (Figure 1: Row 2) the EPC is similar to the one of flat surfaces. Instead, SiO_2 features using ZEP mask (Figure 1: Row 1) have an EPC 50% higher than expected. Polymer mask (ZEP) is a source of carbon, hydrogen and oxygen, which interfere with the etch process bringing it out of the self-limiting window. SiO_2 features etched using lower DC bias (17 V) are aspect-ratio independent and results in a low degree of physical/ionic etching.

A successful application of the FC-ALE approach has been demonstrated. Overall, the cyclic CHF_3/Ar etch has proven to pattern features well with an hard mask, with great potential for significant improvement in overall etch performance.

8:15am **ALE1-TuM-2 Damaged Layer Control for Atomic Level Processes*, Masanaga Fukasawa,*** *T Tatsumi,* Sony Semiconductor Solutions Corp., Japan **INVITED**

Atomic layer etching (ALE) is one of the most attractive methods for overcoming the limitations of conventional processes. One of the advantages of ALE is low-damage etching. However, it is impossible to stop plasma-induced damage from occurring because ions, radiation, and radicals are irradiated on a surface simultaneously. In the case of low-energy incidences of ions (~ 50eV), the effect of radiation and radicals also has an impact on damage generation. In this presentation, I review the results of ion/radiation damage analysis.

Suppression of Si substrate damage caused by energetic ion bombardment is one of the most critical issues in advanced devices. The threshold energy for atomic displacement (Ed) of bulk Si crystal is reported to be 10-30 eV. When we use ion energy higher than the Ed, it is possible to generate damages in Si substrate. Si substrate damage during gate electrode etching causes a "Si recess" structure to form, which is reported to degrade device performance. Although the damage basically consists of a surface oxidized layer and underlying dislocated Si, the damage structure strongly depends on the incident ion species, ion energy, and oxidation during air and plasma exposure. As both the Si recess and remaining dislocated Si degrade electrical performance, precise control of incident ion energy is indispensable to minimize damage generation.

We also found that photons with longer wavelengths than optical bandgap energy could reach the underlying dielectrics/Si interface and cause interface damage. UV radiation transmitting through the upper dielectrics could cause the electrical characteristics of underlying MOS devices to fluctuate. Thus, we must control VUV/UV radiation from plasma, even in the case of ALE processes.

ALE is one of the pulsed plasma, so we investigated an effect of transient behavior of a pulse modulated inductively coupled plasma on the photon-induced interface defects. The time-resolved OES revealed that the optical emission overshoot appeared after ignition because of the variation of the electron temperature and number density in the early ON phase. As a result, the amount of UV radiation damage increased compared with CW plasma. Thus, control of transient behavior is essential for reducing photon-induced damage in pulsed plasma.

The key challenges of atomic level processes for plasma-induced damage reduction are almost same as CW plasma. The effects of VUV/UV radiation and radicals become particularly apparent in the case of low-energy incidences of ions. In addition, the control and the monitoring of the transient behavior of pulsed plasma become more important for atomic precision etching.

8:45am **ALE1-TuM-4 Selective Thermal Cyclic ALE of Lanthanum Oxide via Formation and Desorption of Organo-lanthanum Complex***, **Yoshihide Yamaguchi**, K Shinoda, S Fujisaki,* Hitachi R&D Group, Japan*; Y Kouzuma, S Sakai, K Kawamura, M Izawa,* Hitachi High-Technologies Corp., Japan

The demand for atomic layer/level etching (ALE) is increasing as the geometries of semiconductor devices continue to shrink. Remarkable progress has been made in the recent years to meet the enhanced requirements for a variety of materials to be atomically etched. One approach for selective isotropic ALE is rapid thermal cyclic ALE, which is cyclic repetitions of a self-limiting surface modification and a thermal desorption. Rapid thermal cyclic ALE of SiN, TiN, and W was developed by the authors [1, 2]. As for high-k lanthanum oxide (La_2O_3) whose boiling point is more than 4000°C, thermal etching via a low temperature (< 250°C) volatile organo-lanthanum complex has also been developed [3], although the cyclic process has yet to be confirmed.

In this work, we present thermal cyclic ALE of La_2O_3 exposed to a mixture of a ketone-based ligand and a stabilizer followed by a thermal annealing. Our preliminary cyclic experiments on powdered La_2O_3 demonstrated that the mass of the powder sample decreased as the number of repetition cycles increased. In one cycle of chemical exposure and annealing, the average loss in mass was 0.074 mg, which corresponds to about 30 nm/cycle for a La_2O_3 film.

Formation of an organo-lanthanum complex was quasi-self-limiting because the change in the mass of the powder sample had shown saturation behavior. The volatile organic species in preliminary experiments were collected and spectroscopically analyzed. The resultant data was identified as an organo-lanthanum complex bearing a ligand moiety and a stabilizer moiety.

Next, we examined the effect of temperature during the chemical exposure. In this experiment, both La_2O_3 and SiO_2 films deposited on silicon substrates were used as sample materials. Substrate temperatures during the chemical exposure were 140°C and 260°C. The films' thicknesses were evaluated by scanning electron microscopy after the exposure. Because the etching of the La_2O_3 film was not detected when the temperature was 140°C, we concluded that the formation of the organo-lanthanum complex is self-limiting. On the other hand, continuous etching of the La_2O_3 film was observed when the temperature was 260°C, at which point the organo-lanthanum complex was volatile. The etching of SiO_2 was not detected at both temperatures. From these findings, we concluded that selective, thermal cyclic ALE of lanthanum oxide was successfully demonstrated.

[1] K. Shinoda et al., J. Phys. D: Appl. Phys. 50, 194001(2017).

[2] K. Shinoda et al., SPIE Advanced Lithography 10589-17 (2018).

[3] Y. Yamaguchi et al., AVS Symposium and Exhibition, PS+NS+SS+TF-ThM13 (2017).

9:00am **ALE1-TuM-5 Thermal Atomic Layer Etching of Silicon Using an Oxidation and "Conversion-Etch" Mechanism***, **Aziz Abdulagatov**, S George,* University of Colorado - Boulder

The thermal atomic layer etching (ALE) of silicon was performed using an oxidation and "conversion-etch" mechanism (see Supplemental Figure S1). In this process, the Si surface is oxidized to a silicon oxide layer using O_2 or ozone. The silicon oxide layer is converted to an Al_2O_3 layer using trimethylaluminum (TMA). The Al_2O_3 layer is fluorinated by HF to an AlF_3 layer prior to the removal of the AlF_3 layer by ligand-exchange using TMA. Si ALE was studied using silicon-on-insulator (SOI) wafers in a warm wall reactor with a hot sample stage. *In situ* spectroscopic ellipsometry was employed to monitor the thickness of both the silicon and the silicon oxide layer during Si ALE. These studies observed that the silicon film thickness decreased linearly with number of reaction cycles while the silicon oxide thickness remained constant.

Using an O_2-HF-TMA reaction sequence, the Si ALE etch rate was 0.4 Å/cycle at 290°C (see Supplemental Figure S2). This etch rate was obtained using static reactant pressures of 250, 1.0 and 1.0 Torr, and exposure times of 10, 5 and 5 s, for O_2, HF and TMA, respectively. Reducing the O_2 pressure below 250 Torr reduced the etch rate. A lower etch rate of 0.2 Å/cycle at 290°C was observed at an O_2 pressure of 30 Torr. The order of the reactant sequence affected the Si etch rate. Changing the reactant sequence from O_2-HF-TMA to O_2-TMA-HF reduced the etch rate from 0.4 to 0.2 Å/cycle at 290°C. Comparable etching rates were observed using ozone instead of O_2 as the oxidant. Using an O_3-HF-TMA reaction sequence, the Si ALE etch rate was 0.5 Å/cycle at 290°C. The Si ALE etch rate decreased with process temperature for both the O_2-HF-TMA and O_3-HF-TMA reaction sequences. An oxide thickness of ~10-20 Å remained after Si ALE at 290°C. However, this oxide thickness could be removed by sequential TMA and HF exposures without influencing the underlying silicon film.

This new thermal Si ALE process is expected to yield isotropic etching. Thermal Si ALE will complement the plasma Si ALE process based on directional Ar^+ ions that yields anisotropic etching. Thermal Si ALE should be useful in advanced semiconductor fabrication. Thermal Si ALE could also be utilized for atomic-scale polishing and cleaning of silicon surfaces. In addition, there may be applications in other areas such as silicon-based optoelectronics, photonics and MEMS fabrication.

9:15am **ALE1-TuM-6 Rapid Atomic Layer Etching of Al_2O_3 using Sequential Exposures of Hydrogen Fluoride and Trimethylaluminum with No Purging***, **David Zywotko**,* University of Colorado - Boulder*; J Faguet,* TEL Technology Center, America, LLC*; S George,* University of Colorado - Boulder

An increase in Al_2O_3 atomic layer etching (ALE) rates versus time was demonstrated using sequential, self-limiting exposures of hydrogen fluoride (HF) and trimethylaluminum (TMA) as the reactants with no purging. The normal purging expected to be required to prevent chemical vapor etching (CVE) or chemical vapor deposition (CVD) is not necessary during Al_2O_3 ALE. The purgeless, rapid atomic layer etching (R-ALE) was studied from 250°C to 325°C using various techniques.

In situ quartz crystal microbalance (QCM) measurements monitored Al_2O_3 R-ALE at 300°C. The Al_2O_3 R-ALE process produced linear etching versus number of R-ALE cycles. The net result of fluorination by HF and ligand-exchange with TMA was a mass change per cycle (MCPC) of -32.1 ng/cm^2 using sequential, 1 s exposures for both HF and TMA with no purging. This mass change equates to a thickness loss of 0.99 Å/cycle or 0.49 Å/s. The Al_2O_3 R-ALE etch amount per cycle at 300°C was nearly equivalent to the previously measured Al_2O_3 ALE etch amount per cycle at 300°C using 30 s purge times. However, the Al_2O_3 R-ALE etch rate versus time at 300°C was 78 times faster than the previously measured Al_2O_3 ALE etch rate versus time at 300°C using 30 s purge times. *Ex situ* spectroscopic ellipsometry (SE) and XRR measurements also revealed temperature-dependent etch rates for Al_2O_3 R-ALE from 0.02 Å/cycle at 270°C to 1.12 Å/cycle at 325°C.

Additionally, patterned SiO_2 wafers were used to compare Al_2O_3 R-ALE and normal Al_2O_3 ALE with purging in high aspect ratio structures. Scanning electron microscope (SEM) images revealed that the etching was uniform for both processes and yielded comparable etch rates per cycle in the high aspect ratio structures. The HF and TMA precursors were also intentionally overlapped by various amounts to explore the behavior when both precursors are present at the same time. Similar to atomic layer deposition (ALD), where precursor overlap produces chemical vapor deposition (CVD), precursor overlap during Al_2O_3 ALE leads to AlF_3 CVD. However, any AlF_3 CVD growth that occurs during precursor overlap is removed by spontaneous AlF_3 etching during the subsequent TMA exposure. This spontaneous AlF_3 etching by TMA explains why no purging is necessary during R-ALE.

9:30am **ALE1-TuM-7 Self-limiting Thermal Atomic Layer Etching of Tungsten Metal Using O_2 Oxidation and WCl_6 or WF_6: Role of Halogen Species in Temperature Dependence of ALE Reaction Rate***, **Wenyi Xie**, P Lemaire, G Parsons,* North Carolina State University

Self-limiting atomic layer etching (ALE) is essential for enabling the manufacturing of complex transistor structures. Thermal ALE, based on thermal desorption of volatile etch products, is appealing for avoiding plasma-induced damages of sensitive device structures. However, thermal ALE process for metals is currently lacking. In our study, we demonstrated two thermal atomic layer etching processes based on the sequential oxidation-etch reaction schemes which allow controlled W to proceed for temperatures ≥ 275 and ≥ 200°C, respectively.

In the first part of our study, we investigated a thermal tungsten (W) ALE process using oxygen (O_2) and tungsten hexafluoride (WF_6). Based on insights gained from thermodynamic modeling, we proposed that W etching could proceed in two sequential reaction steps: 1) oxidation of tungsten, and 2) formation and removal of volatile WO_2F_2 during reaction with WF_6 (Supplemental, Figure 1a). Using in-situ Quartz Crystal Microbalance (QCM) analysis, we found the O_2 and WF_6 half reactions exhibit self-limiting characteristics therefore making the O_2/WF_6 process promising for W ALE. In addition, the etch rate is ~ 6.3 Å/cycle at 300°C but decreases to 0.34 Å/cycle when temperature decreases from 300°C to 220°C (Supplemental, Figure 1b). The significant decrease in etch rate is likely due to the limited volatility of WO_2F_2 at temperatures < 275°C as suggested by thermodynamic modeling results.

W etching with the O_2/WF_6 process is limited to temperatures ≥ 275°C, however lower temperature ALE processes are more desired for enabling selective deposition. Through further thermodynamic modeling studies, we find that a lower temperature W ALE process is viable when tungsten hexachloride (WCl_6) is used as the etchant instead of WF_6. Thermodynamic modeling results revealed that WCl_6 reaction with WO_3 can give rise to formation of volatile WO_2Cl_2 at temperatures ≥ 200°C (Supplemental, Figure 2a). Using in-situ QCM analysis, we found that W etching with O_2/WCl_6 process is self-limiting and proceeds readily for temperatures ≥ 220°C (Supplemental, Figure 2b).

In summary, we demonstrated thermally driven W ALE using O_2/WF_6 and O_2/WCl_6 processes, and our work on thermal W ALE serves to increase the fundamental understanding on ALE reactions and expand the base of available ALE processes for advanced material processing.

9:45am **ALE1-TuM-8 Modifying Thermal HF-based ALE Methods via Secondary Interactions with Alkali Compounds***, **John Hennessy**, A Jewell, S Nikzad,* Jet Propulsion Laboratory, California Institute of Technology

Alternating exposure to trimethyaluminum (TMA) and hydrogen fluoride (HF) has been used previously in the ALD of AlF_3 thin films. At substrate temperatures higher than approximately 225°C, the same exposure can result in the thermal atomic layer etching (ALE) of thin films of Al_2O_3. In previous work, we have shown that TMA/HF exposure performed in the presence of lithium fluoride (LiF) can significantly increase the Al_2O_3 etch rate and reduce the transition temperature where etching dominates over deposition.[1] In this work, we expand this approach to study the effect of other alkali halide compounds such as NaCl, KBr, and CsI. These materials are introduced externally into our vacuum chamber and influence the process behavior over surprisingly large spatial scales. All materials are observed to have an enhancing effect on the ALE process with respect to the etch rate of Al_2O_3 at a given substrate temperature. In some cases these materials can enable the reduction of the substrate temperature where continues etching of Al_2O_3 is observed to as low as 125°C, a regime where the deposition of AlF_3 would otherwise dominate the TMA/HF process. The choice of alkali material, choice of aluminum precursor, and process parameters like substrate temperature and precursor dose, can be exploited to tune the rate and selectivity of the thermal HF-based ALE process. We present characterization of these processes to etch Al_2O_3 in a self-limiting manner, and discuss applications of the method related to the performance improvement of aluminum optical components in the deep ultraviolet for space applications.

[1] J. Hennessy *et al.*, J. Vac. Sci. Technol. A 35, 041512 (2017).

Atomic Layer Etching
Room 104-106 - Session ALE2-TuM

Modeling of ALE

Moderators: Alok Ranjan, TEL Technology Center, America, LLC, Craig Huffman, Micron

10:45am **ALE2-TuM-12 The Role of Modelling in Understanding and Designing Processes for Thermal Atomic Layer Etch***, **Simon D. Elliott**,* Schrödinger, Inc., Ireland*; S Natarajan,* Tyndall National Institute, Ireland **INVITED**

Plasma-free (or so-called 'thermal') atomic layer etch (ALE) is often described as the inverse of atomic layer deposition (ALD). In this talk we discuss whether existing approaches for the atomic-scale modelling of ALD chemistries can also be applied to ALE, what new modelling approaches are being developed for ALE and what needs are still outstanding.

Examples of the successful ALE of oxides from the literature are classified into types according to their assumed mechanisms, focusing on continuous versus self-limiting reactions, on surface conversion versus ligand exchange reactions, and on redox steps. Corresponding thermodynamic and kinetic criteria are then proposed as a framework for the theoretical analysis and prediction of ALD processes. To examine the validity of this framework, energetics computed at the level of density functional theory (DFT) for the sample ALE reactions are presented and discussed. Many of the trends observed in experiment for the ALE of oxides like alumina and hafnia can thus be reproduced and understood with relatively little computational effort. The observed temperature dependence is broken down into entropy effects in individual ALE pulses. Moving beyond this simple framework, we discuss the most important reaction steps that need to be explicity modelled for a full understanding of ALE. Early results are presented, including progress towards simulating the volatility of etch by-products. Comparisons are drawn with past work on ALD. A wish-list of future modelling needs is proposed.

11:15am **ALE2-TuM-14 Physical Damage Analysis of Atomic Layer Etching of Silicon using Molecular Dynamic Simulations***, **Ryoko Sugano**, M Kurihara,* Hitachi R&D Group, Japan*; K Kuwahara,* Hitachi High-Technologies Corp., Japan*; S Hamaguchi,* Osaka University, Japan

As the device structures shrink to atomic dimensions, more precise etch processes are required with atomic-scale controllability and lower damage. Atomic layer etching (ALE) is considered to fulfill such requirements in the fabrication of next-generation 3D devices, rather than conventional reactive ion etching [1]. Anisotropic ALE can transfer the exact dimensions of mask patterns to the underlying layer. ALE is typically achieved by two sequential self-limiting surface reactions. For example, anisotropic silicon ALE (Si-ALE) was demonstrated by the use of cyclic repetitions of cryogenic adsorption of F atoms and the subsequent Ar ion irradiation [2]. Since then, various Si-ALE has been investigated with halogen gases for the Si surface modification and Ar ion bombardment for the removal of halogen-bonded Si atoms. Ar ion bombardment in a removal step, however, causes plasma induced damages even at energy below the sputtering threshold. Experiments with low-electron-temperature plasmas showed that surface damage was considerably mitigated when ion energy was less than -10 eV [3]. With an increase of the incident ion energy, both the etched depth and damage thickness increased. Hence, for a better control of anisotropic Si-ALE, the relationship between the etched depth and damage thickness must be clarified.

In this work, to obtain low-damage process conditions for anisotropic Si-ALE, we have used molecular dynamic (MD) simulations and examined the effects of adsorbed halogen species and ion energy. The Si-ALE process analyzed in this study is based on cyclic repetitions of Br or Cl adsorption and Ar ion bombardment steps. Interatomic potential functions used in the MD simulations are of Stillinger-Weber type [4]. Plasma induced damages were estimated by the structural change in the Si lattice of the underlying Si substrate. It has been found that both the damage and the halogen penetration-depths are larger in the case of Cl than in Br, presumably due to the atomic-size difference between Cl and Br. When Cl is used for adsorption, the number of desorbed $SiCl_x$ is more than twice that of $SiBr_x$ when Br is used under similar conditions. This is because the number of Si-Cl bonds in the damaged layer is much larger than that of Si-Br bonds. MD simulations have also shown that Si-ALE with Ar ion irradiation below 20 eV causes no damage in the underlying layer below 1 nm-depth from the surface in both cases of Br and Cl.

[1] K Shinoda et al., J. Phys. D **50** 194001 (2017).

[2] Y. Horiike et al., J. Vac. Sci. Technol. A **8**, 1844 (1990).

[3] L. Dorf et al., J. Phys. D **50** 274003(2017).

[4] K. Miyake et al., Jpn. J. Appl. Phys. 53, 03DD02 (2014).

11:30am **ALE2-TuM-15 Dimer Products from Ligand-Exchange Reactions During Thermal Atomic Layer Etching**, ***Andrew Cavanagh**, J Clancey, S Sharma, S George,* University of Colorado - Boulder

Thermal atomic layer etching (ALE) can be accomplished using sequential, self-limiting fluorination and ligand-exchange reactions. One example is Al_2O_3 ALE using sequential exposures of HF and $Al(CH_3)_3$. Fluorination by HF converts Al_2O_3 to AlF_3. The ligand-exchange reactions are then believed to involve transmetalation where ligands are exchanged between the surface metal fluoride (AlF_3) and the gas phase metal precursor ($Al(CH_3)_3$). The products of these transmetalation reactions have been assumed to be monomeric metal species (e.g. $AlF(CH_3)_2$). In contrast, our recent quadrupole mass spectrometry (QMS) investigations have observed very little of the monomeric $AlF(CH_3)_2$ etch product. Instead, the main etch products are dimer species in form of $AlF(CH_3)_2$-$AlF(CH_3)_2$ and $AlF(CH_3)_2$-$Al(CH_3)_3$ (see supplemental Figure S1). These dimers are formed from the monomeric $AlF(CH_3)_2$ etch product with itself and with the $Al(CH_3)_3$ metal precursor.

To understand the relative stability between monomer and dimer reaction products, calculations were performed on all possible monomers and dimers that could be produced by the $Al(CH_3)_3/AlF_3$ ligand-exchange reaction. The potential energy surface for the reaction of $Al(CH_3)_3$ and AlF_3 confirms that dimers are the preferred etch product (see supplemental Figure S2). The dimers consist of a pair of bridging ligands between the Al metal centers and four terminal ligands. The bridging ligands can be (F, F), (F, CH_3) or (CH_3, CH_3). The (F, F) bridges result in the most stable dimers while the (CH_3, CH_3) dimers result in the least stable dimers. In agreement with the QMS results, these calculations predict that the $AlF(CH_3)_2$-$AlF(CH_3)_2$ dimer with a (F,F) bridge and four terminal methyl groups is the most stable etch product.

The computational methodology has been applied to additional ligand-exchange reactions involving fluorinated Al_2O_3, Ga_2O_3 and ZrO_2 substrates and various metal precursors including $Al(CH_3)_3$, $Al(CH_3)_2Cl$, $SiCl_4$, $GeCl_4$, $SnCl_4$, and $TiCl_4$. In all the systems, the calculations indicate that dimeric metal species are the most stable etch products. The ligand-exchange reactions occur, but the reaction products of the ligand-exchange remain associated in dimer metal species. The calculations predict that dimer metal species should be the stable, volatile etch products observed in future QMS studies.

11:45am **ALE2-TuM-16 Molecular Dynamics Simulation of SiO_2 Atomic-layer Etching (ALE) by Fluorocarbon and Argon Plasmas**, *Y Okada, M Isobe, T Ito, K Karahashi, **Satoshi Hamaguchi**,* Osaka University, Japan

As the sizes of modern semiconductor devices approach near-atomic scales, processing to create such devices in mass production scale also requires atomic-scale precisions. Recent technological advancement for atomic-scale processing includes the development of atomic-layer etching (ALE), where etching processes take place layer by layer with each step having self-limiting chemical reactions on the surface. In such a process, self-limiting reactions result in not only atomic-scale accuracy of processed structures but also process uniformity over a large area regardless of structure densities. In this study we have examined mechanisms of ALE processes of SiO2 based on digital or pulsed application of fluorocarbon plasmas, using molecular dynamics (MD) simulations. In MD simulations, chemically reactive fluorocarbon radicals are first supplied to a SiO_2 surface with extremely low incident energy and a thin fluorocarbon layer is deposited there. Then the surface is irradiated with low-energy Ar+ ions, which induces reactions between fluorocarbon and SiO_2, typically forming volatile SiF_x and CO atoms, and the SiO_2 surface is etched until fluorocarbon on the substrate is essentially exhausted. In MD simulation, we have found that the actual reactions are not as simple as described above. In the Ar+ ion irradiation step, preferential sputtering of O atoms occurs even at small ion incident energy, which makes the surface more Si rich and also promotes the formation of Si-C bonds in the presence of a deposited fluorocarbon layer. C atoms bonded with Si are hard to remove by low-energy Ar+ ion irradiation and C tends to accumulate as fluorocarbon deposition steps are repeated, which may eventually lead to a complete etch stop and carbon deposition. On the other hand, a small amount of oxygen added to Ar+ ion irradiation steps can contribute to more efficient removal of carbon from the surface and also supplement the loss of oxygen due to low-energy ion bombardment. The physical sputtering yield of SiO_x is lower when its oxygen content is closer to stoichiometric SiO_2, so addition of a small amount of oxygen can also help self-limit the physical sputtering in the Ar+ ion irradiation step.

Area Selective ALD
Room 113-115 - Session AS-TuM

Area Selective Deposition I

Moderators: Rong Chen, Huazhong University of Science and Technology, Woo-Hee Kim, Chonbuk National University

8:00am **AS-TuM-1 Selective Area Deposition of BN using Electron Enhanced ALD**, ***Jaclyn Sprenger**, A Cavanagh, H Sun,* University of Colorado - Boulder*; A Roshko, P Blanchard,* National Institute of Standards and Technology*; S George,* University of Colorado - Boulder

Electron-enhanced atomic layer deposition (EE-ALD) is a line-of-sight technique and can produce selective area deposition. The electron beam activates surface sites for precursor adsorption. If a portion of the substrate surface is masked or is parallel to the electron beam, then no active sites will be generated and EE-ALD will not occur. The prospect of selective area deposition by EE-ALD was investigated by depositing boron nitride (BN) EE-ALD films on a trench structure.

EE-ALD of BN has been demonstrated using sequential exposures of borazine ($B_3N_3H_6$) and electrons (50-450 eV) at room temperature. GaN [1] and Si [2] have also been deposited using EE-ALD. EE-ALD uses electron stimulated desorption (ESD) to remove surface species. The ESD step in the EE-ALD of BN removes surface hydrogen. The result of ESD is a substrate surface terminated with dangling bonds. These dangling bonds are reactive and serve as sites for precursor adsorption.

Selective area deposition was investigated by growing an EE-ALD BN film on a trench structure. For a trench structure with vertical walls aligned parallel to the electron beam, there should be no electron flux and no film growth on the vertical walls. In contrast, the top and bottom of the trench will receive the full flux of the electron beam and should obtain film growth. To test these ideas, high resolution TEM images were recorded after 1000 cycles of BN EE-ALD on a trench structure (see supplemental Figure S1). BN films were observed on the top and bottom of the trench and very little BN film growth was measured on the side walls. STEM/EELS elemental mapping of B, N, Si, O and a false-color composite also showed a thick BN film on the top and bottom of the trench. Very little BN film growth was observed on the trench wall (see supplemental Figures S2).

The walls of the trench structures used in this work did not have vertical walls. In addition, the present experimental configuration did not allow for the exact alignment between the substrate surface normal and the electron gun. Even with this set-up, the effects of selective area deposition were apparent on the trench structure. The results show the promise of EE-ALD for applications such as the bottom-up-fill of trenches or vias.

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8:15am **AS-TuM-2 Reactive Monolayers for use in Area Selective Atomic Layer Deposition**, ***Rudy Wojtecki**,* IBM Research - Almaden*; E De Silva,* IBM Research - Albany*; N Frederick Fine Nathel,* IBM Research - Almaden*; H Shobha,* IBM Research - Albany*; N Arellano, A Friz, G Wallraff,* IBM Research - Almaden

Despite critics declaring an end to Moore’s law scaling continues as technology roadmaps target feature sizes below 10nm. As we advance these roadmaps, the lithography used to define features experience increasingly significant scaling errors that include edge placement, overlay and critical dimension uniformity, which can all lead to device variation and ultimately impact device performance. Selective area atomic layer deposition (SAALD), offers the unique advantage of exploiting surface chemistry to deposit a material in a targeted area and could, in principle, eliminate a lithography step – and therefore an alignment step – that introduce these errors. This would offer not only a significant cost savings but may also relax upstream design rules and enable access to non-traditional structures (e.g. 3D patterning).

Monolayers formed from a collection of well-organized small molecules can be utilized as effective barriers to block the deposition of hundreds of ALD cycles, or in combination with repair strategies to extend selective deposition capabilities. This is an attractive strategy as it enables the implementation of well-established head group chemistry to selectively deposit the monolayer on one surface vs. another. However, in SAALD there have only been reports of monolayers where weak Van der Waals interactions are used to drive the formation of well ordered crystalline monolayers, generally long chain alkanes. When the monolayer component has a high vapor pressure this can lead to process requirements where to provide a good barrier may take as long as 48hrs. We have designed monolayer components bearing supramolecular interacting groups that aide in alignment and reduce formation time. Furthermore, functional groups can be incorporated that are subsequently reacted to produce a robust barrier that deactivate surfaces for significantly more ALD cycles in comparison to monolayers that simply exploit the weak Van der Waals interactions.

These masking materials may provide the ability to replace a lithography step in semiconductor manufacturing provided SAALD can achieve a resolution relevant to current technology nodes. Therefore, we have also evaluated these reactive monolayer blocking schemes on planar structures with critical dimensions at and below 200nm allowing us to quantify the limiting resolution of these monolayer masks. Furthermore, these schemes may provide the ability to relax design rules and enable the selective deposition on fabrication of 3D structures, an area we are currently investigating.

$^+$ Author for correspondence: rjwojtec@us.ibm.com

8:30am **AS-TuM-3 Area-selective Atomic Layer Deposition using Si Precursor Inhibitors*, Mohammad Rizwan Khan,*** Incheon National University, Korea, Republic of Korea

Area-selective atomic layer deposition (AS-ALD) is envisioned to play a key role in next-generation semiconductor processing and can also provide new opportunities in the field of electronic devices. In this work, studies will be carried out to deposit the small size of Si precursor i.e., new inhibitors namely (N, N-dimethylamino) dimethylsiliane (DMADMS) and (N, N-dimethylamino) trimethylsiliane (DMATMS) on different substrates using various temperature for improving the packing quality and a highly ordered structure with uniformity and defect free, and have excellent blocking properties. A smaller size of the tail group increases the packing quality because of less steric hindrance, so less bulky tails such as DMADMS and DMATMS are more effective than branched or aryl tails such as octadecyltrichlorosilane (ODTS). Meanwhile, the other advantage of small size inhibitor is easy vaporization deposition which could be easily integrated into ALD process. The SiO_2 substrate coated with the inhibitors, yielding a hydrophobic surface with a water contact angle of about 80°-90°. For example, adsorption of DMADMS molecules with methyl ($-CH_3$) tail groups on an oxide substrate transforms the surface from an OH-terminated hydrophilic surface into a CH_3-terminated hydrophobic surface. The DMADMS molecules selectively adsorbed to the OH-terminated oxide areas, and AS-ALD of metal and metal oxide (Ru, Al_2O_3) was obtained on part of the surface not covered with the hydrophobic DMADMS molecules. The DMADMS adsorption on SiO_2 was investigated with techniques that include surface potential, ellipsometry, and DFT calculation. Surface reactivity of SiO_2 is decreased by adsorption of DMADMS, and thus adhesion of DMADMS coated SiO_2 is lower than DMADMS free SiO_2. The study thus provides useful information on the design of efficient ALD Si precursors with conformal, dense, and high-purity films for area selective growth.

8:45am **AS-TuM-4 *In situ* and *ex situ* Monitoring and Metrology for the Development of a Selective Deposition Process*, Christophe Vallee,*** LTM-UGA, France*; R Gassilloud,* CEA-Leti, France*; B Pelissier, R Vallat, V Pesce, O Salicio,* Univ. Grenoble Alpes, LTM, France*; T Grehl, P Brüner,* ION-TOF GmbH, Germany*; N Posseme,* CEA-Leti, France*; P Gonon, A Bsiesy,* Univ. Grenoble Alpes, LTM, France

Different approaches are currently used for the development of Area Selective Deposition (ASD) processes such as Selective ALD using SAM, Selective ALD using block copolymer, Selective ALD using temperature and inherent selectivity, Selective ALD using spatial ALD, Selective ALD using ABC cycle, as well as Selective ALD using an etching cycle in a ALD cycle (our process). For all these approaches it is necessary to precisely control and understand the interactions and mechanisms between the precursor, the reactant and the surface. Therefore, in this paper we will show how metrology and more precisely *in situ* and *ex situ* surface characterization can play an important role for the development of an ASD process.

The ASD process used for this work is based on the idea of combining ALD and ALE (Atomic Layer Etching) and is a 3 step ASD process. Firstly, inherent selectivity or surface plasma treatment is used to start the growth on one surface versus the other. Secondly, when the growth is starting on the second surface, an etching step is added. Thirdly, after or during the etching step a surface passivation step must be used to prevent any other growth during a given number of ALD cycles. These “super ALD cycles” can be repeated as many times as wanted to obtain the desired selective thickness [1].

Key steps for the process are that we need a precise control of the etching at the atomic scale and a control of its selectivity. Controlling the nature and density of defects induced by the etching step or the passivation steps and understanding their impact on the physical and electrical properties of the selectively deposited films are also required. Moreover, for the optimization of the process we need to precisely understand why after a given number of ALD cycles, the passivation is no more effective. Therefore, *in situ* as well as *ex situ* monitoring and metrology are bringing key advantages for these processes studies and developments. Among others, quasi *in situ* XPS [2] allows to access accurately to the chemical nature of the deposited film at each step of the process while avoiding any atmospheric unwanted oxidation. As an example, thanks to quasi *in situ* XPS, it is shown that after a passivation step on Si and TiN surfaces, more than 10 PEALD cycles are needed to start the growth of TiO_2 on Si while it is starting from the first cycle on TiN surface. Hence, with this presentation we will show how to optimize an ASD process using *in situ* ellipsometry, XPS, and OES, in addition to *ex situ* XRR and LEIS measurements.

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9:00am **AS-TuM-5 Area-Selective Atomic Layer Deposition of TiN, TiO_2, and HfO_2 on Si_3N_4 in Sub-50 Nanometer Si_3N_4/Amorphous Carbon Structures*, Eric Stevens,*** IMEC*; Y Tomczak, B Chan, E Altamirano Sanchez,* IMEC, Belgium*; G Parsons,* North Carolina State University*; A Delabie,* IMEC, Belgium

This work investigates initial growth of TiN, TiO_2, and HfO_2 thin films during thermal atomic layer deposition (ALD) onto an amorphous carbon (aC). ALD of TiN ($TiCl_4/NH_3$ 390ºC), TiO_2 ($Ti(OCH_3)_4/H_2O$ 250ºC), and HfO_2 ($HfCl_4/H_2O$ 300ºC) on pristine aC films resulted in uninhibited thin-film growth. A H_2 plasma treatment resulted in surface reduction and passivation of aC films, with delayed film coalescence for TiN, TiO_2, and HfO_2 ALD on aC. After 200 TiN cycles on H_2 plasma-treated aC, Ti levels were below the Rutherford backscattering spectrometry detection limit (8×10^{13} at/cm^2), whereas Si_3N_4 substrates show ~6 nm of TiN growth (selectivity ~200:1). Exposing plasma-treated aC to H_2O induces nucleation for TiN ALD, consistent with favorable nucleation on hydroxyl sites. We demonstrate selectivity scaling using 45 nm aC/Si_3N_4 line/space patterns, where a 5.8 nm TiN film was deposited on Si_3N_4 with minimal particle formation on aC, with selectivity loss primarily on feature corners and edges. We conclude that improved scaling of selectivity to nanometer scale patterns can be achieved by optimizing surface loading and extent of plasma exposure, and by further understanding shape effects in nanoscale surface plasma modification.

9:15am **AS-TuM-6 Toward Area Selective ALD on Metal/Dielectric Patterns: Comparison of Cu, Co, W and Ru*, Dara Bobb-Semple,*** *S Bent,* Stanford University

Device fabrication today is based on ‘top-down’ processes with multiple lithography and etching steps which serve as a bottleneck as well as a source of errors in device miniaturization. Area-selective atomic layer deposition (AS-ALD), which combines a surface modification technique and atomic layer deposition (ALD) in a ‘bottom-up’ approach to nanopatterning, shows promise in addressing these issues. A common approach in AS-ALD is to use densely-packed, self-assembled monolayers (SAMs) to modify the substrate surface and block ALD.

Incorporating this selective ALD process into fabrication schemes requires understanding how SAMs interact with different surfaces and also determining whether they can block ALD. In this work, we perform comparative investigations of the formation of octadecylphosphonic acid (ODPA) SAMs on four metal substrates: Cu, Co, W and Ru. After SAM deposition, model metal and metal oxide ALD processes were performed to assess the blocking ability of the SAM layer on each substrate. X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), water contact angle (WCA) goniometry, and X-ray reflectivity were used to characterize the modified samples before and after ALD.

Solvent choice and deposition temperature were found to affect ODPA SAM formation. The most passivating SAMs of ODPA were formed on Co and Ru in t-butanol whereas on W the most passivating SAM was formed in toluene. The ODPA covered substrates showed a C/P ratio of ~20 and average WCA of 110 ± 2° which confirm SAM formation.

Testing against ALD showed that ODPA SAMs could block ALD on Cu, Co and W to varying degrees, but not on Ru. ODPA SAMs were successful in preventing growth of at least 17 nm of ZnO ALD on W, whereas only 7 nm was blocked on Co and ~5 nm on Cu. Similarly, 3-4 times more Al_2O_3 ALD was blocked using ODPA SAMs on W versus that on Cu and Co. These results suggest that a higher quality SAM is being formed on the W surface than on the other metals, which may be explained in terms of the Lewis acid character of that substrate. By implementing a sequential deposition and etch process using acetic acid as the etchant, selectivity could be extended to over 20 nm of Al_2O_3 growth on Co/SiO_2 patterns with feature sizes as small as 20 nm. These studies provide insights that are important for consideration in the development of fabrication processes which incorporate SAMs for AS-ALD. Finally, we will present developments toward SAM-free processing for achieving selective ALD on metal/dielectric patterns.

9:30am **AS-TuM-7 Advanced Cycles for Area-selective Atomic Layer Deposition***, **Adrie Mackus,*** Eindhoven University of Technology, Netherlands **INVITED**

Area-selective ALD is currently gaining momentum, motivated by its potential application in self-aligned fabrication schemes. Conventional approaches for achieving area-selective ALD were predominantly based on the local deactivation of the surface *prior* to the deposition using self-assembled monolayers or resists films, followed by standard AB-type (i.e. two-step) ALD cycles. Many of the recently developed approaches for area-selective ALD rely on adding steps *during* the ALD process to influence the selectivity of the deposition, for example in the form of ABC-type cycle,[1] or supercycle[2] processes.

In this contribution, two approaches based on advanced ALD cycles will be discussed and illustrated by recent work on area-selective ALD of SiO_2 and Ru. An ABC-type ALD cycle was developed for area-selective ALD of SiO_2, in which an inhibitor is dosed in step A that selectively adsorbs on specific surfaces and subsequently blocks the precursor adsorption in step B.[1] One of the merits of this approach is that it is compatible with the use of plasmas or ozone as the co-reactant in step C. Furthermore, the selectivity for area-selective ALD of Ru was improved by combining ALD cycles with selective etching cycles in a supercycle recipe.

The main requirements for these advanced ALD cycles will be discussed. In addition, new opportunities that are opened up by the development of these novel area-selective ALD strategies will be described.

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Nanostructure Synthesis and Fabrication
Room 113-115 - Session NS-TuM

Nanostructures I

Moderators: Seong Keun Kim, Korea Institute of Science and Technology (KIST), Mato Knez, CIC nanoGUNE

10:45am **NS-TuM-12 The Precise Tailoring of Catalyst Interface by Atomic Layer Deposition***, **Yong Qin,*** Institute of Coal Chemistry, Chinese Academy of Sciences, China **INVITED**

The active sites of the supported nano-catalysts may include the surface sites of the metal nanoparticles and the interface sites between the metal nanoparticles and the support. The metal-support interfaces considerably affect the catalytic performances, and in many cases, are even more effective than the surface sites. Therefore, the precise tailoring of the surface/interface structure is the most important approach to improve the catalytic performance, especially the selectivity of heterogeneous catalyst. Surface modification and encapsulation of the metal nanoparticles are used extensively for the surface/interface tailoring. In order to obtain highly effecient catalyst and understand the catalytic mechanism, it is critically important to precisely control the particle size distribution, the location and content of the modification materials, and the composition and microstructure of the interface. However, in general, it is difficult to regulate these parameters accurately by traditional methods, such as chemical vapor deposition, sol-gel method, precipitation, impregnation, and so on. Atomic layer deposition (ALD) is an advanced thin-film technology, which possesses thickness control at the atomic level, excellent uniformity and conformality, and good reproducibility. In view of the limitations of traditional methods on the tailoring of the surface/interface structures, we developed new methods for the controllable synthesis of metal nanoparticles, dense/porous oxide films, and carbon films by ALD. Based on these synthesized materials, the tailoring of the surface/interface structure were performed by coating, ultrathin coating, confining in nanospace, ultrathin coating of confined catalyst, and assembling of double-interface structure. These catalysts were characterized and evaluated deliberately, and the mechanisms of how the surface/interface structures affect the catalytic performances were discussed. These results will provide new guidance for the design and synthesis of highly effective catalysts.

11:15am **NS-TuM-14 Improving the Anti-sintering Ability of Au/TiO_2 Catalysts by Constructing Semi-embedded Structure via Selective Atomic Layer Deposition***, **Yuanting Tang**, X Liu, B Shan, R Chen,* Huazhong University of Science and Technology, China

Au nanoparticles are very active for various important catalytic reactions, such as CO oxidation, partial oxidation of hydrocarbons and so on [1]. However, Au nanoparticles are highly susceptible to sinter at elevated temperature, which leads to serious decrease in catalytic activity . In this work, TiO_2-Au/TiO_2 catalysts are fabricated with semi-embedded structure via area selective atomic layer deposition (ALD). The area selective ALD method is realized through passivation of metal nanoparticles with self-assembled monolayers [3]. CO oxidation is performed as probe reaction. The results show that TiO_2-Au/TiO_2 catalysts exhibit outstanding room-temperature CO oxidation activity even after calcination. The key feature of the embedded structure lies in its ability to anchor Au nanoparticles and effectively limits the growth of Au nanoparticles via strong metal–oxide interactions, while still leaving active metal facets exposed. The reported method shows great potential for the simultaneous enhancement of thermal stability and activity of precious metal nanoparticles.

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[3] Liu X, Zhu Q, Lang Y, et al., Angew. Chem. Int. Ed. 2017, 56, 1648

11:30am **NS-TuM-15 Tuning of Boron Nitride Nanotubes, Nanopores and Nanoporous Membranes by ALD***, **Matthieu Weber**, B Koonkaew, S Balme,* Institut Européen des Membranes, France*; I Utke,* EMPA, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; F Picaud,* Université Bourgogne Franche-Comté, France*; I Iatsunskyi, E Coy,* Adam Mickiewicz University in Poznan, Poland*; D Cornu, P Miele, M Bechelany,* Institut Européen des Membranes, France

In this presentation, we report the design and the fine-tuning of boron nitride nanotubes, nanopores and nanoporous membranes by atomic layer deposition (ALD).

First, we developed an ALD process based on the use of BBr_3 and NH_3 as precursors in order to synthesize BN thin films. The deposited films were characterized in terms of thickness, composition, microstructure and mechanical properties.[1,2]

Next, we report the scalable synthesis of BN nanotubes that can be tuned in terms of diameters dimensions through a novel and easy route combining ALD and annealing steps. Carbon nanofibers templates are used as initial supports. In order to obtain the crystallization of BN and to eliminate the carbon initial supports, the samples were first placed at a temperature of 1350°C in nitrogen atmosphere for 5 hours, and then annealed at 600°C for 4 hours in air. The inner diameter can be controlled by choosing the initial carbon nanofibers supports. High resolution TEM imaging has been carried out to characterize the obtained BN nanotubes. The self-limiting reactions of ALD provide a clear control over the diameter thickness of the BN layer deposited with sub-nanometer accuracy as a steady-state ALD growth of $\sim$0.8 Å/cycle has been observed on all our samples. The self-supported BN nanotubes synthesized present good mechanical properties and are easy to handle. Furthermore, the sorption performances of the BN nanotubes have been assessed, and the results showed that the nanotubes absorb up to 110 times their weight in oil while repelling water. These proof-of-concept results are thus very promising for water purification purposes.

For the first time, this BN ALD process was also used to tune the diameter of fabricated single transmembrane nanopores by adjusting the BN thickness and to enable studies of the fundamental aspects of ionic transport on a single nanopore. At pH=7, we estimated a surface charge density of 0.16 $C.m^{-2}$ without slip and 0.07 $C.m^{-2}$ considering a reasonable slip length of 3 nm. Molecular dynamic simulations performed with experimental conditions confirmed the conductivities and the sign of surface charges measured.[2] The high ion transport results obtained and the ability to fine-tune nanoporous membranes by such a scalable method paves the way towards applications such as ionic separation, energy harvesting and ultrafiltration devices.

1 Weber M et al. Boron Nitride Nanoporous Membranes with High Surface Charge by Atomic Layer Deposition,

ACS Applied Materials and Interfaces 9, 19, 16669 (2017).

2 Weber M et al. Mechanical Properties of Boron Nitride Thin Films Prepared by Atomic Layer Deposition. *CrystEngComm*, 19, 6089 (2017).

ALD Applications
Room 113-115 - Session AA-TuA
Active Matrix Device and Material

Moderators: Soo-Hyun Kim, Yeungnam University, Ganesh Sundaram, Ultratech

4:00pm **AA-TuA-11 Amorphous In-Ga-Zn-O Thin-Film Transistor-Based Nonvolatile Memory Devices***, **Shi-Jin Ding**,* Fudan University, China **INVITED**

In recent years, amorphous indium-gallium-zinc-oxide (a-IGZO) thin-film transistor (TFT) nonvolatile memor ies have been widely researched as next-generation memory devices for flexible electronic systems and transparent panel systems. This is because a-IGZO has many advantages over conventional amorphous or polycrystalline silicon, such as high electron mobility, good uniformity, low processing temperature, and transparency in the visible region of the spectrum.

In this talk, I will talk about several types of a-IGZO TFT memory devices: (1) the a-IGZO TFT memory device with ALD Zn-doped Al_2O_3 charge storage layer. It exhibited fast programming characteristics and very good electron retention. The light emitting from a halogen tungsten lamp could be used to erase the programmed device, and the monochromatic light-assisted electrical erasing could increase the erasing efficiency, which was further enhanced with reducing the wavelength of the monochromatic light; (2) The a-IGZO TFT memory device with ALD Pt or Ni nanocrystals. It exhibited a high programming efficiency, and the programmed device could be erased efficiently by UV light or bias-assisted monochromatic light; (3) multi-level cell a-IGZO TFT memory with an IGZO or ALD ZnO charge trapping layer. When the fresh device was programmed at a positive or negative gate bias, a positive or negative threshold voltage shift was obtained compared with the fresh device. Therefore, a large memory window was achieved at relatively low operating voltages. Moreover, the memory device demonstrated electrically programmable and erasable characteristics between different states as well as good data retention.

In conclusion, the above memory devices could have promising applications in one-time programmable memory, light-erasable memory, UV detectors and electrically programmable and erasable memory.

4:30pm **AA-TuA-13 Atomic Layer Deposition of Elemental Tellurium for Composition Tuning Of Ovonic Threshold Switching Materials***, **Stephen Weeks**, G Nowling, V Adinolfi, V Narasimhan, K Littau,* Intermolecular, Inc.

Recent work on resistive switching based non-volatile memory (NVM) technologies has shown their potential for use in next generation data storage applications. In these next generation applications, NVM devices are required to be packed densely in cross-bar memory arrays that require a selector device, such as the ovonic threshold switch (OTS), in series with the memory element to minimize parasitic currents in the memory array.[1] To be cost competitive, the NVM architecture must also be of a high areal density, making three dimensional (3D) integration of both the memory and selector active layers attractive. To obtain this, there is a need for the development of atomic layer deposition (ALD) processes for the materials used in both the memory and selector elements deployed in these memory arrays.

In this work, we focus on the $GeTe_x$ material system. This system is known to exhibit phase change memory (PCM) behavior near the GeTe composition[2] and OTS behavior at the $GeTe_x$(x=4-6) compositions.[3,4] While a number of processes have been reported demonstrating the ALD of GeTe,[5,6] to date no report exists of ALD for the OTS relevant range of this material system, $GeTe_x$(x=4-6). Here, we report for the first time the ALD of elemental tellurium and use this process to tune the composition of $GeTe_x$. Elemental Te ALD was accomplished by reacting $[(CH_3)_3Si]_2Te$ with the alkoxide $Te(OC_2H_5)_4$. The Te deposition was observed to be conformal (see supplemental information). We discuss growth and nucleation behavior of ALD Te observed on Si, TiN, and GeTe substrates. Beyond this, we report the development of a TeO_2 ALD process utilizing $Te(OC_2H_5)_4$ and H_2O to encourage Te growth on surfaces where island like nucleation is observed to limit film closure. Finally, we deposit ALD GeTe using the recently reported $HGeCl_3$+$[(CH_3)_3Si]_2Te$ process of Gwon et al.[6] and utilize the ALD Te process to increase the Te content of the film to compositions relevant for OTS applications. These results provide a pathway towards using conformal elemental Te to tune the composition of chalcogenide films deployed in PCM and OTS applications using an all ALD approach.

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4:45pm **AA-TuA-14 Plasma Enhanced Atomic Layer Deposition of Low Temperature Silicon Nitride for Encapsulation Layer using Novel Silicon Precursor***, **SungGi Kim**, S Jang, J Park,* DNF Co. Ltd, Republic of Korea*; H Jeong,* DNF Co. Ltd*; J Park, G Park, S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

OLED(Organic Light Emitting Diode) has characteristics of self-emission, high-speed response, wide viewing angle, ultra-thin type, and high image quality, and is the spotlight in the display field. However, in the case of an OLED device, there is a problem that the lifetime is shortened and the device performance is lowered due to deterioration and oxidation of a light emitting material and an electrode material due to oxygen and moisture. In order to overcome these disadvantages, encapsulation techniques capable of blocking oxygen and moisture are very important in OLED devices. Recent thin encapsulation technology and hybrid encapsulation technology in flexible OLED panels. Thin film encapsulation technology is used by laminating organic film, inorganic film or inorganic film. Typical inorganic films include Al_2O_3, SiO_2, and SiN_x.

In this paper, a silicon nitride film was deposited with NH_3 and N_2 PEALD (plasma enhanced atomic layer deposition), using a new silicon precursor (Figure 1) on PEN (polyethylene naphthalate) films at various RF time conditions. The PEALD one cycle is made of 6 steps (Si precursor - Purge - NH_3 Reactant - Reaction Purge - N_2 Reactant - Reactant Purge) and the deposition temperature is 90℃. The encapsulation layer property was measured by WVTR(Water Vapor Transmission Rate) using a MOCON AQUATRAN Model 2 and the measurement time is over 100 hours. The deposited silicon nitride film with a 300Å thickness showed excellent WVTR characteristics below 1.00×10^{-4} g/m^2·day. It looks like a saturation behavior at above 300Å thickness, but we expect to be lower. Because it was measured below the detection limit ($1.00x10^{-4}g/m^2$•day) of MOCON AQUATRAN Model 2.

5:00pm **AA-TuA-15 Atomic Layer Delta Doping and Deposition of Ultrathin Metallic TiN-based Channel for Room-temperature Field Effect Transistor***, **Yu-Tung Yin**, P Cheng, C Wang, T Chang, T Shen, Y Cai, M Chen,* National Taiwan University, Republic of China

Under sub-10 nm technology node, the metallic channel transistors have been proposed as one of the possible candidates. However, the conductivity modulation in metallic channels can only be observed at low temperature, which is usually below 100 K. By using the atomic layer delta doping and deposition (AL3D) technique, the thickness and electron concentration of oxygen-doped TiN metallic channel has been precisely controlled, and the room-temperature field effect and modulation of the channel conductivity on TiN metallic channel were achieved in this study. The reduction in electron concentration and the blue shift of absorption spectrum were observed with the decrease of the channel thickness, which can be explained by the onset of quantum confinement effect. Similarly, the oxygen incorporation using the AL3D tehnique also results in the reduction in electron concentration and the blue shift of absorption spectrum, which can be deduced from the increase of the interband gap energy due to the oxygen oncorporation. Since the electron concentration was significantly modulated by the AL3D process, the screen effect was dramatically suppressed in the oxygen-doped TiN metallic channel. In addition, owing to the quantum confinement effect and the suppressed screening effect, the modulation of channel conductivity from the gate electric field can be achieved at room temperature in the precisely controlled oxygen-doped TiN ultrathin-body channel with the thickness down to 4.8 nm and the oxygen content up to 35%.

5:15pm **AA-TuA-16 Influences of Annealing Conditions on Characteristics of Sn-doped Zinc Oxide Thin Film Transistors Fabricated by Atomic Layer Deposition***, **Tao Wang**, H Lu, J Yang, W Liu, S Ding, D Zhang,* Fudan University, China

Transparent oxide semiconductors employing a tin-doped zinc oxide (TZO) thin film generated via atomic layer deposition (ALD) at low temperature (150°C) are investigated for their feasibility into high performance thin film transistor (TFT). The resistivity of the as-deposited uniform TZO film is as low as $1.9 \times 10^{-2}\Omega$ cm. The carrier concentration is high up to $4.9 \times 10^{19}cm^{-3}$ and the optical transparency is greater than 80% in visible range. The TZO thin film transistors exhibit excellent electrical and optical properties. In addition, the insights into the dependency of the impurities within the channel layer upon thermal annealing of the oxide film are presented. Studies towards an optimized annealing temperature (300°C) result in a high device performance in enhancement mode with a field effect mobility (μ_{FE}) of $13.7 cm^2/Vs$ and a subthreshold swing (S.S.) of 0.15V/dec. The performance of the TZO TFTs relies on carriers and defects in SnZnO and near the back-channel surface of SnZnO as well as the quality of the gate dielectric/SnZnO interface. Compared with the pristine devices, the TFT performance turned out to be dependent on the annealing temperature because of growing grain size and decreasing interface defects. These findings on the influence of annealing conditions allow for a better understanding on the formation of the active semiconductor channel and serve towards the applicability of ALD based transparent oxide semiconductors in next generation electronics.

ALD Fundamentals
Room 116-118 - Session AF1-TuA
Characterization

Moderators: Sean Barry, Carleton University, Canada, HyeongTag Jeon, Hanyang University, Korea

1:30pm **AF1-TuA-1 Studying Metal ALD Processes through X-ray Based in situ Characterization***, J Dendooven,* Ghent University, Belgium*; E Solano,* ALBA Synchrotron Light Source, Spain*; R Ramachandran, M Minjauw,* Ghent University, Belgium*; G Portale,* University of Groningen, Netherlands*; D Hermida-Merino,* ESRF, France*; A Coati,* SOLEIL, France*; **Christophe Detavernier,*** Ghent University, Belgium **INVITED**

Initial nucleation is particularly important during metal ALD. Using three different case studies, we aim to demonstrate that x-ray based characterization techniques such as x-ray fluorescence (XRF), grazing incidence x-ray scattering (GISAXS) and x-ray diffraction (XRD) can offer unique insights in metal ALD processes, offering approaches towards the conformal deposition of metal nanoparticles with carefully controlled loading, size and composition, as required for e.g. applications in catalysis and plasmonics.

A first case study concerns Ag ALD. We recently reported that combining the $Ag(fod)(PEt_3)$ precursor with NH_3 plasma results in a six-fold increase of the steady growth rate (0.24 ± 0.03 nm/cycle) when compared to H_2-plasma as reactant (0.04 ± 0.02 nm/cycle). The film morphology was investigated by electron microscopy and GISAXS, and it was found that films grown with the NH_3-plasma process exhibit a much higher particle areal density and smaller particle sizes on oxide substrates compared to those deposited using the H_2-plasma process (Chem. Mater. 29, 7114 (2017)).

A second case that will be discussed concerns initial nucleation during Pt ALD. The $Me_3(MeCp)Pt$ precursor was combined with different reactants (O_2, O_2 plasma, O_3 and N_2 plasma), and in situ XRF and GISAXS measurements provided detailed information about the evolution of Pt loading, average particle dimensions, and mean center-to-center particle distance during the initial stages of ALD, revealing that the choice of reactant had a significant impact on the nucleation and growth of the Pt nanoparticles. In the case of oxidizing reactants, there was a clear impact of the mobility of Pt surface species on the evolution of island morphology. The particle areal density could be controlled by tailoring the number of ALD cycles using oxygen as reactant, while subsequent growth using the same Pt precursor in combination with nitrogen plasma as reactant allowed for tuning of the particle size at the atomic level (Nat. Comm. 8, 1074 (2017)).

A third case concerns a recently reported ALD-based synthesis of bimetallic Pt-In nanoparticles. First, a Pt/In_2O_3 bilayer is deposited by ALD, where the thickness control inherent to ALD enables an accurate control of the Pt/In composition ratio. After ALD, annealing in H_2 ambient results in a reduction of the In_2O_3 and the controlled agglomeration of the bilayer structure into a film of bimetallic nanoparticles. In situ XRD and GISAXS were used to study the annealing process, and illustrate the accurate phase and size control that is offered by this two-step approach (ACS Nano 10, 8770 (2016)).

2:00pm **AF1-TuA-3 Stresses in ALD Films: Aiming for Zero Stress Thin Films***, R Ritasalo,* Picosun Oy, Finland*; O Ylivaara,* VTT Technical Research Centre of Finland, Finland*; **Tero Pilvi**, T Suni,* Picosun Oy, Finland

When grown films by atomic layer deposition (ALD) both intrinsic and thermal stresses are formed into the film; latter due to the mismatch in the thermal expansion coefficient of the substrate and the grown film. Films under high residual stress may cause problems for further processing, and for device performance and reliability. High residual stress can induce film delamination or buckling; bend released structures or the materials where the films are attached. Especially in microelectromechanical system (MEMS) manufacturing, zero or well-controlled residual stress is desired, as the stress effect is more prominent on released structures. Here, the residual stress measured from most common metal oxides deposited by thermal ALD processes on silicon substrates are presented. The thermal processes have an advantage that those can be scaled up to batch processing to achieve through-put and cost efficiency required for volume production. By varying the process parameters (e.g. temperature, chemicals) we aim for zero stress films or film stacks as well as for comprehensive stress data set to help for example MEMS designers and process integrators choosing proper thin film material, and ALD process chemistry and process conditions.

All films were grown in Picosun™ R-200 advanced reactors using thermal ALD processes. Deposited materials were HfO_2, TiO_2, SiO_2, Al_2O_3 and Ta_2O_5 and combinations of these. The ALD temperature was varied between 150°C and 300°C. The substrates used were 150 mm diameter double side polished silicon wafers, which have been pre-measured for stresses before the ALD. For stress measurement we used TOHO FLX-2320-S wafer curvature measurement tool and the measurements were carried out at room temperature. Deposited film thicknesses were measured with Semilab SE-2000 ellipsometer.

Residual stress data from most common metal oxides are presented. For some of the films there is also comparison for the same film material made with different precursors. In Figure 1 the residual stress data for the HfO_2 film grown at varying temperature is presented. The stress changes from compressive to tensile as the ALD temperature was increased from 150°C to 200°C.

Acknowledgements: This work has been done in the ECSEL Joint Undertaking project InForMed (An integrated pilot line for micro-fabricated medical devices) coordinated by Philips Electronics Netherlands BV.

2:15pm **AF1-TuA-4 High-throughput Screening of Atomic Arrangements of Surface and Interfacial Structures of ALD-deposited Thin Films***, **Orlando Trejo**, N Dasgupta,* University of Michigan

Atomically-precise engineering of surfaces and interfaces is critical for the development of PV technology. To address such atomic-scale engineering challenges, it is necessary to exploit advances in atomic-scale synthesis and characterization techniques by leveraging advances in corresponding theoretical understanding, modeling algorithms, and computational performance. However, there is a lack of software and modeling platforms to enable user-friendly and systematic investigation of surface and interfacial structure/disorder. Therefore, in this work we are developing a computational procedure for high-throughput screening of atomic arrangements of surface and interfacial structures.

Atomic structures of interfaces are typically a few Angstroms thick, not well-defined, multi-phase, non- periodic, and have intermixing of chemical species. Techniques like X-ray absorption near edge structure (XANES) and electron energy less spectroscopy (EELS) are promising to characterize interfacial structure as they capture element-specific geometric and electronic information [1]. However, identifying viable atomic configurations to simulate XANES spectra with density functional theory (DFT) is challenging due to computational time limitations. In my previous work [2,3], no more than 40 atomic arrangements were explored due to computational time limitations.

A statistical screening method for empirical fitting of experimental XANES spectra with simulated spectra is performed by a regression on critical geometric descriptors (e.g. space groups, unit cell parameters, and fractional coordinates). This process narrows down the range of atomic arrangements that produce simulated XANES spectra that resemble the experimental spectra. To determine the fit quality, the coefficient of determination (R2) is calculated between normalized experimental and simulated spectra over a defined X-ray energy range. The atomic arrangements yielding the best-matched XANES spectra are ran in DFT packages in order to determine their relative energetic stability and likelihood of representing the actual surface or interfacial structure.

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2:30pm **AF1-TuA-5 Application of Low Energy Ion Scattering for Characterization of Modern ALD Films of Industrial Relevance***, **Philipp Brüner**, T Grehl,* ION-TOF GmbH, Germany*; G Saheli, Y Uritsky, Y Xu, Y Lei, Y Yang, W Tang,* Applied Materials

ALD has become an essential part of the semiconductor manufacturing process. More and more materials are deposited using this technique, and its application will become even more relevant in the future. It is therefore of high importance to also expand the means of characterization of the films during and after growth, supporting both process development and quality control.

One technique that is well suited for this purpose is Low Energy Ion Scattering (LEIS). Noble gas ions of a few keV are scattered back from the surface; by measuring the energy spectrum of these ions, the composition of the outer atomic layer is determined in a quantitative way. Even more, LEIS determines information about the depth distribution of the elements over the first few nm of the film. In this way, the film can be monitored from nucleation to film closure and beyond. While the surface coverage is measured directly, information of the thickness distribution can be deducted from the tails in the spectrum. The combination of surface coverage and thickness distribution allows determining the growth mode. The minimal continuous thickness can be identified either by looking for the film reaching a coverage of 100%, or by the substrate signal disappearing. Depending on the masses of the elements involved, one of the two approaches is more sensitive. Also diffusion and surface segregation can be studied, and contaminations monitoring is possible.

Due to the ultimate surface sensitivity, the focus of LEIS studies is usually the nucleation phase, from the first cycle to formation of a closed film. In this presentation, a range of samples systems are studied to demonstrate the application of LEIS in the industrial R&D context. These examples include W on SiO_2 substrate for contact application with a thickness range of 0 – 1.5 nm. These films were grown under two different conditions and the effect of these conditions is shown. Another set of samples – again under two different growth conditions – includes 0.2 – 1.7 nm TaN on 1.5 nm TiN for barrier and work function applications. Time permitting, one or two other examples will be shown to illustrate the range of information that can be deducted from the LEIS results.

2:45pm **AF1-TuA-6 Characteristic Evaluation of ZrO_2 Thin Films by PEALD to Semiconductor and Display using Cp-Zr Precursor***, **Sang-Yong Jeon**, G Park, S Lee, W Chae, S Yim, J Park, S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

ZrO_2 has been widely used for high-k material and studied in various fields such as hardmask, thin film transistor (TFT), and encapsulation layer of Organic light-emitting diodes (OLEDs) due to its low dry etch characteristics and low moisture permeability.

In this study, we used $CpZr(DMA)_3$ as a precursor to evaluate characteristics of ZrO_2 by PEALD method and confirmed high applicability to high-k, hardmask, encapsulation, and TFT due to its electrical characteristics, dry etch rate, and WVTR characteristics.

ZrO_2 grown on Si substrate showed ALD window up to 280℃, which is relatively high temperature as shown in Fig. 1, and self-limited reaction was observed in linearity evaluation as shown in Fig. 2. The deposition rate was 29Å/min, which is relatively fast. The XPS results showed that the films were free of N and, C, and pure films with an O/Zr ratio of about 1.9. The dielectric constant and leakage current density of the ZrO_2 thin films were about 23 and 5E-8A/cm^2, respectively. In addition, it was confirmed to be HT-ACL of less than 40% of that of HT-ACL in a dry etch atmosphere based on C4F8 gas.

The WVTR of ZrO_2 deposited on PEN film at low temperature (<100℃) for OLED application was 10 times better than SiO_2 of the same thickness as shown in Fig. 3.

As can be seen from the above results, it was confirmed that the ZrO_2 thin film deposited with PEALD can be applied to various areas such as high-k, hardmask, TFT and encapsulation.

3:00pm **AF1-TuA-7 Hybrid Electronically Tailorable Dielectric Thin Films and Substrate Effects on Electrical and Chemical Properties of ALD Al_2O_3***, **Jessica Kopatz**,* Pennsylvania State University*; J Daubert, W Xie,* North Carolina State University*; A Meddeb, Z Ounaies, M Lanagan,* Pennsylvania State University*; G Parsons,* North Carolina State University

Our study is focused on the fundamental understanding of electronic transport and reliability of dielectric interfaces resulting from both MLD and ALD-grown thin films on two technologically important substrates: silicon and polymers. Based upon the deposition sequence and deposition time, the hybrid film possesses a range of properties incorporating both inorganic and organic natures. The organic alucone is grown via ethylene glycol and trimethylaluminum (TMA) precursors, while the use of water and TMA enables the growth of Al_2O_3. By capping 80 nm of MLD alucone with 20 nm ALD Al_2O_3, the permittivity was found to exceed the permittivity of Al_2O_3 itself, while the low loss remained in the same order of magnitude. This was unexpected because organic materials generally have a lower polarizability compared to inorganic metal oxides, thus causing lower permittivity values. The focus was then directed towards investigating the capacitive behavior and the nature of charge transport at the substrate-ALD interface by depositing Al_2O_3 onto different types of substrates. Herein, we examine the effect of substrate interface on the electrical and chemical properties of atomic layer deposited 100 nm Al_2O_3 thin films at deposition temperatures ranging from 100-300°C. Our substrates included platinized silicon (1500 Å) and low-resistivity (0.001-0.005 Ω*cm) p-type and n-type silicon. Electrical measurements consisted of utilizing current-voltage sweeps, dielectric spectroscopy, and capacitance-voltage sweeps. The use of platinized silicon was found to have a significant improvement on the dielectric permittivity of the deposited Al_2O_3 compared to the highly doped silicon substrates with values of 9 as opposed to 7.5, respectively. Capacitance-voltage measurements will help determine trapped states present within the highly doped silicon substrates. Chemical measurements regarding the refractive index of the deposited films were obtained using a Woollam Ellipsometer and Cauchy model. According to Ellipsometry, the refractive index of all Al_2O_3 films deposited at 300 °C was 1.66. This similarity demonstrates the difference in permittivity values must result from the interfacial reactions and not from film quality. At 300°C, the growth rate of 0.80 Å/cycle was calculated. Atomic force microscopy images of the Al_2O_3 films will offer insight on the relationship between surface roughness, deposited thickness, and deposition temperature.

3:15pm **AF1-TuA-8 Atomic Layer Deposition of Pyrite FeS_2, CoS_2, and NiS_2***, **Xinwei Wang**,* Peking University, China

The pyrite-type transition-metal disulfides (MS_2, M = Fe, Co, Ni) form a series of compounds that are highly interesting in many aspects. These compounds share the same cubic pyrite crystal structure but differ in the progressive increase of an anti-bonding *d* electron in the conduction band, and as a result, the metal pyrites exhibit very diverse and intriguing electrical magnetic properties from diamagnetic semiconductive to itinerant-electron ferromagnetic and to antiferromagnetic semiconductive. This diversity of the material properties has not only offered a model system platform for fundamental science studies but also enabled tremendous engineering possibilities for practical applications, such as solar cells, lithium/sodium-ion batteries, and electrocatalytic hydrogen evolution, oxygen evolution, and oxygen reduction.

In this presentation, we will show our latest progress on the development of atomic layer deposition processes for the metal pyrites of FeS_2, CoS_2, and NiS_2 (*Angew. Chem.Int. Ed.* 2018, doi:10.1002/anie.201803092). We use the metal amidinate compounds as the precursors for the metals and H_2S plasma as the sulfur source, and we will show that the deposition processes for FeS_2, CoS_2, and NiS_2 all follow ideal layer-by-layer ALD growth behavior over a wide temperature range to produce fairly pure, smooth, pyrite-structure metal disulfide films. We will further show that the ALD FeS_2, CoS_2, and NiS_2 films can be conformally deposited into deep narrow trenches with aspect ratios as high as 10:1, which thereby highlights the broad and promising applicability of these ALD processes for conformal film coatings on complex high-aspect-ratio 3D architectures in general.

ALD Fundamentals
Room 116-118 - Session AF2-TuA
High Aspect Ratio

Moderators: Scott Clendenning, Intel Corporation, Han-Bo-Ram Lee, Incheon National University

4:00pm **AF2-TuA-11 Modeling the Infiltration Kinetics of Porous, High Surface Area Materials in ALD: Effective Diffusivities, Saturation Times, and Densification*, Angel Yanguas-Gil, J Elam,*** Argonne National Laboratory

Understanding the infiltration dynamics in high surface area materials is crucial to evaluate the scale up of ALD processes involving the functionalization or densification of these materials. One of the challenges in ALD is that, due to the time dependent nature of the chemistry, modelling infiltration involves three very different timescales: the timescale of the transport of individual species inside high surface area materials, the surface kinetics, and the evolution of the internal porosity with the number of cycles.

In this work we apply an approach that we have recently developed to model ALD infiltration on disordered porous materials. Based on the treatment of the reactive transport of ALD precursors and other gas phase species as a Markov chain, the model allows us to obtain local sticking probabilities in a very efficient manner. Our simulation consists of two steps: we first generate random structures through the simulation of a particle sedimentation process, with various degrees of freedom to allow for the formation of materials with different porosity and pore size distribution, as well as their inverse structures. We then use these substrates as a starting point to model both the reactive transport of gas phase species within the porous material, and the evolution of the densification process as the ALD coatings grow to fill the pores.

Finally, we also model the impact of ALD processes on the electronic properties of the resulting scaffolds: using the simulated, coated structures as a starting point, we have modeled the carrier transport efficiency of a hypothetical nanostructured electrode under two assumptions: one in which charge transport is enhanced via ALD infiltration, and a second in which the simulated coating acts as a passivation layer reducing recombination.

4:15pm **AF2-TuA-12 Thin Film Conformality Analysis, Reliability and Modeling using All-silicon Lateral High Aspect Ratio Structures*, Oili Ylivaara,*** *M Ylilammi, V Korpelainen,* VTT Technical Research Centre of Finland, Finland*; R Puurunen,* Aalto University, Finland

Device downscaling in semiconductor and microelectromechanical device industry brings new challenges from the process perspective as increased three-dimensionality sets demands towards higher aspect ratio structures which have to be filled conformably. 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 a promising technique especially from the conformality point of view. Traditionally thin film conformality has been analysed with cross sectional specimens. Our approach is to turn the analysis to horizontal plane with all-silicon lateral high aspect ratio structures (LHAR) and reflectometry line-scans.

This work continues on earlier work on conformality analysis [1–6]. The LHAR structures consist of a lateral gap of typically 500 nm in height while the gap length varies from 1 to 5000 µm, giving aspect ratios of 2:1 to 10 000:1. LHAR chips were coated with ALD Al_2O_3 and TiO_2 films, the effects of pulse and purge times were inspected from conformality point of view, and the measurement reliability was characterized with atomic force microscopy and QuickVision optical coordinate measuring tool. Diffusion model [6] was used to study the propagation of the ALD growth in the narrow channel. According to reflectometry measurements longer pulse time increased the penetration depth of the film to the narrow channel. The diffusion model was well in agreement with the experimental results. Measurement reliability and uncertainty components of the measurement were studied systematically. Therefore realistic uncertainty estimates can be given for the results. The LHAR structures presented here with thin film analysis and theoretical diffusion model accelerate the process up-scaling from small to large industrial scale.

Acknowledgements: Funding for this work comes from Academy of Finland's Finnish Centre of Excellence in Atomic Layer Deposition and Tekes PillarHall project.

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4:30pm **AF2-TuA-13 High Step Coverage Properties of New Zr Precursors with High Thermal Stability for High-k*, Haeng-Don Lim,*** *S Jeon, J Cho, W Chae, J Park, S Yim, S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

New Zr precursors have been developed using a tri-amine structure with enhanced thermal stability. Currently precursors of Cyclopentadienyl structure (Cp-Zr), which have high thermal stability, are used as precursors of ZrO_2 thin films. We synthesize Zr precursors of tri-amine structure (ZTA-01) with further improved thermal stability, and analyze characteristics according to structure difference with Cp structure.

The ALD window of ZTA-01 is 220 to 320℃ (Fig. 1(b)). Compared with Cp-Zr, the high-temperature stability of ZTA-01 was found to be about 20℃ higher. As a result of XRD analysis, distinct tetragonal peaks of ZrO_2 were clearly observed at 310℃ (Fig. 2). The stoichiometric ratio of O / Zr was found to be close to ideal ZrO_2 (O / Zr = 2.00) with ZTA-01 of 1.96 by XPS at 310℃. Impurities C and N were not detected.

The hole structure pattern of aspect ratio 60-65: 1 is used and the step coverage characteristics are analyzed at the ALD window temperature of 290 ~ 330℃ of ZTA-01. (Fig. 3) The step coverage is 97% at wafer temperature 290℃, 98% at 300℃, 99% at 310℃, 97% at 320℃, and 94% at 330℃. The ZTA-01 step coverage in the ALD window is more than 97 to 99%, which is evidence of the high thermal stability of ZTA-01 and the ideal self-limited reaction. Under the same conditions, the step coverage characteristic of the ZrO_2 thin film using Cp-Zr is 90% (Fig. 4(a)). This experiment shows that the Zr precursors of the tri-amine series are improved by at least 8% in the step coverage characteristics when compared with the Zr precursors of the cyclopentadienyl structure. Similar to the step coverage characteristic of ZrO_2 single layer using ZTA-01, the step coverage characteristic is 99% even in ZAZ laminated structure for reducing the leakage current (Fig. 4(b)).

This result shows that the inter-molecular stability and the intra-molecular stability of the Tri-amine structure are all high, so that it is not subjected to thermal decomposition to the bottom of the high aspect ratio and shows step coverage of 99% through a self-limited reaction.

4:45pm **AF2-TuA-14 Atomic Layer Deposition: Tailoring High Aspect Ratio TiO_2 Nanostructures*, Raul Zazpe,*** *H Sopha, J Prikryl, M Krbal, J Macak,* University of Pardubice, Czech Republic

The ongoing advances in the fabrication techniques over the last decades have allowed the shrinking of the devices to nanoscale dimensions, yielding a new generation of promising nanostructures as nanowires, nanorods or nanotubes. Among such nanostructures, anodic self-organized 1D TiO_2 nanotube layers have received significant scientific and technological interest, motivated by the semiconductive nature of the TiO_2, unique tubular architecture, chemical and mechanical stability, unidirectional electron transport through nanotube walls, biocompatibility, as well as simple and low cost fabrication process.[1,2]

An encouraging further step lies on the fabrication of TiO_2 nanotubular composite structures with new functionalities by the deposition of secondary materials. However, the shrinking to nanoscale dimensions brings the challenge of attaining conformal, homogeneous and continuous secondary material coatings. Conventional thin film deposition methods result inefficient and display serious limitations for the secondary material coating of high aspect-ratio nanostructures.[3] To date, atomic layer deposition (ALD) is the only deposition method capable to deposit continuous and conformal layers into high aspect-ratio nanostructures with an unprecedented sub-nanometer thickness control.[4] Thus, TiO_2 nanotubular composite structures have been produced via ALD by the deposition of ultrathin films of materials as TiO_2,[5] Al_2O_3,[6] ZnO,[7,8] or CdS,[9] or homogeneous decoration with noble metal nanoparticles.[10] The composite nanostructures display synergetic effects resulting in enhanced performance in a wide range of applications, such as photocatalytic,[5] sensing,[8] solar cell,[9] catalytic,[11] and battery.[12]

The presentation will focus on fabrication and experimental details, and recent photocatalytic,[5] sensing,[8] solar cell,[9] catalytic,[10] and battery[11] reports will be presented and discussed.

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5:00pm **AF2-TuA-15 Mechanisms Limiting Conformality in Thermal and Plasma-assisted ALD Investigated by Lateral High Aspect Ratio Structures***,* ***Karsten Arts****, V Vandalon,* Eindhoven University of Technology, Netherlands*; F Gao, M Utriainen,* VTT Technical Research Centre of Finland, Finland*; R Puurunen,* Aalto University, Finland*; E Kessels, H Knoops,* Eindhoven University of Technology, Netherlands

This work investigates the processes governing conformality achieved by ALD, using Lateral High Aspect Ratio (LHAR) test structures supplied by VTT.[1] We show that these structures are well suitable for investigating the underlying ALD chemistry, as the shape of the thickness profile and the penetration depth are indicative for the growth regime and provide insight into parameters such as sticking probabilities.

In the new PillarHall™ LHAR3 structures the reacting species diffuse underneath a removable membrane which is supported by pillars giving a 500 nm spacing. This configuration offers new possibilities compared to traditional vertical structures. Among others, top-view diagnostics can be applied to straightforwardly determine the thickness profile and material properties. A range of diagnostics is validated in this work for this top-view analysis. Moreover, the structure has features with aspect ratios up to 10000. Therefore a non-fully saturated profile is acquired for even the most conformal processes, which provides information on the limiting mechanisms.

Two cases are discussed to exemplify these possibilities. Firstly, in the case of thermal ALD of Al_2O_3 using TMA and water it is known from recent work that at low temperatures the growth is limited by the reduced reactivity of H_2O towards $–CH_3$ groups.[2] We examine how this reactivity affects the conformality, by measuring and simulating Al_2O_3 thickness profiles for different substrate temperatures. For example, at 200°C table temperature a sloping profile is observed with a half-thickness-penetration-depth (HTPD) of ~400 µm (AR=800). This profile seems to be consistent with the low sticking probability of water at these temperatures ($s\sim3\cdot10^{-5}$).[2] That is, from Monte Carlo simulations a growth regime in between reaction-limited and diffusion-limited growth is expected for this sticking probability and penetration depth, yielding such a sloping profile.

Secondly, in the case of plasma-assisted ALD of Al_2O_3 recombination-limited growth is observed, as the HTPD is reduced to ~30 µm (AR=60) through recombination of the reactive O radicals. As even these short profiles can be resolved using top-view diagnostics, the LHAR3 structures can be employed to investigate recombination probabilities in plasma-assisted ALD as well. On the basis of the aforementioned studies, these and other insights into ALD chemistry relevant to conformal growth will be provided.

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2. V. Vandalon and W.M.M. Kessels, Appl. Phys. Lett. **108**, 011607 (2016)

5:15pm **AF2-TuA-16 Multilayers on Reinforcement Fiber Fabrics with ALD***,* ***Pauline Dill****, F Pachel, M Scharf, W Goedel,* Chemnitz University of Technology, Germany

Carbon fiber fabrics, with a size of 30x8 cm, were coated smooth in a homebuilt reactor with combinations of three different ALD-layers. We used inorganic ALD coating (Al_2O_3, TiO_2, $Ti_3(PO_4)_4$) as well as an organic-inorganic TiO_2/furfuryl alcohol coating.[1] The coatings were combined in such a way that stacks of inorganic/organic-inorganic/inorganic were produced. The layer thickness and the homogeneity of each layer and the combination of the three layers were investigated with scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The elemental analysis of the coating was investigated with energy-dispersive X-ray spectroscopy (EDXS). The coated fabrics will be embedded in a ceramic matrix to give a fiber reinforced ceramic, in which the coating should provide oxidation protection for carbon fibers and also the coating may be helpful for crack deflection in the composite. Each of the coating in the combination has at least one task to protect the carbon fiber in the ceramic matrix composites. The first coating should protect the fiber from oxidation environment, the second one is needed for crack deflection and the top coating is needed to protect the remaining coated carbon fiber fabrics, when it will be sintered at high temperatur. For good crack deflection the three coatings should not stick too tight to each other, so that the fiber is able to move along the fiber axis. The delamination behavior of the coatings was also seen in SEM images.

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Atomic Layer Etching
Room 104-106 - Session ALE1-TuA

Applications for ALE

Moderators: Fred Roozeboom, TNO-Holst Centre & Eindhoven University of Technology, The Netherlands, Harm Knoops, Eindhoven University of Technology

1:30pm **ALE1-TuA-1 Mechanism of HF Pulse in the Thermal Atomic Layer Etch of Al_2O_3***,* ***Suresh Kondati Natarajan,*** Tyndall National Institute, Ireland*; S Elliott,* Schrödinger, Inc., Ireland

Alumina has excellent electrical insulation properties, which makes it an important material in the fabrication of semi-conductor devices. As the critical dimensions of such devices are decreasing rapidly, advanced material processing techniques with atomic precision have become necessary. Recently, a thermal atomic layer etch (ALE) process for alumina has been reported where HF and $Sn(acac)_2$ / tri-methyl aluminium (TMA) are used as precursors. Thermal ALE is different from conventional ALE in using thermally activated ligand exchange reactions for material removal instead of energetic ion bombardment or plasma. In the ALE of alumina, the HF pulse modifies alumina surface by forming a non-volatile AlF_3 layer and the subsequent $Sn(acac)_2$/ TMA exposure exchanges ligands with the surface resulting in the formation of volatile etch products.

In this talk, insights in to the mechanism of HF adsorption on alumina will be provided with the help of first principles calculations using density functional theory. On adsorption, a HF molecule dissociated spontaneously at the surface of alumina and formed surface bound Al-F and O-H species. At higher coverages, a hydrogen bonded network of dissociated and intact HF molecules was observed at the alumina surface. Partial dissociation of the adsorbed HF molecules was found to be energetically favorable than the dissociation of all adsorbed molecules. Energetic barriers ranging from +0.9 eV to +1.8 eV were found to be impeding the formation of water molecules. The desorption energy of water molecules were found to be ranging from +0.2 eV to +1.2 eV. Finally, based on the saturated coverage of dissociated F atoms (13.7 ± 0.3 F/nm^2), the theoretical maximum of the etch rate was estimated to be -1.28 ± 0.03 Å/cycle.

1:45pm **ALE1-TuA-2 Low-K Dielectric Etch Challenges at the 7nm Logic Node and Beyond: Continuous-wave vs. Quasi-atomic Layer Plasma Etching Performance Review***,* ***Yen-Tien Lu,*** Tokyo Electron

For logic nodes beyond 7nm, back-end-of-line (BEOL) patterning critical pitch is less than 40nm, which has direct impacts on low-K etch process window. As the pitch is reduced, RIE lag becomes more significant resulting in wider trenches having a faster etch rate compared to narrower trenches (Figure 1). Hence, the trench profile, via CD and height, and chamfer angle will vary in trenches depending on their width. Hard mask selectivity also becomes a concern for the dense trenches where the hard mask at smaller dimensions is more significantly affected by sputtering. Recently, the concept of atomic layer etching and quasi-atomic layer etch (Q-ALE) has been widely used in various applications for high selectivity requirements and ideal bottom trench profile engineering[1,2]. However, little studying has been done on sub 40nm pitch BEOL dielectric etch with Q-ALE.

In this work, we investigate the impacts of Q-ALE on low-K materials compared to continuous wave (CW) plasma and pulsed plasma. We demonstrate that Q-ALE can be successfully used to suppress RIE lag in BEOL low-K materials at advanced pitches. In order to minimize low-K damage generated during the etching process, an inverse RIE lag process was also developed. These processes can be used with conventional etching processes to compensate RIE lag and result in optimum process performance (Figure 2). In addition, Q-ALE technique shows improved hard mask selectivity and results in lower pattern roughness. Finally, combining Q-ALE and CW processes can minimize wafer throughput impact from Q-ALE processes, which usually take significantly longer than CW processes (Figure 3).

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Keywords: RIE lag, quasi-ALE, pulsed plasma, low-K damage

2:00pm **ALE1-TuA-3 Precise Etching Profile Control by Atomic-scale Process**, ***Yoshihide Kihara**, T Katsunuma, M Tabata, T Hisamatsu, M Honda,* Tokyo Electron Miyagi Ltd., Japan **INVITED**

In recent years, with the progress of device miniaturization and increased challenges in the scale of integration as semiconductor devices, fine control of the surface reactions is required in the fabrication processes. In self-aligned contacts (SAC) process, ultra-high selectivity of SiO_2 etching towards SiN is required, for which we developed Quasi-ALE technique for SiO_2 etching. Quasi-ALE precisely controls the reaction layer thickness of the surface, by controlling the radical and ion flux independently. In Quasi-ALE, adsorption step contains radical supply onto the surface and activation step contains etching by ion bombardment. Quasi-ALE was able to improve the conventional trade-off between the etching ability on the micro slit portions and SiN selectivity in the SAC process [1].

We have advanced Quasi-ALE technology for control of etching profile. The advanced technology is called as rapid advanced cyclic etching (RACE) process. The RACE process is divided by process gas into several steps that have a different purpose as a function of each process gas. As a result, we can easily set optimum radical and ion fluxes and ion energy for each step. Therefore, RACE process enables even more precise control of the surface reactions.

TiN mask pattern is transferred to the underlying SiO_2 and low-k film in metal hard mask trench process of BEOL where TiN mask selectivity, chamfer profile control and critical dimension (CD) variation at wafer very edge are the big patterning challenges. In the conventional method, the process results show that there is a trade-off between TiN mask selectivity and chamfer profile. To address this issue, RACE process was adopted in BEOL trench process. With this method, we were able to control the chamfer profile while keeping a low TiN mask loss. This is because RACE process achieves very fine control of the surface reactions by maximizing the effect of each step in RACE process. In addition, RACE process was able to reduce the CD variation at wafer very edge. This is demonstrating that RACE process is effective technique for not only the etching performance but also the CD uniformity.

On the other hand, we developed new CD shrinking technique without CD loading that combines Atomic Layer Deposition (ALD) and etching [2]. To control etching profile precisely, ALD was adopted to various applications. In the presentation, we will introduce some etching performances.

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2. M. Honda, "New Innovative Dielectric Etching Approaches by Controlling the Surface Reaction at Atomic-Level" 4th ALE 2017

Atomic Layer Etching
Room 104-106 - Session ALE2-TuA

Selective ALE

Moderators: Fred Roozeboom, TNO-Holst Centre & Eindhoven University of Technology, The Netherlands, Harm Knoops, Eindhoven University of Technology

2:30pm **ALE2-TuA-5 Thermal Selective Etching on Metal Oxide and Nitride Film**, ***Jinhyung Park***, Air Liquide Laboratories Korea, Republic of Korea

Highly selective etching of metal oxide, nitride and metal has been demonstrated by using metal fluoride. In addition, this etching was taking thermal dry etching without plasma assisted. Reports of thermal dry etching by using metal fluoride are very limited.1 In this work we conducted etching test between 150 and 450oC on various metal oxides, nitrides and metal substrate. Some results showed selective etching that only desired film was etched and non-desired film was not etched under same conditions. Etching rate and selective tendency was also compared. Not only flat surface, it was confirmed that metal fluoride worked for dry etching of a film in patterned wafer.

Figure 1

Figure 1. SEM image of thermal etching of ZrO2 deposited in patterned wafer

Figure 1 showed one example that etching of ZrO2 in trench by using NbF5 under different conditions. All etching results are analyzed by several methods such as ellipsometry, scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS) and x-ray photoelectron spectroscopy (XPS). In this presentation, individual etching result of metal oxides (Nb2O5, Ta2O5, TiO2, ZrO2, HfO2, SiO2, Al2O3, Y2O3), metal nitrides (TiN, TaN, SiN), metal (W) and their comparison will be shown and discussed.

[1] P. C. Lemaire, G. N. Parsons, Chem. Mat. 29, 6653(2017).

2:45pm **ALE2-TuA-6 Benefits of Atomic Layer Etching for Material Selectivity**, ***Thorsten Lill**, K Kanarik, S Tan, I Berry, V Vahedi, R Gottscho,* Lam Research Corp.

For most critical etch applications such as pattern-transfer and 3D structure formation, an essential requirement is material selectivity. By material selectivity we refer to etching one material (X) preferentially to another material (Y), where the extent of selectivity is commonly denoted by the ratio X:Y for the relative amounts etched. Etching has had to be selective since the earliest years and the development of selective processes has been developed at least over the last 40 years of plasma etching. in this talk, we will discuss the strategies of selective etching and how atomic layer etching (ALE) helps. Both directional and isotropic ALE schemes will be discussed, as well as the basic underlying strategies in both. The insights will be vital for exploiting ALE in the fabrication of future devices.

3:00pm **ALE2-TuA-7 Approaching Atomic Scale Precision for Etch Technology Needs in the Semiconductor Industry**, ***Robert Bruce**, J Papalia, M Sagianis, D Montalvan, H Miyazoe, N Marchack, S Engelmann,* IBM TJ Watson Research Center **INVITED**

As we advance beyond the 7nm technology node, the semiconductor industry has implemented ever more complex architecture for logic and memory devices. For example, stacked nanosheets are a potential successor to finFETs and the number of levels continue to rise in 3D-NAND memory. To enable manufacture of new 3D devices at this unprecedented level of scale and intricacy requires atomic precision in etching and patterning, both anisotropic and isotropic, with high selectivity of etching one material over a host of other materials. Atomic layer etching (ALE) is a concept with goal to achieve this atomic scale precision by separating the etch process into controlled, self-limited reactions.

Because a large part of integrated devices are composed of insulating materials such as SiOx and SiNx, it is essential to understand their fundamental etching behavior at the atomic scale. In this talk, the interaction of SiOx and SiNx in hydrofluorocarbon-based plasmas was investigated. Due to their differences in surface modification behavior, the etching process could be tuned so that SiOx etches selectively to SiNx, and vice versa. The etch process parameters that influence material selectivity were evaluated, and it was found that hydrogen content, ion energy and substrate temperature had significant impact to the etching behavior of SiNx. The possibility of improving selectivity by separating deposition and etching in a quasi-ALE approach is also studied. These important observations provide essential guidance to a wide range of dielectric etch applications, such as self-aligned contact etching and spacer etching.

ALD for Manufacturing
Room 107-109 - Session AM-TuA

ALD for Manufacturing

Moderator: Se-Hun Kwon, Pusan National University

4:00pm **AM-TuA-11 Open Air Processing of Innovative Transparent Conductive Materials with Spatial ALD***, **David Muñoz-Rojas,*** Grenoble INP/CNRS, France **INVITED**

Spatial Atomic Layer Deposition (SALD) is an alternative approach to ALD that is gaining momentum in the last years due to the high deposition rate that it offers. In combination with the unique properties of ALD, namely, film homogeneity, precise thickness control, high quality materials at low temperatures and unique ability to conformably coat high aspect ratio features, the high throughput offered by SALD widens the potential industrial applications of ALD.

Additionally, SALD can be performed at atmospheric pressure, and even in the open air. One approach to do so is to use a deposition manifold head in which the different precursors and inert gas flows are injected along parallel channels. By placing the substrate to be coated close enough to the deposition head, efficient precursor separation is achieved (Figure 1). Such close proximity approach is indeed very convenient to couple SALD with other deposition and processing methods, in order to fabricate functional devices. [1]

On type of materials that can benefit for the unique assets of SLAD are transparent conductive materials (TCMs). TCMs are currently widely used in different type of devices raging from solar cells or LEDs to touch screens or transparent heaters. Depending on the applications, the properties of TCMs in terms of conductivity, transparency and stability need to be tuned. But in most cases, the ability to deposit TCMs at low temperatures and with high throughput is required in order to be compatible with other delicate components in the device (organic active materials, soft substrates such as plastic) and to be convenient for industrial application (were high deposition rates are needed).

In this communication I will show several examples of application of open air SALD to the deposition and surface engineering of innovative TCMs. The effect of processing in the open air in the properties of the deposited films will also be discussed.

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4:30pm **AM-TuA-13 Conformality of SiO_2 and Al_2O_3 Coatings Produced using High Speed Spatial ALD with a DC Plasma***, **Eric Dickey**, B Danforth, W Barrow,* Lotus Applied Technology

For substantially smooth planar surfaces, spatial ALD has been demonstrated to allow the use of very short cycle times by eliminating the transient periods associated with precursor introduction and removal from the reactor for each ALD cycle. To achieve the highest overall deposition rates, the exposure times to the precursors, and to the plasma if used, must also necessarily be minimized. However, in order to achieve high levels of conformality, the duration of exposure to the precursor must be sufficient to allow diffusion into the bottom of features. For plasma-based processing, sufficient amounts of reactive radicals must be delivered to the bottom of the features, without recombining into less reactive species on the way down. In this study we examine the limiting factors to the deposition rate of highly conformal metal oxide films grown using spatial PEALD. The reactor used is a batch tool with a rotating disc as the substrate holder, configured to expose the substrate to a metal precursor on one side, and a DC plasma on the other. The substrate is exposed to the metal precursor for about 18% of the circumferential substrate path length, and to the plasma for about 8% of the path length. Substrate rotation rates were varied between 300 RPM and 30 RPM, resulting in exposure times ranging from 36 to 360 milliseconds for the precursor and 16 to 160 milliseconds for the plasma. Two types of patterned silicon substrates were used to characterize conformality of the coating, including substrates with conventional deep trenches of varying width and aspect ratios up to 50:1, and substrates patterned with a novel re-entrant overhang feature. This overhang provides surfaces that are not in the line of sight of the plasma source or the precursor showerhead, as well as an aperture to comparatively larger volume features. To identify the parameters that limit conformality at high deposition speeds, precursor concentration, substrate temperature, and plasma conditions were varied and relative conformality was compared.

4:45pm **AM-TuA-14 Characterizing Precursor Delivery from Vapor Draw Ampoules***, **James Maslar**, B Sperling, W Kimes,* National Institute of Standards and Technology*; W Kimmerle, K Kimmerle,* NSI

Vapor draw ampoules (no dip tube: the gas in and gas out ports open directly into the ampoule headspace) are commonly employed for precursor delivery in atomic layer deposition processes, typically for solid precursors but sometimes for liquid precursors. Unlike a bubbler (an ampoule with a dip tube) for which a constant precursor output is readily achievable for a given set of process conditions, the precursor output from a vapor draw ampoule typically exhibits a transient decrease upon startup, even for constant process conditions. Such behavior has been observed for both solid precursors, e.g., pentakis(dimethylamido) tantalum (PDMAT) and trimethyl indium, and liquid precursors, e.g., μ^2–η^2–(^{t}Bu–acetylene)dicobalthexacarbonyl (CCTBA). This characteristic can complicate ALD recipe development and process optimization. Different factors have been proposed to explain this transient, including sublimative/evaporative cooling of the precursor (i.e., cooling reduces the precursor vapor pressure and hence the amount of material entrained in the carrier gas), incomplete saturation of the carrier gas (i.e., the precursor sublimation/evaporation rate is too low to permit saturation of the carrier gas for the gas residence time in the ampoule), or slow mass transport processes in the ampoule. The goal of this work is a better understanding of the processes involved in precursor delivery from vapor draw ampoules. Such an understanding should facilitate ALD process optimization and development of improved ampoule designs. To achieve this goal, the amount of precursor delivered under a range of conditions was measured using custom-designed non-dispersive infrared gas analyzers and tunable diode laser spectroscopy systems employed as optical mass flow meters. In addition, validated analytical and numerical process models were developed to describe the dependence of precursor delivered on process parameters. Compounds were selected for investigation based on industrial relevance, e.g., PDMAT, CCTBA, and water, or availability of physical-chemical properties, e.g., water, hexane, and hexadecane. The focus of this investigation was on commercial 1.5 L ampoules (with a maximum fill of 1.2 L), although different designs were examined.

5:00pm **AM-TuA-15 Monitoring Conformality in ALD Manufacturing: Comparing Lateral and Vertical High Aspect Ratio Test Structures***, **Mikko Utriainen**,* VTT Technical Research Centre of Finland, Finland*; S Riedel, A Kia,* Fraunhofer IPMS, Germany*; F Gao,* VTT Technical Research Centre of Finland, Finland*; R Puurunen,* Aalto University, Finland

Atomic Layer Deposition (ALD) technology enables manufacturing of conformal thin films into such deep microscopic trenches and cavities that the film characterization becomes a true challenge. In ALD applications these 3D microstructured substrates are typically vertically oriented high aspect ratio (HAR) structures. Monitoring and control of conformality relies predominantly on cross-sectional sample preparation and SEM/TEM characterization. This approach has several challenges, e.g. need to break the wafer, seeing only thin slice, cleavage plane inaccuracy, multiple repeated samples to get reliable data and long response times.

A potential approach to circumvent the challenges is a MEMS-based all-silicon lateral high aspect ratio (LHAR) test structure, PillarHall® developed at VTT [1-2]. The LHAR test chip is IC cleanliness proven and thus potentially compatible to any cleanroom environment. This study focuses to research questions: How reliable and accurate is LHAR test in 300 mm wafer manufacturing environment and, especially, how does it compare to vertical HAR structures.

The LHAR Test Chip (LHAR3 -series, AR range 2:1 - 10000:1, 500nm gap height) was employed for the first time on the carrier wafer in 300 mm wafer ALD process (Jusung Eureka 3000) in Fraunhofer IPMS. The ALD process was foundry's default ZrO_2/Al_2O_3 laminate process, 22 nm, carried out in two process variation runs (A=optimized for 3D, B=planar) at same temperature and cycle numbers. In the same run was employed LHAR and vertical trench test structures (AR 20:1). Conformality of both structures were analyzed by SEM cross-sections, with appropriate sample preparations.

Findings show that conformality in LHAR is comparable to vertical HAR within accuracy limits of step coverage metrology within the comparable AR range. Furthermore, in this study, higher aspect ratios in LHAR test chip shows significant differences between the process variations while in VHAR they are small. Therefore, even optical microscope metrics from LHAR provides fast relative insight to the process variations and can be utilized in monitoring. LHAR enables also access to gain more detailed compositional information on the trench wall e.g. by ToF-SIMS, which is under examination and a topic of further studies.

REFERENCES

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5:15pm **AM-TuA-16 A Remote Plasma Spectroscopy Based Method for Monitoring of Atomic Layer Deposition Processes***, **Joseph Brindley**, B Daniel, V Bellido-Gonzalez,* Gencoa Ltd, UK*; O Zabeida, L Martinu,* Polytechnique Montreal, Canada*; R Potter, B Peek,* University of Liverpool, UK

Atomic layer deposition (ALD) is an exciting emerging technology in the deposition of many functional thin films. Effective monitoring of individual gas concentrations during the ALD processes offer a unique insight into the process behaviour as well as being an important step in the eventual wide-spread industrialisation of the ALD technique.

Conventional quadrupole residual gas analysers have difficulty monitoring ALD processes due to the high process pressures and the presence of contaminating hydrocarbons contained within many ALD precursors. For these reasons monitoring of precursor gas concentrations during the ALD process is rarely undertaken.

An alternative gas sensing technique that operates directly at pressures above $1E^{-4}$ mbar has been built around plasma emission monitoring. This technique involves the generation of a small, remote plasma using an inverted magnetron placed within the ALD vacuum system. Consequently, species that are present within the vacuum become excited in the sensor's plasma, emitting a spectrum of light, which can then be used to identify and monitor the emitting species.

This work will demonstrate that the sensing method is robust when exposed to the ALD processing environment. Photomultiplier and CCD spectroscopy based methods were investigated for analysing the plasma emission. It was found that by synchronising the spectrum acquisition with the precursor injection, it was possible to consistently capture the fast gas dynamics of the ALD process. Sensitivity limitations of the technique are also investigated, in particular the effectiveness of plasma emission monitoring in being able to distinguish between similar precursors.

Examples of this sensing technique's practical uses for ALD processes are discussed; this includes detection of contaminants, optimising purge cycle length and monitoring the reaction dynamics in terms of precursor gas consumption.

Area Selective ALD
Room 113-115 - Session AS-TuA
Area Selective Deposition II

Moderators: Adrie Mackus, Eindhoven University, Netherlands, Bonggeun Shong, Hongik University

1:30pm **AS-TuA-1 Integrated Isothermal Atomic Layer Deposition and Thermal Atomic Layer Etching: "Atomic-Level Processing" for Area-Selective Patterning of TiO_2***, **Seung Keun Song**,* North Carolina State University*; P Lemaire,* Lam Research Corp.*; G Parsons,* North Carolina State University

Area-Selective Atomic Layer Deposition (AS-ALD) is attracting more attention from the semiconductor industry as a possible solution to alignment issues typically faced when scaling down transistor feature sizes. To address this challenge we show a new approach to AS-ALD, where self-limiting thermally-driven atomic layer etching (ALE) is chemically coupled with self-limiting thermal atomic layer deposition (ALD) to yield several nanometers of TiO_2 thin film formation on receptive SiO_2 surfaces at 170°C, with no measurable grown on adjacent areas of hydrogen-terminated silicon (100). When TiO_2 ALD using $TiCl_4$ and H_2O is done 170°C on non-oxidized hydrogen-terminated silicon, we find an incubation time of ~30 cycles is required before substantial TiO_2 nuclei appear. On SiO_2 surfaces, however, TiO_2 nucleation proceeds rapidly, allowing 10-20 Å of deposition before nucleation on Si-H. Using this inherent nucleation delay combined with a novel self-limiting thermal ALE procedure employing sequential doses of WF_6 and BCl_3, we create a new isothermal "Atomic-Level Process", where the atomic-scale chemical control of ALD is intimately coupled with that of thermal ALE to build up on a prepared surface, precise nanoscale constructs with pre-selected location and dimension. Using the integrated ALD/ALE sequence, we achieve in excess of 200 TiO_2 ALD cycles, yielding ~ 4 nm of TiO_2 on SiO_2, before visible nuclei form on Si-H, as determined by SEM, ellipsometry and TEM analysis. Process and materials analysis using in-situ QCM and ex-situ AFM and XPS further confirm our findings. To date, extending the ALD/ALE sequence to more than 500 ALD cycles leads to incomplete TiO_2 etch removal from Si-H, ascribed to changes in Si-H during prolonged exposure to deposition and etch species. This demonstrated Atomic Level Process for improved control in selective deposition offers substantial opportunities for integrated area-selective ALD, and provides a viable pathway to explore other Atomic Level Processes for parallel and wafer-scale synthesis of nanoscale and sub-nanoscale constructs.

1:45pm **AS-TuA-2 Inherent Substrate Selectivity and Nucleation Enhancement during Ru ALD using the RuO_4-Precursor and H_2-gas.***, **Matthias Minjauw**,* Ghent university, Belgium*; H Rijckaert, I Van Driessche, C Detavernier, J Dendooven,* Ghent University, Belgium

Ruthenium is a candidate to replace copper in future sub-10 nm interconnects. At these dimensions the resistivity of Ru lines is expected to be lower compared to Cu due to the lower sensitivity to size effects.[1] In addition, it is likely that Ru interconnects won't require a diffusion barrier, and will show a better electromigration performance.[2] At feature sizes below 10 nm it will be difficult to align subsequent lithography steps, and the conformality of the deposition method is increasingly important, such that area selective atomic layer deposition (ALD) of ruthenium is of high interest.[3]

We first report inherent area selective ALD of Ru on H-terminated Si (Si-H) versus SiO_2, using the thermal RuO_4 (ToRuS^{TM})/ H_2-gas ALD process.[4] In situ spectroscopic ellipsometry (SE) on blanket substrates shows that Ru growth initiation occurs from the first cycle on Si-H, while on SiO_2 the growth is delayed, resulting in a substrate selectivity window of ~ 70 cycles (Figure 1, a). Area selective Ru ALD was evaluated using a patterned substrate of 1-10 µm wide Si-H lines separated by 10 µm wide SiO_2 regions, and exposing it to 20 cycles of the RuO_4 / H_2-gas ALD process. Ex situ scanning electron microscopy (SEM) and cross section high resolution transmission electron microscopy (HRTEM) measurements show that a 4.5 nm Ru film could be deposited on the Si-H, with no Ru detected on the SiO_2 (Fig. 2). In vacuo X-ray photoelectron spectroscopy (XPS) experiments showed that exposure of Si-H to a single RuO_4 pulse leads to the oxidation of the Si surface, together with the deposition of RuO_2. On SiO_2 however, the surface is already oxidized, and in vacuo XPS shows that for the same exposure to RuO_4 no Ru is deposited on the surface (Fig. 3). Therefore, we propose that the mechanism behind the inherent substrate selectivity is the oxidation of the Si-H surface by RuO_4. Secondly, we report for a methodology to enhance the nucleation of the RuO_4 / H_2-gas process on oxide substrates. In vacuo XPS and in situ SE experiments show that a single exposure of SiO_2 to trimethylaluminum (TMA) makes the surface reactive towards RuO_4, which allows for Ru growth initiation from the first cycle (Fig. 1, b; Fig. 3). We propose that this is due to the combustion of surface CH_3-groups by RuO_4. As TMA is known to be reactive towards many oxide substrates, this methodology presents a way to achieve Ru metallization of virtually any surface.

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2:00pm **AS-TuA-3 Surface Preparation and High Nucleation for Selective Deposition using Anhydrous Hydrogen Peroxide***, D Alvarez, **Jeffrey Spiegelman**, K Andachi,* RASIRC

Creative surface protecting agents are being used in efforts to explore novel methods for Area Selective Deposition (ASD). These agents include self-assembled monolayers, patterned photoresists, plasma deposited films and others. At the same time, fast nucleation and growth of metal oxide films require creation of fully covered reactive surfaces. Surface treatment ideally will:

- Generate high density or complete surface functionalization
- Eliminate or minimize sub-surface oxidation
- Increase speed and uniformity of nucleation compared to H_2O
- Not react with organic functionality or photoresist on adjacent surfaces

Anhydrous hydrogen peroxide has been largely ignored as a potential novel reactive chemistry. There are several reasons for this. First, there is no precedent in the literature. Second, when delivered H_2O_2 is typically mixed with H_2O, which dominates the reaction. Third, this material has only recently become available in a packaged form that could integrate into selective deposition process equipment.

Hydrogen Peroxide is an attractive chemistry for area selective deposition because of both its oxidation properties and proton transfer properties. The chemistry compares favorably to Ozone (oxidation potential = 2.1V versus 1.8V for H_2O_2). It also has slightly stronger proton transfer than water (water pKa = 7.0 versus 6.5 for H_2O_2). Most critically, H_2O_2 has a very weak O-O bond, with Bond Energy = 36 kcal/mole, suggesting more energetically favorable reactivity at reduced temperatures.

Results from our work show good correlation with selective deposition requirements:

- Nucleation surface density of hydroxyl groups (-OH) is 3-5 times greater using anhydrous hydrogen peroxide versus water on metal surfaces
- No sub-surface oxidation on Si surfaces using anhydrous H_2O_2 for monolayer hydroxyl (-OH) surface functionalization
- Faster nucleation and growth of Al_2O_3 on Si-H surfaces when using anhydrous H_2O_2 versus water
- Little to no photoresist removal at temperatures up to 300°C with anhydrous H_2O_2

Other testing shows that metal oxide film quality grown using anhydrous H_2O_2 are nearly identical to those grown with ozone methods. Metal oxide films include aluminum oxide, hafnium oxide, and zirconium oxide.

The presentation will discuss details of newly discovered reactivity of anhydrous H_2O_2 on several surfaces and will outline potential ASD pathways.

2:15pm **AS-TuA-4 An Inherently Selective Atomic Layer Deposition of $MoSi_x$ -on Si (001) in Preference to Silicon Nitride and Silicon Oxide*, Jong Youn Choi,*** *C Ahles,* University of California San Diego*; R Hung, N Kim,* Applied Materials*; A Kummel,* University of California San Diego

As metal-oxide-semiconductor field effect transistors (MOSFETs) shrink into the <10 nm regime, it becomes a significant challenge to minimize electrical loss with a decreasing pitch especially at the contact regions. To reduce resistance in a compact geometry, selective atomic layer deposition (ALD) of transition metal disilicides is of great interest. In previous studies, selective ALD of tungsten (W) via a fluorosilane elimination process was demonstrated using WF_6 and SiH_4 or Si_2H_6.[1,2] Selectivity was achieved by an inherently favorable reactivity of the precursors on hydrogen-terminated Si versus OH-terminated SiO_2. In this study, sub-stoichiometric $MoSi_x$ (x= 0.7–1.4) was selectively deposited by ALD on H-terminated Si (001) in preference to SiO_2 and SiN using MoF_6 and Si_2H_6 at 120°C. In-situ, X-ray Photoelectron Spectroscopy (XPS) was used to investigate the chemical composition of $MoSi_x$ ateach experimental step. To confirm selective deposition on the nanoscale, $MoSi_x$ was deposited on a Si sample patterned with SiO_2 and Si_3N_{4-} and cross-sectional Tunneling Electron Microscopy (TEM) was performed. It was observed that the Si-H surface termination allowed nucleation of $MoSi_x$ on Si in contrast to the inherently chemically passive (non-reactive) SiO_x and SiN surfaces. This substrate-dependent selectivity was retained for $MoSi_x$ growth of up to 10 nm with a proper N_2 purge gas to prevent any CVD components on SiO_2 and SiN. Performing additional Si_2H_6 doses after the ALD cycles allowed the incorporation of more Si into the film and increased the stoichiometry to be closer to $MoSi_2$. The $MoSi_x$ catalyzes this self-limiting CVD of Si while retaining selectivity over SiO_2 and SiN. In-situ Scanning Tunneling Microscopy (STM) showed that $MoSi_x$ ALD on Si produced an atomically flat surface with a root mean square (RMS) roughness of 2.8 Å. Post-annealing in ultra-high vacuum at 500°C for 3 minutes further decreased the RMS roughness to 1.7 Å. A depth profiling XPS study revealed that the bulk of the $MoSi_x$ film is close to stoichiometric $MoSi_2$ with <10% oxygen and fluorine. The TEM imaging shows that the selectivity is retained on the nanoscale and that $MoSi_x$ can be selectively deposited on Si without substrate consumption. This is enabled by just taking advantage of the selective ALD of substiochiometric $MoSi_x$ combined with the ability of the substiochiometric $MoSi_x$ films to selectivity induce self-limiting Si deposition from Si_2H_6.

1. Ph. Gouy-Pailler *et al.*, Thin Solid Films, **241**, 374 (1994)

2. B. Kalanyan *et al.*, Chem. Mater., **28**, 117-126 (2016).

2:30pm **AS-TuA-5 Investigating the Difference in Nucleation during Si-based ALD on Different Surfaces (Si, SiC, SiO_2 and SiN_x) for Future Area-Selective Deposition (AS-ALD)*, Ekaterina A. Filatova,*** Tyndall National Institute, University College Cork, Ireland*; A Mameli, A Mackus,* Eindhoven University of Technology, Netherlands*; F Roozeboom,* Eindhoven University of Technology and TNO, Netherlands*; W Kessels,* Eindhoven University of Technology, Netherlands*; D Hausmann,* Lam Research Corp.*; S Elliott,* Schrödinger, Inc., Ireland

Area-selective atomic layer deposition (AS-ALD) allows nanostructures of arbitrary composition and lateral shape to be built with atomic precision on pre-selected substrate locations. Most current approaches for AS-ALD are based on local inhibition (e.g. with self-assembled monolayers) or activation. However, for some applications of AS-ALD (e.g. in self-aligned fabrication) it is relevant to be able to exploit differences in chemical behavior of a pre-patterned substrate. For this reason, investigating inherent differences in nucleation on diverse substrates is of crucial importance for developing future AS-ALD processes. In this paper we are focussing on substrates of silicon and silicon-based dielectric materials (SiC, SiO_2 and SiN_x) used in electronics.

In order to investigate the possibility of area-selective deposition of Si-based materials using aminosilane precursors, nucleation on four different Si-based surfaces (Si:H, SiC:H, SiO_2:OH and Si_3N_4:NH_2/NH) was analyzed. First, we investigated the difference in precursor adsorption on these surfaces during the exposure of di(isopropylamino)silane (DIPAS), di(sec-butylamino)silane (DSBAS) and bis(t-butylamino)silane (BTBAS) precursors by calculating their adsorption energies using ab-initio modelling. From density functional theory (DFT) calculations, we found that DSBAS is thermodynamically favorable to react with Si_3N_4 and SiO_2, but not with SiC and Si at 0K. To experimentally corroborate these results, SiN_x was deposited using Plasma-Enhanced ALD from DSBAS precursor and N_2 plasma on three different surfaces (H_2 plasma-exposed SiC, HF-last c-Si and c-Si with native SiO_2). In-situ spectroscopic ellipsometry (SE) measurements were performed after every half-cycle to analyze the DSBAS adsorption reaction on these surfaces. During the first DSBAS dosing cycle on the SiO_2 surface a change in the SE signal was observed, suggesting initial DSBAS adsorption, while no changes were observed on the Si and SiC surfaces. The selective adsorption of DSBAS on SiO_2 is in agreement with the DFT predictions. The subsequent N_2 plasma half-cycle modifies the non-growth surface into SiN_x, after which the selectivity is lost. These results illustrate that it is generally difficult to achieve area-selective ALD for nitrides, because of the nitridation of all the exposed substrate surfaces during the plasma step.

We conclude, that during ALD on Si-based substrate materials DSBAS reacts selectively with SiO_2 and SiN_x surfaces but not with Si and SiC surfaces. Our results highlight the role of DFT calculations in predicting possible routes towards AS-ALD process development.

2:45pm **AS-TuA-6 Strategies for Area Selective Atomic Layer Deposition and Applications in Catalysis*, Rong Chen,*** *K Cao, X Liu, J Cai, B Shan, J Zhang,* Huazhong University of Science and Technology, China **INVITED**

Atomic layer deposition (ALD) is a mainstay technology for the semiconductor industry since it allows deposition of nanometer-thin layers of desired materials onto a substrate in a very controlled and uniform manner. Recently, ALD has been adapted to design and synthesize composite catalysts that allow them to promote multiple chemical reactions. In fabrication of composite catalysts, the selective approaches of ALD are of great importance to exert spatial control of deposition to fabricate three dimensional nanostructures.

In this talk, strategies for selective ALD and enabled nanostructures for catalytic applications will be discussed. Selective ALD allows directional and precise tailoring of the structural size, composition, interfaces, and active sites, that is of great importance for catalysis applications. Two major types of selective ALD approaches are introduced, template selective method via surface modification of self-assembled monolayers (SAMs) and reverse SAMs passivation, as well as inherently selective deposition. With these methods, core shell nanoparticles, oxide overcoating structures ranging from porous coating to ordered structures, and oxide surrounding structures could be fabricated controllably. Theoretical simulations, spectroscopic and microscopic analysis, and catalytic performance are carried out to verify the results. These strategies of selective ALD demonstrate unique advantages to design and fabricate highly stable and active catalysts on the atomic scale, providing unique opportunities to understand the structure–property relationship of catalysis.

Emerging Materials
Room 107-109 - Session EM-TuA

Organic-Inorganic Hybrid Materials

Moderator: Virginia Wheeler, U.S. Naval Research Laboratory

1:30pm **EM-TuA-1 Simultaneous Enhancement of Toughness and Elimination of the UV Sensitivity of Kevlar with a Combined ALD/MPI Process***, **Itxasne Azpitarte**, M Knez,* CIC nanoGUNE, Spain

Kevlar® is among the most prominent high-strength polymers for a use in mechanically demanding applications, such as personal safety, sport equipment and aircrafts. In many of these applications Kevlar is exposed to UV radiation and/or moisture, which seriously affect its mechanical properties. Thus, strengthening or protection of Kevlar is of great interest. So far, the most efficient approaches resulted in heavy and rigid composite materials consisting of Kevlar fibers embedded in a resin [1]–[3].

Kevlar´s outstanding strength arises from the highly ordered crystalline structure formed during the extrusion of the polymer. Astonishingly, little attention has been paid to the possibility of enhancing the mechanical properties and stability via chemical post-processing of the polymer. In our previous work [4], we demonstrated that the thermal and UV sensitivity of Kevlar can be suppressed by infiltration of ZnO through Multiple Pulsed Infiltration (MPI). However, still only 90% of the modulus of toughness was retained in this way.

In this work, we present an extraordinary improvement of the properties of the fibers after applying a combined ALD/MPI process. Kevlar fibers have been infiltrated with ZnO and coated with Al_2O_3 in the same process. In this way, not only the loss of the modulus of toughness was suppressed, but the fibers even gained 10% of toughness. Simultaneously its sensitivity to UV-induced degradation was completely eliminated. This new processing strategy is a breakthrough in the improvement of Kevlar and promises further optimization with refinement of the processing conditions and precursors.

[1] J. R. Yeh, J. L. Teply, and A. Laboratories, “Compressive Response of Kevlar / Epoxy Composites,” vol. 22, no. March 1988, pp. 245–257, 2015.

[2] a Mittelman and L. Roman, “Tensile properties of real unidirectional Kevlar / epoxy composites,” vol. 21, no. 1, pp. 63–69, 1990.

[3] R. J. Morgan, C. Pruneda, and W. J. Steele, “The Relationship between the Physical Structure and the Microscopic Deformation and Failiure Processes of Poly(p-Phenylene Terephthalamide) Fibers,” *J. Polym. Sci. Polym. Phys. Ed.*, vol. 21, pp. 1757–1783, 1983.

[4] I. Azpitarte ***et al.***, “Suppressing the Thermal and Ultraviolet Sensitivity of Kevlar by Infiltration and Hybridization with ZnO,” *Chem. Mater.*, vol. 29, no. 23, pp. 10068–10074, 2017.

1:45pm **EM-TuA-2 Mutual Synergistic Doping in Conductive Hybrid Materials Obtained after Vapor Phase Infiltration***, W Wang, I Azpitarte, **Mato Knez**,* CIC nanoGUNE, Spain

Hybrid materials are in most cases blends of inorganic and organic materials and are considered to be key for the next generation of materials research. The main goal while fabricating such materials is to bridge the worlds of polymers and ceramics, ideally uniting the most desirable properties within a singular material. Furthermore, in a well performing hybrid material the individual components will add value to their counterpart in a synergistic way.

In this work, an innovative approach towards creating flexible electronic materials will be presented. Rather than growing thin conformal films, the ALD process technology is applied to controllably infiltrate metals into polymeric substrates, which leads to novel strategies for obtaining conductive polymers. On the one hand, single precursor infiltration processes are applied to dope conductive polymers such as polyaniline or P3HT in a post polymerization process, opening the pathway to easier structuring of the polymer substrates and a more precise control of the doping levels. This is of great importance for those conductive polymers, which upon doping do not allow further shaping anymore due to dopant-induced brittleness.

On the other hand, a completely new concept for fabricating conductive polymers will be presented, which also shows a paradigm shift. Namely, the infiltration strategy with multiple precursors is applied to fabricate polymer-inorganic hybrid materials that are able to mutually dope each other in a synergistic way. The interaction of the semiconducting and the polymeric phase increases the conductivity of the hybrid material by up to 5 orders of magnitude in comparison to the conventionally doped polymer or the semiconductor. This strategy opens a new pathway to construct flexible conductive materials and enables thousands of new material combinations for the fabrication of flexible electronic materials.

2:00pm **EM-TuA-3 Infiltration Synthesis of ZnO in a Non-reactive Polymer Facilitated by Residual Solvent Molecules***, X Ye, J Kestell, K Kisslinger, M Liu,* Brookhaven National Laboratory*; R Grubbs,* Stony Brook University*; J Boscoboinik, **Chang-Yong Nam**,* Brookhaven National Laboratory

Infiltration synthesis is an atomic-layer-deposition (ALD)-derived organic–inorganic material hybridization technique that enables unique hybrid nanocomposites with improved material properties and inorganic nanostructures replicated from polymer templates. The process is typically perceived to be driven by the binding reaction between reactive chemical groups of polymers and infiltrating vapor-phase material precursors. In this work, we discover that residual solvent molecules from polymer processing can react with infiltrating precursors to enable the infiltration synthesis of metal oxides in a nonreactive polymer. The experimental investigation, combining in situ quartz crystal microgravimetry, polarization-modulated infrared reflection–absorption spectroscopy, X-ray photoelectron spectroscopy, and transmission electron microscopy, reveals that the ZnO infiltration synthesis in a nominally nonreactive, cross-linked SU-8 polymer is mediated by residual processing solvent cyclopentanone, a cyclic ketone whose Lewis-basic terminal carbonyl group can react with the infiltrating Lewis-acidic Zn precursor diethylzinc (DEZ). Additionally, we identify favorable roles of residual epoxy rings in the SU-8 film in further assisting the infiltration synthesis of ZnO. The discovered rationale not only improves the understanding of infiltration synthesis mechanism, but also potentially expands its application to more diverse polymer systems for the generation of unique functional organic–inorganic hybrids and inorganic nanostructures.

2:15pm **EM-TuA-4 Thermal Conductivity in Layer-engineered Inorganic-Organic Thin Films***, **Fabian Krahl**,* Aalto University, Finland*; A Giri, J Tomko,* University of Virginia*; T Tynell,* Aalto University, Finland*; P Hopkins,* University of Virginia*; M Karppinen,* Aalto University, Finland

The combined atomic/molecular layer deposition (ALD/MLD) offers unprecedented opportunities to design exciting layer-engineered film structures not readily achievable by any other fabrication technique. We utilize this to design hybrid inorganic-organic thin films structures that suppress the thermal conductivity of the inorganic component. Such thin films are desired for example for thermal barrier coatings and wearable thermoelectrics.

Our material system is the semiconducting ZnO matrix with thin benzene layers embedded within the the thicker oxide layers. In our previous works we already could show that a significant reduction in thermal conductivity can be achieved by introducing a superlattice, most likely caused by phonon scattering at the layer interfaces.[1,2] Now we extend our work towards irregular and gradient structures in which the layer thickness is not constant (as it is in regular superlattices), see Figure 1.[3] Our results show that the layer design is playing an important role and that a cleverly designed gradient structure can surpass the superlattices in regards to the suppression of thermal conductivity.

Our research extends the data for engineered hybrid thin films to gradient layered systems that have, to the best of our knowledge, not been provided before. We believe this approach is not limited to our present ZnO:benzene material system and hope it can help understanding the interaction of film design and properties in thin films.

[1] T. Tynell, A. Giri, J. Gaskins, P. E. Hopkins, P. Mele, K. Miyazaki, M. Karppinen, *J. Mater. Chem. A***2014**, *2*, 12150.

[2] Giri, J.-P. Niemelä, T. Tynell, J. T. Gaskins, B. F. Donovan, M. Karppinen, P. E. Hopkins, *Phys. Rev. B***2016**, *93*, 115310.

[3] F. Krahl, A. Giri, J.A. Tomko, T. Tynell, P.E. Hopkins, M. Karppinen, *Adv. Mater. Interfaces*, in press (**2018**).

[4] J. Alvarez-Quintana, E. Martínez, E. Pérez-Tijerina, S. A. Pérez-García, J. Rodríguez-Viejo, *J. Appl. Phys.***2010**, *107*, 063713

2:30pm **EM-TuA-5 Reversible Trans-cis Photoisomerization of ALD/MLD-fabricated Azobenzene-based Inorganic-Organic Thin Films***, **Aida Khayyami**, M Karppinen,* Aalto University, Finland

We report the successful incorporation of photoresponsive azobenzene molecules through atomic/molecular layer deposition (ALD/MLD) in inorganic-organic thin films. Together with azobenzene-4, 4’-dicarboxylic acid as the organic precursor we use diethyl zinc (DEZ) as the inorganic precursor for our hybrid thin films of the $(Zn\text{-}O\text{-}C_{14}H_9N_2\text{-}O_4\text{-})_k$ type. The fabrication route developed for the hybrid films was then combined with the diethylzinc/H_2O ALD process for ZnO in order to grow $[(ZnO)_m(Zn–O–C_{14}H_9N_2\text{-}O_4\text{-})_{k=1}]_n$ superlattice structures where single azobenzene layers are sandwiched between thin crystalline zinc oxide blocks. The ratio of the ALD-ZnO and MLD-($Zn\text{-}O\text{-}C_{14}H_9N_2\text{-}O_4$-) cycles was varied between 199:1 and 1:1. The kinetics of the trans-cis-trans photoisomerization were studied by alternate exposures to UV radiation and visible light ($\lambda > 450$ nm). Our inorganic-organic hybrid and superlattice structures were found to be photoreactive upon 360 nm irradiation. This observation confirms that switching processes with photochromic compounds, such as azobenzene, can be implemented in inorganic-organic thin films prepared by the ALD/MLD technique. This underlines the exciting new possibilities provided by the ALD/MLD technique for preparing novel light-sensitive materials.

2:45pm **EM-TuA-6 Organic/Inorganic Nanocomposite Synthesis through Sequential Infiltration of 3D Printed Polymer Parts: A Microstructural Study***, **David J. Mandia**,* Argonne National Laboratory*; R Waldman,* University of Chicago*; P Kozak,* Argonne National Laboratory*; S Letourneau,* Boise State University*; G Sterbinsky, D Gosztola, L Ocola, A Yanguas-Gil, J Elam,* Argonne National Laboratory

The modification of polymer 3D printed parts using chemical vapor infiltration methods, such as sequential infiltration synthesis, can be used to impart novel functional properties to 3D printed parts. In this work, we describe the infiltration and characterization of 3D printed parts composed of polymers including poly(lactic acid) (PLA), poly(methyl methacrylate) (PMMA) and acrylonitrile butadiene styrene (ABS), with ZnO using diethyl zinc and water. This results in the formation of a hybrid organic/inorganic composite in the sub-surface region of the polymer whose thickness depends on processing conditions. Through a combination of X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and photoluminescence, we have studied the bonding environment, medium range order, and electronic properties of the resulting material. We discovered that through control of the purging step, growth can proceed in two different regimes, one in which the growth seems to be dictated by precursor molecules coordinating with reactive sites within the polymer, and another that is consistent with infused precursors reacting within the polymer itself. This results in a higher incorporation of inorganic material and a change in microstructure from a coordination environment characteristic of atomic-size inorganic cluster to denser, wurzite-like domains.

3:00pm **EM-TuA-7 Reactivity of Common ALD Precursors with OH/H_2O-containing Metal Organic Framework Materials***, **Kui Tan**,* University of Texas at Dallas*; S Jensen,* Wake Forest University*; L Feng,* Texas A&M University*; H Wang,* Rutgers University*; J Klesko, R Rahman, J Cure, K Wei,* University of Texas at Dallas*; H Zhou,* Texas A&M University*; J Li,* Rutgers University*; T Thonhauser,* Wake Forest University*; Y Chabal,* University of Texas at Dallas

The ability to incorporate metal atoms into nanoporous materials such as metal organic frameworks (MOFs) in a well-controlled fashion provides new opportunities to prepare functionalized and modified materials for potential applications such as catalysis and gas separation. There are however new challenges that need to be overcome such as understanding the reaction mechanisms in order to develop structural and process optimization. MOFs possess three-dimensional structures, with complex pore architecture, leading to a number of possible processes (gas transport, adsorption and reaction) that are much more complex than on flat surfaces. To address these issues, we have combined *in-situ* infrared spectroscopy, X-ray-photoelectron spectroscopy and *ab initio* calculation to study the reaction of a number of common ALD precursors -- trimethylaluminium (TMA), diethylzinc (DEZ), titanium tetrachloride ($TiCl_4$)-- with in several Zr-MOFs containing hydroxyl (OH) and water (H_2O) groups. Differentiating reaction with OH and H_2O groups is particularly interesting since their reactivity highly depends on both the chemical and structural (i.e. sterics) environments. We find that the OH groups in the $Zr_6(\mu_3\text{-}OH)_4(\mu_3\text{-}O)_4(OH)_x(OH_2)_y$ cluster node do not all react at similar rates (i.e., the reaction pathway and energetics are highly dependent on their location, accessibility and chemical environment). For different OH-containing MOFs without H_2O groups, the activation temperatures for the TMA reaction with bridge OH of Zr_6 clusters decrease with their node connectivity, and are 250°C, 150°C and 24°C for UiO-66-NH_2, Zr-abtc and MOF-808, respectively. Interestingly, the amine group in UiO-66-NH_2 is found to act as a catalytic active site by anchoring TMA molecules and facilitating their reaction with nearby hydroxyl groups, which is not observed in un-functionalized UiO-66. This synergistic effect between -NH_2 and -OH is fully elucidated by first-principles calculations. In addition, we find that TMA easily reacts with water adsorbed on the external surfaces of wet MOFs crystals at room temperature, forming a thick Al_2O_3 blocking layer on the periphery of MOFs crystals. These findings provide a basis for the design and synthesis of new MOFs structures requiring ALD for new applications.

3:15pm **EM-TuA-8 Atomic/Molecular Layer Deposition of Inorganic-Organic Carboxylate Network Thin Films for Possible Sensing Applications***, **Jenna Penttinen**, M Nisula, M Karppinen,* Aalto University, Finland

We introduce novel atomic/molecular layer deposition (ALD/MLD) processes for the fabrication of crystalline inorganic-organic coordination network thin films with different s-block elements and different aromatic polycarboxylates. The deposition processes fulfill the basic principles of ALD/MLD-type growth including the sequential self-saturated gas-surface reactions and atomic/molecular-level control of the film thickness, and yield crystalline thin films in a wide deposition temperature range. We have investigated the stability of the films in heat and humidity treatments to verify that some of the films reversibly absorb water molecules forming well-defined crystalline water-derivative phases. This suggests that the materials could be utilized e.g. for gas storage and sensing applications. Also interestingly, for some of our as-deposited crystalline thin-film materials there are no bulk structures reported in literature. Our work thus underlines the strength of the ALD/MLD technique in discovering new exciting coordination network thin-film materials that may ultimately be potential material candidates for the next-generation application in, e.g., electronics, sensors, and other high-technology products.

Nanostructure Synthesis and Fabrication
Room 104-106 - Session NS+ALE-TuA

Nanostructures II + ALE

Moderators: Robert Clark, TEL Technology Center, America, LLC, Yong Qin, Institute of Coal Chemistry, Chinese Academy of Sciences

4:00pm **NS+ALE-TuA-11 Atomic Layer Etching and Chemical Vapor Etching of 2D Materials and Metal Oxide Films using MoF_6-H_2O***, **Anil Mane**, D Choudhury, S Letourneau, J Elam,* Argonne National Laboratory

To meet the milestones outlined in the semiconductor technology roadmap, precisely controlled layer-by-layer etching processes for metal oxides are required to enable the fabrication of 3D-semiconductor microelectronic devices. In addition, 2D-layered transition metal dichalcogenides (TMDs) with tunable electronic properties exhibit attractive material properties and are under intense investigation as alternatives to silicon. Therefore, integration of 2D-materials with compatible dielectric metal oxide growth as well as etching can pave the way to successful device fabrication. Moreover, both selective material growth and selective etching are required for the cost effective manufacturing of advanced microelectronics.

Here we have developed etching processes using alternating exposures to molybdenum hexafluoride (MoF_6) and H_2O vapor for ALD grown metal oxides and 2D-TMDs. The MoF_6-H_2O precursors offer several advantages including low cost, low processing temperature, and rapid and effective etching spanning the range from continuous etching to atomic layer etching (ALEt).

We have used in-situ quartz crystal microbalance (QCM) and Fourier-transform infrared spectroscopy (FTIR) measurements to monitor the deposition and etching of the metal oxides and 2D-TMDs layers. Next, the etched metal oxides and 2D-TMDs thin films were analyzed by spectroscopic ellipsometry to determine the thickness and refractive index, and the composition was determined by X-ray photoelectron spectroscopy (XPS). These ex-situ measurements confirmed the etching behavior findings from our in-situ studies. Here we will discuss the details of the MoF_6-H_2O based etching chemistry.

4:15pm **NS+ALE-TuA-12 Membranes by Atomic Layer Deposition: Design and Applications***, **Mikhael Bechelany**,* Institut Européen des Membranes, France **INVITED**

Atomic layer deposition (ALD) is a thin film technology that in the past two decades rapidly developed from a niche technology to an established method. It proved to be a key technology for the synthesis of ultrathin film, the surface modification and the fabrication of complex nanostructured materials as well as the membrane tuning. [1]

In this work, we will give an overview about our activities on ALD, from the design of nanomaterials to membrane applications. After a short introduction to ALD, the versatility of the technique for the fabrication of novel nanolaminates thin films [2] and functional nanomaterials [3, 4] will be showed. Selected examples, focused on its use for the engineering of nanostructured functional materials and membranes targeting applications in energy (osmotic energy, biofuel cells and gas separation), environmental ((bio)-sensor and water purification) and health (DNA and proteins sensing) fields [5-9] will be discussed.

[1] **Advanced Materials**, 2012, 24, 1017

[2] **J. Phys. Chem. C**, 2016, 120, 5124–5132

[3] **Nano Energy** 1 (2012) 696

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[5] **Journal of Materials Chemistry A**, 2016, **4**, 6487-6494

[6] **Journal of Materials Chemistry A**, 2016,4, 17686-17693

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[8] **Journal of Materials Chemistry A**, 2014, 2 (48), 20650 – 20658

[9] **ACS Appl. Mater. Interfaces**, 2017, 9, 16669–16678

4:45pm **NS+ALE-TuA-14 Field-effect Transistor using Two-dimensional Electron Gas in ALD Al_2O_3/TiO_2 Ultrathin (<10 nm) Film Heterostructure Interface**

***Tae Jun Seok**, Y Liu,* Hanyang University, Republic of Korea*; H Jung, S Kim,* Ajou University, Republic of Korea*; D Kim,* Hanyang University, Republic of Korea*; S Kim, J Jang,* Korea Basic Science Institute, Republic of Korea*; D Cho,* Chonbuk National University, Republic of Korea*; S Lee,* Ajou University, Republic of Korea*; T Park,* Hanyang University, Republic of Korea

Recently, two-dimensional electron gas (2DEG) has attracted great attention due to the observation of 2DEG at various heteroepitaxial perovskite oxide interfaces. Typically, epitaxial $LaAlO_3$/single-crystal $SrTiO_3$ (LAO/STO) heterostructure shows high density of electrons (~10^{13}-10^{14} cm^{-2}) confined at the oxide interface, where the density is about ~100 times higher than those of a typical semiconductor interface (~10^{11}-10^{12} cm^{-2}). Despite its high electrical performance, process schemes are not suitable for practical device applications because of their high cost in the production of the oxide single crystal and epitaxial layer. Although the formation of 2DEG using γ-Al_2O_3 and amorphous LAO with Al_2O_3 over-layers on STO substrate was demonstrated recently, single crystalline STO substrates are still required. Therefore, 2DEG at an oxide interface has not been realized *via* a mass-production compatible thin film deposition process, in contrast to 2DEG at the semiconductor interfaces.

In this work, we demonstrate a realization of 2DEG at the interface in an extremely thin film (< ~10 nm) heterostructure comprised of two binary oxide stacks of Al_2O_3/TiO_2 *via* atomic layer deposition (ALD) on a SiO_2/Si substrate without using an oxide single crystal or epitaxial substrate. The Al_2O_3/TiO_2 heterostructure was composed of a few nm-thick amorphous Al_2O_3 over-layer and poly-crystalline anatase-TiO_2 bottom layer. We achieved high electron density (~10^{13}-10^{14} cm^{-2}) and mobility (~4 $cm^2/V{\cdot}s$) in the 2DEG at the interface of ultrathin Al_2O_3/TIO_2 heterostructures, comparable to those obtained from epitaxial oxide heterostructures. More importantly, we demonstrate a new type of field-effect transistors (FETs) using Al_2O_3/TiO_2 heterostructures with a high on-current (I_{on}, > 12 A/m), high on/off current ratio (I_{on}/I_{off} > ~10^8), low off current (I_{off}, ~10^{-8} A/m), and low sub-threshold swing (SS, ~100 mV/dec.), which outperforms the oxide heterostructure-based FETs reported so far. Ultrathin (< ~7 nm) TiO_2 bottom layer in the proposed Al_2O_3/TiO_2 heterostructure prone to be fully depleted, allows an extremely low I_{off}, high I_{on}/I_{off} ratio and low SS with maintaining high I_{on} *via* 2DEG channel with a high carrier density at the interface. The proposed new-type devices would provide a great opportunity for practical applications and mass-production of 2DEG devices, allowing a multi-level three-dimensional (3D) integration scheme. The detailed experimental results including new materials systems will be presented.

5:00pm **NS+ALE-TuA-15 Increased WS_2 Crystal Grain Size by Controlling the Nucleation Behavior during Plasma Enhanced Atomic Layer Deposition**

***Benjamin Groven**, A Nalin Mehta,* KU Leuven, Belgium*; H Bender, J Meersschaut, T Nuytten, T Conard, A Franquet, W Vandervorst, M Heyns, M Caymax, I Radu, A Delabie,* IMEC, Belgium

Two-dimensional (2D) transition metal dichalcogenides such as molybdenum and tungsten disulfide (MoS_2, WS_2) emerge as semi-conducting three-atom-thick layers that are widely applicable, for example as the complement of Si in ultra-scaled nanoelectronic devices at the back-end-of-line (BEOL) [1]. To exploit the potential of 2D layers in BEOL structures, they need to be grown using manufacturable deposition techniques in a highly crystalline structure with control over the orientation of the basal plane at low deposition temperatures (< 450°C).

When grown by atomic layer deposition (ALD) for atomistic growth control and compatibility with temperature sensitive structures, the crystallinity and structure of 2D materials is determined by the nucleation mechanisms, which are currently not yet understood. In our earlier work, polycrystalline WS_2 with well-controlled composition (S/W ratio ~2) and 2D structure was grown by PEALD from WF_6, H_2 plasma and H_2S on Al_2O_3 at 300°C [2]. The WS_2 layers suffered from a nanocrystalline grain structure (< 20 nm).

In this work, we show that the WS_2 crystal grain size can be increased from ~20 nm to beyond 200 nm by lowering the nucleation density. The latter is achieved by using a starting surface with a lower reactivity towards the PEALD precursors (i.e., thermally grown SiO_2), and by enhancing the mobility of the adsorbed species at higher deposition temperature (< 450°C) and reactor pressure (Figure 1).

By analyzing the morphology of the WS_2 crystals, we derive a qualitative model for the nucleation behavior of WS_2 during the PEALD process. The SiO_2 starting surface is less reactive to the PEALD precursors compared to Al_2O_3 starting surfaces, which results in growth inhibition on SiO_2. The PEALD precursors preferentially adsorb on the existing WS_2 nuclei. In combination with enhanced surface diffusion of the adsorbed species across both the SiO_2 starting surface as well as the growing WS_2 nuclei, lateral growth from WS_2 crystal edges is promoted which maximizes the WS_2 crystal grain size and develops a strong (0002) texture.

This work demonstrates how insight in the nucleation behavior of 2D materials can be used to increase the crystal grain size and control the basal plane orientation during ALD. A better understanding of these nucleation mechanisms is crucial to advance the field of ALD of 2D materials.

[1] 47th IEEE European Solid-State Device Research Conference (ESSDERC) **2017**, pp. 212–215. T. Schram, et al.

[2] *Chem. Mater.***2017**, 29 (7), 2927–2938. B. Groven, et al.

5:15pm **NS+ALE-TuA-16 Controlling Material Properties of Nanostructured WS_2 during Plasma ALD for Improved Electrochemical Performance**

***Shashank Balasubramanyam**, L Wu, V Vandalon, M Verheijen, E Kessels, J Hofmann, A Bol,* Eindhoven University of Technology, Netherlands

Transition metal dichalcogenides like WS_2 are promising candidates for sustainable production of H_2 through electrochemical hydrogen evolution reaction (HER), when engineered into nanostructures with exposed reactive edge sites. Controlling the various parameters during the plasma exposure step of plasma-enhanced ALD (PEALD) allows tailoring of material properties which can influence the HER performance. In this work, we demonstrate a novel approach to maximize the density of reactive edge sites in nanostructured WS_2 by tuning the composition of co-reactant gas mixture during the plasma exposure step of PEALD.

H_2S+Ar and H_2 diluted H_2S+Ar were used as co-reactant gas mixtures for tuning the plasma composition during PEALD of WS_2. The addition of the strong reducing agent H_2 to the H_2S+Ar plasma gas mixture can significantly influence the WS_2 growth behaviour and resulting material properties. The H_2S+Ar plasma yielded a GPC of 0.8Å while the H_2S+Ar+H_2 plasma increased GPC to 1.4Å for the same metalorganic precursor bis(tertbutylimido)-bis(dimethylamido)-tungsten, at a low temperature of 300°C. Transmission electron microscopy (TEM) studies revealed the growth of WS_2 'nanoflakes' when using H_2S+Ar plasma, while H_2S+Ar+H_2 plasma resulted in the growth of WS_2 'fins'. The nanoflakes comprised of closely packed basal planes with their edges predominantly terminating on the top surface, while the fins appeared to have higher surface area and were observed to taper out on the top surface. Rutherford backscattering spectroscopy studies indicated an excess S content for nanoflakes (S:W=2.2), while a S deficiency was observed for fins (S:W=1.9). In line with TEM studies, X-ray diffraction measurements showed differences in preferential orientation of crystals for nanoflakes and fins.

The HER performance of WS_2 nanoflakes was significantly better than of WS_2 fins. To reach a current density of $10mA/cm^2$, a relatively lower overpotential of ~390mV was sufficient for the nanoflakes while a significantly higher overpotential of ~460mV was required for the fins. In line with HER results, copper underpotential depositions on the respective nanostructures revealed a three-fold increase in the amount of reactive edge sites for nanoflakes when compared with fins. In order t o further enhance the HER performance, catalytically superior WS_2 nanoflakes were grown on top of high surface-area WS_2 fins. This WS_2 stack yielded the best HER performance in our work (overpotential of ~365mV). To summarize, we demonstrate how PEALD can be used as a new approach to nanoengineer and enhance the HER performance of WS_2 by maximizing the density of reactive edge sites at low temperature.

ALD Fundamentals
Room Premier Ballroom - Session AF-TuP

ALD Fundamentals Poster Session

AF-TuP-1 Kinetic Study on Atomic Layer Deposition of Zinc Oxide from Diethylzinc and Water*, **Sungjoon Kim**, Y Min,* Konkuk University, Republic of Korea

Zinc oxide is a semiconducting material used in various applications due to its easily tunable electrical conductivity and transparency. Atomic layer deposition (ALD) is a preferred method when depositing thin films of ZnO due to its ability to deposit conformal layers of material even on high aspect ratio substrates. Despite ALD's advantages, the mechanisms and reaction pathways regarding the deposition processes are still under investigation, even for the most widely operated processes. The complex nature of the deposition environment make accurate predictions difficult, and although calculative methods such as the density functional theory (DFT) offer some insight to the reaction kinetics, their usefulness is somewhat limited in real applications. In this study, we propose a mechanism for diethylzinc adsorption on ZnO film which incorporates a molecular adsorption equilibria before the precursor molecule irreversibly adsorbs on the surface. The saturation curves at various deposition temperatures and precursor exposure times were analyzed to evaluate the effect of temperature on the rate of adsorption reaction. Reaction parameters such as the effective activation energy and the steric hindrance factor were extracted from the proposed model. The effective activation energy of the adsorption of diethylzinc on ZnO film was around 0.14 eV, and the decrease in growth-per-cycle may be attributed to the shift in adsorption/desorption equilibria at high temperatures. The effect of de-hydroxylation of the film's surface was found to be insignificant in the temperature range of this work.

AF-TuP-2 Effects of Organic Doped on the Performance and Stability of ALD Grown ZnO Thin Film Transistor*, **Hongbum Kim**, S Yu, M Sung,* Hanyang University, Republic of Korea

We fabricate zinc oxide thin-film transistors (TFTs) using 4-mercaptophenol (4MP) doped atomic layer deposition (ALD) grown ZnO that results in highly stable and high performance. The 4MP concentration in ZnO films were varied from 1.7% to 5.6% by controlling Zn:4MP pulses. The n-type carrier concentrations in ZnO thin films were controlled from 1.017×10^{20}/cm^3 to 2.903×10^{14}/cm^3 with appropriate amount of 4MP doping. The 4.8% 4MP doped ZnO TFT revealed good device mobility performance of 8.4 cm^2/Vs and the on/off current ratio of 10^6. Such 4MP doped ZnO TFTs exhibited relatively good stability (ΔV_{TH} : 0.4 V) under positive bias-temperature stress while the TFTs with only ZnO showed a 4.3 ΔV_{TH} shift, respectively.

AF-TuP-3 Investigation of Annealing Effects on Structural and Compositional Properties of AlN Films Deposited by Atomic Layer Deposition*, **Jun Chen**, F Zhang, X Liu, G Yan, Z Shen, Z Wen, L Wang, W Zhao, G Sun, Y Zeng,* Institute of Semiconductors, Chinese Academy of Sciences, China

We have investigated and compared the influence of annealing temperature on properties of AlN thin films grown on Si (100) substrates by atomic layer deposition using trimethylaluminum and ammonia as precursors at 400℃. Those as-deposited films were annealed by rapid thermal annealing at 700℃, 800℃, 900℃ and 1000℃ for 1 min in N_2 atmosphere, respectively. The thickness, refractive index, and surface morphology and composition of AlN films were measured by spectroscopic ellipsometer, scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS).

As the annealing temperature increased, the thickness of AlN thin films decreased because annealing temperature increased the density of the AlN film, as shown in Figure 1. This result was in good agreement with the surface morphology measured by SEM, as shown in Figure 2. We observed that there were obvious grains on the surface of the as deposited AlN films, which indicates that nucleation and island growth were simultaneous. With the increase of annealing temperature, the grain size of AlN thin films gradually became smaller. The possible reason is that the annealing temperature increased the kinetic energy of atoms and then the films tended to form the stable structure and became denser.

Moreover, the refractive index increased with the increase of the annealing temperature,as shown in Figure 3, which is probably due to the changes of the components in the films. In the as-deposited films, the value of refractive index was small because of the high content of AlON contained, as shown in Figure 4(a). As the annealing temperature increased, Al-O-N bond decreased and more Al-N bond increased in the films, as shown in Figure 4(b) and Figure 4©. Since the refractive index of AlN is higher than AlON[1], the increase of AlN in the films resulted in an increase of the refractive index.

[1] Hong-Yan Chen et al. ACS Appl. Mater. Interfaces, 9, 44(2017).

AF-TuP-4 PE-ALD Growth of GaN on Various Substrates and their Device Applications*, **Xinhe Zheng**, Y He, M Li, S Liu, Y Song, H Wei, M Peng, P Qiu, Y An,* University of Science and Technology Beijing, China

Gallium nitride (GaN) based films and devices on various substrate or templates can produce different potential in electronic and/or optoelectronic applications. The device systems include high-frequency hot electron transistors (HETs) relying on the vertical transport of a controlled source of hot-electrons implementing two-dimensional (2D) materials, such as graphene and Molybdenum disulfide (MoS_2), etc., in the base region to form GaN/2D materials heterojunction systems on silicon and thin-film transistors (TFTs) on flexible substrates. To reap this benefit, one of great challenges is to grow high-quality GaN films on various templates at reasonably-high deposition temperature, but no damage of templates or flexible substrates is allowed. This challenge implies that the overall thermal budget of the device processing should be as low as possible, especially in the case of GaN deposition. The two device systems share the same requirements from endurable temperature processing of templates and/or flexible substrates and reasonably-high deposition temperature for high crystalline quality and realization of good performing device.

Therefore, the trade-off of temperature choices on various templates or substrates will play a critical role in the ALD processing. In this presentation, we report some detailed growth results of GaN films on graphene, MoS_2 templates and flexible KAPTON substrates at lower and higher temperatures, respectively. It is found that during the ALD window, all GaN films show a polycrystalline with wurtzite structure and have a tendency to form preferential crystallization with increasing of the thickness. While the window temperature increases, the crystalline quality and GaN density are intriguingly enhanced. For the case of GaN films over templates onto SiO_2/Si substrates, a very sharp interface between them is observed. While in the case of KAPTON substrates, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) measurements reveal a back diffusion of GaN into the KAPTON. Possible reasons behind these intriguing observations are in detail discussed in the presentation.

AF-TuP-5 Novel Tin Precursors for Atomic Layer Deposition of Tin Oxide Thin Films*, **Seong Ho Han**, T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; S Son,* Sungkyunkwan University (SKKU), Republic of Korea*; B Park, C Kim,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

In the past decade, oxide semiconductor materials have attracted great attention for various applications in thin film transistors (TFTs), gas sensors, lithium batteries, and solar cells. Especially, tin(II) monoxide (SnO) which is a p-type material, has attracted material because of wide optical band gap energy (2.7~3.0 eV), which highlights the possibility of completely transparent electronic devices. Moreover SnO based TFT recently showed the record field effect mobility of ~6.75 cm^2/V·s and Hall mobility of ~18.71 cm^2/V·s. On the other hand, tin(IV) dioxide (SnO_2) is an n-type material, which has also wide band gap energy (~3.6 eV) with excellent optical, electrical, and chemical properties. SnO_2 is transparent under visible light and the resistivity of SnO_2 films can vary at wide range. Doped SnO_2 films can be applied as transparent conducting electrodes. Generally, chemical vapor deposition (CVD) or atomic layer deposition (ALD) are required for uniform and conformal thin film growth. Moreover, SnO or SnO_2 can be deposited selectively by the oxidation state control with Sn(II) precursors and oxygen source. In the cases of ALD, various Sn precursor/reactant combinations have been studied to grow SnO or SnO_2 films, and many cases resulted in n-type SnO_2 films.

In pursuit of novel tin(II) precursors for thin film applications, we have synthesized new tin complexes using tin(II) chloride as starting material. The resulted complexes were characterized by various analysis equipments such as nuclear magnetic resonance (NMR), elemental analyses (EA), thermogravimetric analysis (TGA), and single crystal X-ray diffraction.

AF-TuP-6 Preparation of Transition Metal Molybdenum Precursors and MoS_2 Thin Films Growth by Atomic Layer Deposition (ALD)*, **Sunyoung Shin**, J Kim, B Park, C Kim, T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Molybdenum disulfide (MoS_2) has in recent years become one of the most intensely studied subjects in materials chemistry and materials science, because MoS_2 is a layered semiconductor with a thickness-dependent optical band gap in the range of 1.2–1.8 eV. 2D MoS_2 has been utilized for battery, gas, and biosensor applications, and extensively for catalytic hydro-desulfurization and hydrogen evolution processes. Precursor used in the ALD requires volatility, stability, and low deposition temperature. Precursors using a heteroleptic ligands with different reactivity have advantage of selective reaction of the heteroleptic ligands on substrate during ALD process. In this study, we have synthesized new heteroleptic molybdenum precursors with aminoalkoxides which have been widely used for the development of precursor because of their chelating effects by increasing the coordination number of the metal, and advantages to synthesize a single precursor. A newly synthesized Mo(IV) precursors will be adopted for MoS_2 thin films by ALD.

AF-TuP-7 Synthesis and Characterization of Molybdenum Precursors Containing Aminoalkoxide and Aminothiolate Ligands for MoS_2 Thin Films by Atomic Layer Deposition*, **Jahee Kim**, S Shin, B Park, C Kim, T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Transition metal dichalcogenides (TMDCs), MX_2 (M = Mo, W; X = S, Se, Te), have been widely studied for various applications such as future electronic materials and various catalysts due to their interesting properties of two-dimensional layered structure. The unique structure of TMDCs is attracting attention as a next generation flexible devices. Among them, molybdenum disulfide is most interesting because MoS_2 has a band gap of 1.2-1.8 eV and excellent optical and mechanical properties. It can be applied to wide variety of applications to such as semiconductor devices, batteries, supercapacitors, optoelectronics, hydro cracking and hydrodesulfurization catalysts.

In order to produce uniform and high-quality MoS_2 thin films by atomic layer deposition, it is essential to develop reactive molybdenum precursors without producing harmful or corrosive by-products.

In this study, we synthesized molybdenum precursors containing aminoalkoxide and aminothiolate ligands to fabricate MoS_2 thin films. Newly synthesized molybdenum complexes were characterized by elemental analysis (EA), FT-IR, ^{1}H NMR and Mass, and the crystal structure was analyzed by single crystal X-ray analysis. The thermal stability and volatility were confirmed by thermogravimetric analysis (TGA).

AF-TuP-8 Synthesis of Manganese Nitride Precursors*, **Sunju Lee**, B Park, T Jung, C Kim,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Cu diffusion barrier materials are important to prevent Cu diffusing onto substrate. Among a variety of Cu diffusion barrier materials, TaN has high resistance against Cu migration, robust mechanical properties, and high chemical stability. For the Cu diffusion barrier, TaN film has thickness of more than 10 Å includes a TaN layer above Ta layer. However, for smaller nodes (less than 32 nm), a thinner TaN thin film (5 nm) is required. TaN thin film with the thickness is non-continuous, resulting in larger wiring resistance and lower copper barrier properties. Therefore, manganese nitride thin film can be presented as one of the most promising material in back-end of line copper wiring of next-generation devices.

Precursors for manganese nitride thin film are Mn(amidinate)2, Mn(guanidinate)2, Mn(β-diketiminate)2, etc. However, the precursors have some issue such as volatility, thermal stability, and reactivity to use in the ALD method. Therefore, development of new manganese precursor is required. Recent in precursor chemistry are developments of heteroleptic precursor bonded to different types ligands. The heteroleptic precursors can have a distinct advantage of having a different dissociation pattern for each ligand.

Herein, we report the synthesis of new heteroleptic manganese precursors for thin films containing manganese. Also, the precursors were fully characterized by IR, thermogravimetric analyses (TGA), microanalyses, and structural analysis through X-ray single crystallography.

AF-TuP-9 Atomic Layer Deposition of HfO_2 Thin Film using a Novel Linked Cyclopentadienyl-amido Hf Precursor*, J Park, **Min Hyuk Nim**, M Park, K Moon, J Park, K Lim, J Seok,* Hansol Chemical, Republic of Korea

Hafnium oxide (HfO_2) is presently considered as one of the most promising candidates for alternative gate oxide insulating layers in CMOS (complementary metal oxide semiconductor) devices because of its thermal stability, high permittivity, and relatively large bandgap. Other possible applications for HfO_2 thin film include DRAM (dynamic random access memory) capacitors and optical coatings. In this study, we introduce a novel linked cyclopentadienyl-amido Hf precursor, CMENHa. Also, we compared the properties of the HfO_2 thin film of CMENHa to those of CpHf(NMe2)3 grown by atomic layer deposition (ALD).

The physical characteristics of CMENHa, CpHf(NMe2)3 and Hf(NEtMe)4 were investigated by NMR and viscometer. It was notable that the viscosity of CMENHa was similar to CpZr(NMe2)3. The thermal stability of CMENHa was also investigated by thermogravimetric analysis (TGA). The amount of residue was about 0.6% for CMENHa, which had a less residue compared to CpHf(NMe2)3 (2.5%) and Hf(NEtMe)4 (3.2%). The ALD characteristics of CMENHa compare to CpHf(NMe2)3 will be discussed in the conference. Based on suitable viscosity and good thermal stability, the CMENHa is expected to be promising precursor for insulating layer in gate oxide and DRAM capacitors.

Figure 1. (a) Thermogravimetric analysis of Hf precursors, (b) Physical characteristics of Hf precursors

AF-TuP-10 Al_2O_3 Thin Film Fabrication by UV-assisted Atomic Layer Deposition*, **Gyu Sang Yi**, M Sung,* Hanyang University, Republic of Korea

We have deposition Al_2O_3 thin films at room temperature by UV light enhanced atomic layer deposition on poly(ethylene terephthalate) (PET) substrates. We have used trimethylaluminum (TMA) for metal source and H_2O for oxygen source as precursors during UV irradiation. The atomic layer deposition can be done with pulsing of the precursor gases onto the substrate surface followed by chemisorption of the precursors onto surface. In general cases, the surface reactions of the atomic layer deposition are not conducted at low temperature.

In this experiment, by using UV radiation ,the reactions were self-limiting surface reaction and complementary enough to yield uniform and conformal Al_2O_3 thin films at low temperature. The UV light was very efficient to get the high quality Al2O3 thin films without any defect on polymer substrate. The thickness, density, morphology and electrical property of the Al2O3 thin films were measured by AFM, XRR, ellipsometry, and C-V measurement

AF-TuP-11 Fabrication and Characterization of Organic-Inorganic Hybrid Thin Films*, **Thu Huong Chu**, M Sung,* Hanyang University, Republic of Korea

Nowadays, the next generation electronic devices require new materials that have great properties. One way to fabricate new materials is the hybridization of existing materials having different properties. The hybrid materials mixed by organic and inorganic components are expected to have combined properties both of inorganic parts, such as stability and high electrical or optical performance and organic parts, such as flexibility and functionality. Furthermore, the hybrid materials are expected to have synergic effects which are not shown in just one component.

In this report, we fabricated new types of organic-inorganic hybrid thin films by molecular layer deposition. The hybrid thin films were made by sequential surface reactions of metal alkyls and bifunctional monomers. Diethyl zinc and 2,4-hexadiyne -1,6-diol are used as an inorganic precursor and an organic precursor, respectively, in order to fabricate poly(zinc diacetylene). Some methods are used to characterize the microstructure and compositions of the hybrid films such as Raman, XPS and TEM analysis. And, the electric and optical properties were analyzed by a TFT fabrication and photoluminescence spectroscopy, respectively. The high performance of TFTs, on/off ratio of over 107 and saturation electron mobility of over 10 cm^2/V·s, and the low-temperature process indicate the possible use of the hybrid films to flexible devices.

AF-TuP-12 Low Temperature Atomic Layer Deposition of Yttrium Oxide using Plasma Excited Humidified Argon*, **Kentaro Saito**, K Tokoro, K Kanomata, M Miura, B Ahmmad, S Kubota, F Hirose,* Yamagata University, Japan

Yttria (Y_2O_3) is attracting much attention since this material has an excellent corrosion resistance. In the conventional technologies, Y_2O_3 films were deposited by thermal atomic layer deposition with temperatures exceeding 250˚C, where the high temperature process is the biggest obstacle for the organic electronics applications. We newly developed an atomic layer deposition (ALD) of Y_2O_3 using tris(butylcyclopentadiyl)yttrium ($(BuCp)_3Y$) and plasma excited humidified argon and succeeded in Y_2O_3 film formation at 150˚C and room temperature (RT).

In the experiments, we used a double-sided polished p-type Si (100) substrate with a resistivity of 10 Ωcm as a sample. The sample size was 10 ×

45 mm^2. To confirm the Y_2O_3 formation, we carried out an atomic ratio analysis of Y_2O_3 film by X-ray photoelectron spectroscopy (XPS). The XPS shows the Y3d peak of the film when the ALD was performed with 60 cycles with a precursor exposures of 200000 L and an oxidation time of 10 min at 150˚C or RT. These were close to the full oxidized peak position. It is considered that Y_2O_3 was grown at both 150˚C and RT. To determine the growth per cycle of the Y_2O_3 film, the film thicknesses were measured by spectroscopic ellipsometry. The growth per cycle of Y_2O_3 at 150˚C and RT are recorded 0.06 nm/cycle and 0.6 nm/cycle, respectively. The growth per cycle at RT is 10 times larger than that of 150˚C. We consider this is advantageous for the application of Y_2O_3 film as anticorrosion films.

AF-TuP-13 Fabrication of Zeolite Thin Films by Room-temperature Atomic Layer Deposition*, **Yoshiharu Mori**, Y Noguchi, K Kanomata, M Miura, B Ahmmad, S Kubota, F Hirose,* Yamagata University, Japan

In recent years, zeolite thin films are applied in various fileds such as ion absorbers. The zeolite films were deposited by hydrothermal synthesis although it requires high temperature processes. In addition, it is difficult to control the film thickness in nanometer scale. We newly developed room temperature ALD of zeolite using tris [dimethylamino] silane (TDMAS), trimethylaluminum (TMA) and plasma-excited humidified Ar. We demonstrate the adsorption ability of Na and K cations. We show the results of the Na adsorption test. It is confirmed that the adsorption ability of the zeolite thin film was larger than pure SiO_2 or Al_2O_3 . We also demonstrate the ion exchange properties using zeolite thin film formed by this method. The ion exchange rate from Na to K is recorded as 62 % at room temperature for 30 minutes.

AF-TuP-14 Atomic Layer Deposition of Cuprous Oxide Thin Films using bis(1-dimethylamino-2-methyl-2-butoxy)Copper Precursor*, **Seungmin Yeo**,* Korea Research Institute of Chemical Technology(KRICT), Republic of Korea*; J Han,* Seoul National University of Science and Technology, Republic of Korea*; B Park, C Kim, T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Copper oxide is very attractive material due to its many advantages of non-toxicity, earth-abundance, low cost and direct band gap. Specifically, cuprous oxide (Cu_2O) is known to have band gap of 2.1 ~ 2.6 eV, carrier concentration of ~ 10^{16} cm^{-3}, hole mobilities of ~ 100 cm^2/Vs at room temperature. Owing to these properties, Cu_2O thin films have been investigated for various applications such as gas sensor, photodiode, anode materials in batteries, thin film transistors (TFTs), solar cells and photo-catalysts.

In this study, Cu_2O thin films were grown by atomic layer deposition (ALD) using bis(1-dimethylamino-2-methyl-2-butoxy)copper ($C_{14}H_{32}N_2O_2Cu$) and H_2O vapor as precursor and reactant, respectively. Several *ex-situ* characterizations such as X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray fluorescence (XRF) were performed in detail to investigate the properties of Cu_2O films on SiO_2/Si substrate. All the analysis results clearly showed that polycrystalline with cubic structure and pure with negligible C impurity Cu_2O thin films were successfully achieved using Cu(dmamb)$_2$/H_2O chemistry. It was also observed that self-limiting film growth with the growth rate of 0.04 nm/cycle was observed with varying the precursor and reactant pulsing time. The XRD results of the ALD Cu_2O film showed specific six peaks corresponding to the cubic Cu_2O structure. The XPS analysis strongly supports that the films deposited with the optimal conditions in this study mostly consist of the Cu_2O phase, which is well matched with XRD results. From the Tauc plot, estimated band gap of ALD-Cu_2O film was ~ 2.3 eV. We believe that ALD Cu-$_2$O films can be applied to various devices including TFTs, catalyst, anode material in batteries, etc.

AF-TuP-15 Recent Development of Group 4 Transition Metal Precursors for ALD*, **Ga Yeon Lee**, C Kim, B Park, T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

In the case of dynamic random access memory (DRAM), capacitor dielectrics have required new dielectric materials with a higher k-value than that of traditional SiO_2. HfO_2 and ZrO_2 have been extensively investigated as the gate dielectric oxide or the capacitor dielectrics.

A series of novel group 4 transition metal complexes containing amino-alkoxy as stabilizing ligands, were synthesized for the deposition of metal dioxide. The new heteroleptic group 4 metal precursors have two amino ligands and alkoxide ligands containing nitrogen donor.

The synthesized compounds were characterized by FTIR and NMR spectroscopy as well as elemental and thermogravimetric (TG) analysis. The molecular structures of compounds were inspected by single crystal X-ray diffraction, displaying that they crystalized in the monoclinic space group P2(1)/n as monomer.

AF-TuP-16 SAOLs-Al_2O_3 Nanolaminated Thin Films with Ultrahigh Gas Barrier Performance using Molecular Layer Deposition and Atomic Layer Deposition*, **Jinseon Park**, M Sung,* Hanyang University, Republic of Korea

Organic light-emitting diodes (OLEDs) have emerged as a potent candidate for next-generation displays due to their multiple advantages. However, the life span of OLEDs are limited because of their sensitivity to moisture and air. So one of the major challenges in OLEDs industry is the development of protection film with extremely low moisture and oxygen permeabilities. For commercial applications, the water-vapor transmission rate (WVTR) of approximately 10^{-6} g m^{-2} day^{-1} is generally cited as the minimum requirement to assure adequate lifetime stability for most OLED devices. Herein, we presents a novel organic−inorganic nanolaminated thin films that combine self-assembled organic layers (SAOLs) with an inorganic Al_2O_3 layer through MLD and ALD, respectively. This SAOLs- Al_2O_3 thin film achieved a high degree of mechanical flexibility, excellent transmittance (> 95%), and an ultralow WVTR (2.99×10^{-7} g m^{-2} day^{-1}), which represents one of the lowest permeability levels ever achieved by thin film encapsulation. Furthermore, Modulation of the relative thickness ratio of the SAOLs and Al_2O_3 enabled control over the elastic modulus and stress in the films. On the basis of its outstanding barrier properties with high flexibility and transparency, the nanolaminated film was applied to a commercial OLEDs panel as a gas-diffusion barrier film. This demonstrated excellent encapsulation performance, leading to remarkably high durability of the panel in air.

AF-TuP-17 Remote Plasma Enhanced-atomic Layer Deposition of SiON Thin Films with a High Growth Rate (> 0.25 nm/cycle) using Novel Si Precursor*, **Dae Hyun Kim**, H Lee, H Jin,* Hanyang University, Republic of Korea*; H Lee, J Kim, M Yoo, T Kim, J Kim, M Lee, K Cho, J Lee, J Kim,* Dongjin Semichem, Republic of Korea*; T Park,* Hanyang University, Republic of Korea

Silicon oxide (SiO_2) and silicon nitride (Si_3N_4) thin films have been widely used in semiconductor industry as insulating and dielectric materials for electronic devices. Recently, atomic-layer-deposited (ALD) SiO_2 and Si_3N_4 films are used as a physical and electrical passivation layer such as a gate spacer in metal-insulator-semiconductor field-effect transistor and moisture protective layer in flat display panels, and hard mask layer in self-aligned double patterning process. For these processes, the requirements on materials properties and process conditions are quite stringent in common; high growth rate, low process temperature, high physical density, and high physical/chemical uniformity. Especially, low growth rate of ALD film is a critical drawback in view point of mass-production.

Meanwhile, in an era of 3-dimensional device integration the considerable part of direct plasma enhanced ALD (PEALD) processes would be replaced with remote PEALD processes, because physical and chemical non-uniformity become more critical as well as plasma damage on a substrate.

Therefore, in this work, we demonstrated a high growth rate over 0.25 nm/cycle of PEALD SiON films using new Si precursor and ICP-type remote plasma such as N_2 and NH_3 plasma. Furthermore, SiON films can be grown at the temperature lower than 100^{o}C. The experimental results will be presented in detail.

AF-TuP-18 Automation of Reactivity Modelling in Thin Film Process Chemistry*, T Mustard, **H. Shaun Kwak**, L Jacobson, A Bochevarov,* Schrödinger, Inc.*; S Elliott,* Schrödinger, Inc., Ireland

Modern day modeling and simulation of reactive pathways for individual ALD processes often relies on quantum mechanical predictions of energetics of stationary points on the potential energy surface. The predicted free energies of equilibrium states provide direct insight into thermodynamics of the ALD process whereas the transition state barrier heights among them provide control over the kinetics. Finding the relative kinetics of competing reaction steps is particularly useful for understanding saturating reactions, thermal decomposition and selective-area ALD. Unlike computing the energetics of equilibrium stationary points, however, finding transition states of new reaction pathways for these complex chemistries has widely been acknowledged as labor-intensive, non-transparent, and even an art-like process owing to the extreme nonlinearity of the energy and configuration space. In this work we present a fully automated formalism based on density functional theory (DFT) calculations designed to find a transition state between equilibrium surface structures along key ALD reaction pathway. The new automated transition-state search algorithm, referred to as AutoTS[1], has already been presented with its recent success in finding thousands of transition states and predicting reactivity in a wide variety of reactions in purely organic systems such as the Michael addition, Diels-Alder cycloaddition, and hydrogen abstraction. Here we extend our method to reactions relevant to ALD chemistry, particularly those involving semimetal and metal precursors. Examples are presented using a selection of Si and Al half-reactions, and validated against manually calculated and characterized results. The novel automated transition state search can be combined with such techniques as virtual screening and generation of novel precursor libraries, promising faster research and development of new ALD precursor chemistry with tunable processing parameters.

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AF-TuP-19 Development of High Speed Flow Metering on Pulsed Delivery Systems for ALD and ALE Applications., *Patrick Lowery, T Hoke,* HORIBA*; H Nishizato,* HORIBA, Japan

Atomic layer processes, such as atomic layer deposition (ALD), atomic layer etch (ALE), and selective deposition/ etch processes are the becoming some of the predominant methods used to achieve new device geometry shrinks with smaller lithographic nodes. Current fluid delivery solutions used with these atomic layer processes are challenging due to very fast delivery time or pulsation intervals, and the chemical vapors used in ALD processes have to be delivered at elevated temperatures with highly volatile and reactive organometallic chemistries. In this study, we look at the development and implementation of new technologies into pulsation gas delivery systems for ALD/ALE applications. A high speed piezoelectric actuated valve solution allows for fast pulsation time control resolution of less than 10msec, can provide feedback enabled and settable waveform control, and will enable accurate precursor concentration, injection time control, and repeatability. This additional fast flow metering capabilities will allow for precise process calculations, and could greatly reduce precursor waste thru improved injection timing for purge steps, and reduction of excess precursor due to oversaturation of ALD chamber.

AF-TuP-20 Combined XPS-UPS Study of Conduction and Valence Band Offsets for Al_2O_3/HfO_2 High-*k* Dielectric Nanolaminates Grown on Single-crystal GaN and Ga_2O_3 by Atomic Layer Deposition, *David J. Mandia, B Kucukgok,* Argonne National Laboratory*; J Liu,* Northwestern University*; J Libera,* Argonne National Laboratory*; J Leach,* Kyma Technologies, Inc.*; A Yanguas-Gil, J Elam,* Argonne National Laboratory

The search for adequate binary metal oxide dielectric nanolaminates (NLs) to prevent degradation of power semiconductor devices is ongoing and involves the atomic layer deposition (ALD)-growth of a variety of binary metal oxide combinations. In the present work, we explore the ALD growth of amorphous (x)HfO_2/(y)Al_2O_3 NLs on Si (with native SiO_2 layer) substrates and then on both GaN and Ga_2O_3 single crystals. A variety of samples ranging from their homogeneous mixtures to HfO_2 or Al_2O_3-rich NLs are assessed before and after a thermal annealing by spectroscopic ellipsometry (SE), XAS techniques such as X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (EXAFS) measurements in order to elucidate the structural evolution of the NL at the GaN (or Ga_2O_3)-NL interface. By quantifying the HfO_2 incorporation throughout the Al_2O_3 layer and using the programmable nature of ALD to alternate layers of the HfO_2 and Al_2O_3 in an $(AB)_x$-$(CD)_y$ fashion, the influence of HfO_2 mobility within Al_2O_3 layer on the NL dielectric constant can be verified unequivocally. EXAFS is a powerful tool for determining the local coordination environment of the Hf at the GaN or Ga_2O_3(001)-HfO_2 interface and, at low super-cycle numbers (sub-nm scale), the ultimate stability of the NLs can be probed and optimized such that the bulk material properties are retained. Finally, via a modified Kraut's method,[1] Ultraviolet photoelectron spectroscopy (UPS) is used to obtain the valence band maximum of the GaN and Ga_2O_3 substrates and combined with the high-resolution XPS data for the Hf and Ga shallow core-level photoelectrons ejected from the thin HfO_2/Al_2O_3 overlayer in order to assess the conduction band offset (CBO) at the film-substrate heterojunction. Probing the insulator properties imparted by the high-k overlayer on the wide bandgap semiconductor surfaces of GaN and Ga_2O_3 is crucial in order to understand and prevent the degradation problem in Ga_2O_3/GaN-based power semiconductor devices. Moreover, photoluminscence (PL) studies of the coated and pristine samples will corroborate the effect of the bulk defect concentration on the conduction/valence band properties of the material.

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AF-TuP-21 Low Temperature Thermal ALD of Pt Films with Novel Precursor, *Jacqueline Wrench, Y Yang, W Tang, N Yoshida, P Ma,* Applied Materials*; T Enomoto, R Harada,* Tanaka, Japan

Platinum (Pt) has attracted considerable attention for applications in sensing, catalysis and nanoelectronics due to its excellent electric and catalytic properties.[1,2] For use in these applications, uniform, thin films on high aspect ratio structures are necessary making ALD an ideal technique for deposition. The conventional ALD process of Pt films using $MeCpPtMe_3$ and oxygen deposits at processing temperatures >250°C.[3] Lower temperature deposition requires plasma or O_3 to achieve which can cause severe damage to substrates.[4]

In this work, a novel precursor deposited Pt films at 130°C in an ALD process with H_2. The film demonstrated a clear preference for deposition on metallic substrates with a growth rate of 0.3Å/cyc on in situ TiN substrate (fig 1). The films are highly pure Pt(111) with <5% C content and an RMS roughness of 0.3 nm (fig 2). Step coverage on TiN substrates for 30Å Pt films of >95% was achieved making this a useful low temperature, non-destructive ALD procedure.

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AF-TuP-22 By-product HCl Influence on SiN ALD Process using Chlorine-containing Silicon Precursor, *Hayato Murata,* Taiyo Nippon Sanso Corporation, Japan*; N Tajima,* National Institute for Materials Science, Japan*; K Suzuki,* Taiyo Nippon Sanso Corporation, Japan

We found by-product HCl was an inhibitor on the thermal ALD process using chlorine-containing silicon precursor to form the high-quality silicon nitride (SiN) film.

Recently, high-quality SiN films formed below 400°C are required for next-generation semiconductor devices. We have studied the SiN ALD reaction mechanism using ammonia (NH_3) and dichlorosilane (DCS, SiH_2Cl_2) or hexachlorodisilane (HCDS, Si_2Cl_6), and found HCDS/NH_3 was better to form SiN films under lower deposition temperature than DCS/NH_3[1]. On the other hand, low-temperature deposition results in degradation of the SiN film quality in general. Therefore, we focused on HCl, by-product, effect to film quality.

We calculated activation energies (ΔEa) and enthalpies of formation (ΔHf) using quantum chemical calculation to discuss the HCl's reactivity to the nitrided surface structures which were formed by DCS/NH_3 or HCDS/NH_3. The calculation was performed by B3LYP density functional with cc-pVDZ basis set. Table 1 shows ΔEa and ΔHf calculated for chemisorption reactions. Firstly, for the case of HCDS/NH_3, ΔEa of HCDS chemisorption reaction to >NH surface structure was 57 kJ/mol. ΔEa of HCl reaction to the HCDS/NH_3 nitrided surface structure was 56 kJ/mol. So, we found ΔEa's are nearly equal in both reactions. On the other hand, according to the ΔHf values, the HCl reaction is exothermic and the HCDS chemisorption reaction is endothermic. We got similar results in DCS/NH_3. These results indicate the HCl reaction, dry etching of >N-Si bond, is faster than HCDS chemisorption. In addition, the by-product HCl of HCDS/NH_3 process might be generated more than that of DCS/NH_3 process, because HCDS has three times more Si-Cl bond than DCS. And we suppose that HCDS/NH_3 is susceptible to by-product HCl and form rough thin film easily.

From the above, we propose the necessity to develop HCDS/NH_3 process condition to minimize the influence of the by-product HCl.

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AF-TuP-23 Conformality Measurement Needs and Challenges: Survey among ALD professionals, *Mikko Utriainen, R Puurunen,* VTT Technical Research Centre of Finland, Finland

Conformality is a core value proposition of Atomic Layer Deposition (ALD) and related thin film processing methods. However, conformality is challenging to measure and quantify and standardized methods do not exist either.

This study focuses to identify specific needs and problems in the conformality measurements. The method was a survey and questionnaire. Responders were ALD or other thin film R&D and process engineering experts (N=45), representing academic (N=24) and industry (N=21) and geographically 55% Europe, 25% North America, 20% unknown.

All responders considered that it is important or very important to measure conformality, however, only 38% were satisfied with their present measurement methodology. The dominant method is SEM/TEM analysis from microscopic vertical trenches or other high aspect ratio structures. Only few uses alternative approaches (e.g. macroscopic lateral stacks or indirect methods) and those more frequently in academy than in industry. Some responders also state that they try to avoid conformality measurements.

Survey showed that the most important attribute was the reliability and accuracy (98% responded 4-5, in the range 1-5) followed by availability of test structures (87%). Lowest success in the present methodology was the speed of measurement (84% responded 1-3, in the range 1-5), followed by cost (71%) and availability of test structures (67%).

Responders also described their main challenges. Slow speed is due to tedious (cross-sectional) sample preparation, inaccurate dimensional analyses and multiple sample fractions. Test structures should be comparable to dimensions of real substrates, provide variable 3D dimensions and be available at low cost. Avoidance of breaking valuable wafers was also mentioned. Alternative self-made stacks have challenges e.g. in processing condition compatibility. Other accuracy challenges were low film thickness, inadequate resolution in SEM and missing surface area factor. Responses also pointed out the need of mapping the details on the trench wall/ 3D surface, like morphology, composition, evolution of the film and properties of the film.

Significant gap between high importance and low satisfaction of the current measurement approaches leads to conclude that there is a strong need among professionals to get improvements. In this respect, new innovations or joint activities in standardization can support the whole ALD community.

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AF-TuP-24 AlN Films Prepared by PEALD using Different Plasma Sources, *M Kot,* BTU Cottbus-Senftenberg, Germany*; F Naumann,* SENTECH Instruments GmbH, Germany*; S Garain, E Pożarowska, Z Rouissi,* BTU Cottbus-Senftenberg, Germany*; **Hassan Gargouri,*** SENTECH Instruments GmbH, Germany*; K Henkel, D Schmeißer,* BTU Cottbus-Senftenberg, Germany

Aluminum nitride (AlN) has remarkable properties such as wide band gap, low electrical conductivity, high dielectric constant, low thermal conductivity, and shows piezoelectric behavior. Thus, thin AlN films are promising for a broad range of applications in the field of (opto)electronics and sensors, to name a few.

We present a comparative study of thin AlN films grown by plasma-enhanced atomic layer deposition (PEALD) at 350°C on silicon 8" wafers in the SENTECH SI ALD LL system [1,2]. As precursor and co-reactant trimethylaluminium and ammonia were used, and either a capacitively coupled plasma (CCP) or a direct PTSA (planar triple spiral antenna) source was applied.

The films were characterized by ellipsometry, X-Ray diffraction, field emission scanning electron microscopy, atomic force microscopy, X-Ray photoelectron spectroscopy, and electrical measurements. The layer properties are discussed concerning the varied PEALD process parameters (plasma source, plasma power, plasma pulse duration).

In general, the films prepared with the usage of the direct PTSA plasma source posses higher refractive index and better homogeneity over the wafer in comparison to the process applying the CCP source. Furthermore, higher growth rates per cycle (GPC) in reduced total cycle durations were achieved by the PTSA process. Films with refractive index in the range of 2.07 and permittivity around 8 were realized with a GPC of 1.54 Å/cycle.

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AF-TuP-25 Feature-Scale Simulation of ALD: Steric Hindrance and Under-Exposure Effects, ***Paul Moroz,*** TEL Technology Center, America, LLC

Progress in the semiconductor industry allows ever shrinking feature dimensions, in some degree, due to application of such methods as Atomic Layer Deposition (ALD) and Atomic Layer Etching (ALE). Here we are concerned with the ALD processes, and would like to note that while the number of ALD experimental achievements and applications grow dramatically [1-2] since as far back in time as the 1960s – 1970s [3], the realistic simulation of ALD processing is well behind due to significant difficulties. Among major difficulties are the requirements to simulate evolution of relatively large features with the accuracy of a single monolayer, often in addition to very low sticking probabilities and the requirement of high gas pressures when incident fluxes are very large. Another difficulty for simulations comes from the fact that in most ALD cases the rate of deposition is so low that a single monolayer is deposited only after a few identical cycles. In spite of that, a number of semi-analytic models for ALD processes were reported (among recent see, for example [4-5]), However, to our knowledge, so far only simulations via the FPS3D code reported in [6-9], have the capability of modeling the temporal evolution of feature profiles during a general ALD processing. In current presentation, the results of ALD simulations are demonstrated in detail. The non-ideal effects of roughness, film composition change, and reduced step coverage along the surface might appear in conditions of time-exposure limitations and large aspect ratios. Those effects are simulated during profile evolution due to FPS3D. A special role which steric hindrance could play during ALD processes is demonstrated, and computational methods used for simulations are outlined.

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AF-TuP-26 Novel Tungsten ALD Precursors Supported By Chelating Nitrogen-Based Ligand Frameworks, ***Keith Huynh,*** *C Brown, J Dube,* Digital Specialty Chemicals, Canada*; T Knisley, J Anthis, M Saly,* Applied Materials

Tungsten-based thin-films have found widespread applications in advanced microelectronics devices. Gate contacts composed of tungsten metal or tungsten silicide have been reported, while tungsten nitride films are useful as a copper diffusion barrier layers due to their inherent high density. In addition to microelectronics, tungsten carbide thin-films are refractive materials that have high melting points, are chemical resistant with high hardness, which lend applications in aerospace as coatings and turbine components. Thin-films containing tungsten are achieved via deposition techniques such as chemical vapor deposition (CVD) or atomic layer deposition (ALD) where controlled growth of film thickness and conformality are achieved by process design and precursor development. The bench-marking precursor in CVD/ALD applications has been tungsten hexafluoride; yet in recent years, focus has been placed on developing fluoride-free organometallic tungsten precursors due to the release of toxic HF during CVD/ALD processes, and its propensity to induce unwanted etch in other surfaces. To this end, we have centered our attention in developing organometallic tungsten precursors based on a bis-*tert*-butylimido motif. This poster will focus on our developments in bis-*tert*-butylimido tungsten complexes supported by chelating nitrogen-based ligands and their effect in enhancing volatility and thermal stability. Initial findings reveal candidates that exhibit single-step weight losses and clean sublimations; which have the potential to displace current state-of-the-art for tungsten thin-film deposition.

AF-TuP-27 Growth of Titanium Nitride by PE-ALD: Effects of Intermittent Argon Plasma Exposure, *K Keskinbora, **Gül Dogan**, U Sanli,* Max Planck Institute for Intelligent Systems, Germany*; H Karl,* University of Augsburg, Germany*; G Schütz,* Max Planck Institute for Intelligent Systems, Germany

Titanium nitride (TiN) films have been heavily studied for many applications ranging from protective coatings to diffusion barriers and more recently to refractory plasmonics. Polycrystalline TiN thin films have been already produced *via* atomic layer deposition (ALD) which offers unique capabilities like deposition of highly conformal coatings over complex geometries, accurate thickness and composition control. However, highly textured films are more preferable in terms of improved optical and electrical properties. The adatoms during film growth need to have sufficient mobility in order to enhance crystalline quality. Due to that thin film growth is generally carried out at high temperatures. However, this gives rise to desorption of the deposited material in ALD processes. Alternatively, a plasma treatment can be applied to improve crystallinity at low substrate temperatures [1]. In a recent study by Shih *et. al.* low-temperature epitaxial growth of aluminum nitride (AlN) was demonstrated *via* ALD. In each ALD cycle, an additional *in-situ* plasma treatment was performed. They denoted this process step as “atomic layer annealing (ALA)” [2]. It was proposed that ALA treatment could enhance the adatom movement and migration at the surface, which is favorable for improved crystallization of the deposited films. In this study, we applied the ALA approach for the growth of TiN thin films with favorable chemical and electrical properties.

TiN thin films were deposited on sapphire (0001) substrates at 500°C by plasma-enhanced atomic layer deposition (PEALD) using $TiCl_4$ and N_2-H_2 plasma. TiN thin films were exposed to Ar plasma for 40 s after each ALD cycle to achieve a highly textured structure. The deposition rate was around 0.29 nm/cycle according to XRR analysis and the linear increase of thickness as a function of number of cycle was observed by *in-situ* spectroscopic ellipsometry (SE) confirming the ALD type growth. The structural analysis was carried out by X-ray Diffraction (XRD) technique. A low resistivity of 168 µohm.cm was achieved thanks to highly crystalline structure and a low chlorine content revealed by X-ray photoelectron spectroscopy (XPS). Further structural and chemical analysis results and their relation to the achieved properties will be discussed.

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AF-TuP-28 Plasma-assisted Atomic Layer Deposition of Phosphorus Oxide, ***Bodo Kalkofen**, B Ahmed, M Silinskas,* Otto von Guericke University, Germany*; S Beljakowa,* Friedrich-Alexander-Universität, Germany*; B Garke,* Otto-von-Guericke University, Germany*; M Lisker,* IHP, Germany*; E Burte,* Otto von Guericke University, Germany

Plasma-assisted atomic layer deposition (PALD) of thin films of phosphorus oxide on silicon substrates was carried out. The intention of our work is to precisely deposit a finite dopant source on the semiconductor material for creating ultra-shallow junctions close to the surface after subsequent rapid thermal annealing. Phosphorus oxide is known to be extremely sensitive to water vapor. Probably, this is the reason why no recent reports on ALD processes for this material were found in the literature.

The experiments were carried out in a commercial PALD reactor build by Sentech Instruments GmbH Berlin. Tris(dimethylamido)phosphine (TrisDMAP) was used as phosphorus precursor. Dosing was achieved by “vapor-draw” into a nitrogen carrier flow by fast acting valves. Oxygen radicals in the PALD processes were generated by a remote inductively coupled plasma source. Typical process parameters for the phosphorus oxide deposition were: TrisDMAP: 50°C source temperature, 10 ms pulse time, 5 s purge time; oxygen plasma: 50 W, 5 s pulse time, 2 s purge time. Growth per cycle of 0.1 to 0.16 nm was typically achieved. The ALD window for different process temperatures and saturation behavior was investigated by varying the relevant process parameters.

The phosphorus oxide films were, as expected, highly unstable in ambient air and needed to be stabilized for further ex-situ investigation by mixing them with stable oxides (e.g. antimony oxide) or by applying capping films of varying thickness. The films and film stacks were measured by spectroscopic ellipsometry and composition of the film stacks was analyzed in detail by x-ray photoelectron spectroscopy (XPS) and secondary-ion mass spectrometry (SIMS).

AF-TuP-29 Isotopic Tracing of Hydrogen and Oxygen Exchange Reactions in Al_2O_3 Thin Films, ***Sami Kinnunen**, K Arstila, T Sajavaara,* University of Jyväskylä, Finland

ALD thin films can be used as moisture and gas diffusion barriers [1]. In this work hydrogen and oxygen isotope exchange reactions accompanied by diffusion were studied in ALD Al_2O_3 thin films on silicon substrate. Films were deposited using trimethylaluminum and deuterated water, $^{2}H_2{}^{16}O$, and oxygen-18 enriched water, $^{1}H_2{}^{18}O$. Similar isotopic tracing has been used only in post-deposition treatments [2]. After deposition films were annealed at low temperatures in moist conditions in order to accelerate diffusion and isotope exchange reactions. For example deuterium incorporated in the films is exchanged to hydrogen even in room temperature and normal humidity conditions. In addition, post-deposition annealing was made in $^{16}O_2$-atmosphere. Elemental composition of the films was investigated before and after the post-deposition treatment using ToF-ERDA (Time-of-Flight Elastic Recoil Detection Analysis) measurements. ToF-ERDA can resolve different isotopes of an element and enables tracing of hydrogen and oxygen diffusion in the films. Morphology of the films was studied with HIM (Helium Ion Microscopy).

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AF-TuP-30 Plasma Source Diagnostics for Plasma Assisted Atomic Layer Deposition, ***David Boris**, V Wheeler,* U.S. Naval Research Laboratory*; V Anderson,* Kennesaw State University*; N Nepal,* U.S. Naval Research Laboratory*; S Rosenberg,* American Association of Engineering Education*; A Kozen,* The American Society for Engineering Education*; J Hite, S Walton, C Eddy, Jr.,* U.S. Naval Research Laboratory

Plasma assisted atomic layer deposition (PA-ALD) is a low temperature conformal layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas phase chemistry to produce varying film characteristics. The flexibility and lower growth temperatures that plasmas provide come at the cost of a complex array of process variables that often require great care on the part of the user.

In response to this challenge, this work focuses on the use of plasma diagnostics to inform the choice of process conditions for PA-ALD systems. In this work we employ optical emission spectroscopy, vacuum ultra-violet emission spectroscopy and charged particle collectors to characterize the plasma source of a Fiji 200 (Veeco) PA-ALD tool. In particular, we assess the total ion flux reaching the substrate surface, the relative flux of VUV photons reaching the surface, and the relative fractions of atomic and molecular species generated in the plasma under a variety of pressures and gas input flow fractions. This work is relevant to the growth conditions for plasma enhanced atomic layer expitaxy of AlN, InN, TiO_2, and Ga_2O_3 films.

AF-TuP-31 How ALD has Changed: Analyzing Topic Evolution through Text Mining, ***Elsa Alvaro**,* Northwestern University*; A Yanguas-Gil,* Argonne National Laboratory

Using a combination of bibliometric, social network, and text analysis, we recently examined the rate of knowledge production as well as changes in authors, journals, and collaborators, in the field of atomic layer deposition [1]. As a result of this study, we compiled a dataset comprising more than 11,000 individual papers published between 1981 and 2015.

In this work, we analyze the content of the abstracts in our ALD dataset by using topic modelling and other text mining tools. The result provides information on the topics or hidden semantic themes present in our document collection; the study of the evolution of those topics over time can help further understand the history of ALD. In addition, we focus on extracting chemical compounds present in the abstracts as a way of identifying different precursors and ligands in the ALD literature.

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AF-TuP-32 Ruthenium Atomic Layer Deposition on Platinum using the ToRuS Precursor*, ***Daniel Potrepka**,* U.S. Army Research Laboratory*; N Strnad,* University of Maryland*; G Rayner,* Kurt J. Lesker Company

The Ru precursor ToRuS was developed to provide for the growth of Ru thin films at substrate temperatures of 75-100°C. Preventing deleterious Ru film accumulation in a hot-wall reactor while providing sufficient ToRuS reactivity for the deposition of Ru onto the substrate is difficult due to the limitation imposed on the wall temperature by this low-temperature ToRuS ALD window which, in turn, limits the effectiveness of the purge following the ToRuS dose. In contrast, a Ru precursor with an ALD window of 100-150°C has been successfully used to deposit a Ru seed layer onto a metal contact for suitable Cu growth in FERAM and DRAM metal-contact processes [1].

In this study, nanoscale Pt films were obtained by flash RF sputtering depositions that used short RF plasma times to obtain 3-5 nm thick Pt films. The ToRuS precursor and H_2 co-precursor were then used to thermally deposit Ru with a 100°C substrate temperature, 21 °C ampoule temperature, and 40°C chamber and line temperature. The process used will be described and methods for overcoming observed challenges discussed. An analysis of the Ru deposition on the Pt will be presented. Ru growth conditions on 500 nm thermal SiO_2, obtained using the same deposition conditions, will be analyzed to inform our assumptions of growth rate on Pt. Sample characterization techniques used in this work include in-situ and ex-situ spectroscopic ellipsometry, sheet resistance, and scanning electron microscopy.

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AF-TuP-33 Plasma-Enhanced Atomic Layer Deposition of Ruthenium Using Ru(EtCp)$_2$ & O$_2$-Plasma on Platinum*, ***G. Bruce Rayner, Jr.**,* The Kurt J. Lesker Company*; B Johs,* Film Sense*; B Liu,* The Pennsylvania State University*; N O'Toole,* The Kurt J. Lesker Company*; D Potrepka,* U.S. Army Research Laboratory

Ruthenium is a noble metal that continues to be of considerable interest as an electrode material for microelectronic device applications. Thermal and plasma-enhanced atomic layer deposition (PEALD) of Ru using molecular O_2 gas and O_2-plasma requires controlled exposure conditions to ensure the elemental phase is obtained. The Ru precursor utilized for this work was bis(ethylcyclopentadienyl)ruthenium [$Ru(EtCp)_2$].

To address nucleation delay during Ru PEALD using $Ru(EtCp)_2$ and O_2-plasma at 300°C, platinum seed layers were used as starting surfaces for subsequent Ru PEALD nucleation and growth [1]. Pt PEALD using trimethyl(methylcyclopentadienyl)platinum ($MeCpPtMe_3$) and O_2-plasma was performed at 300°C in the same reactor prior to Ru growth. The effects of Pt seed layer thickness on Ru PEALD nucleation and growth, as well as O_2-plasma exposure conditions were investigated in-situ by ellipsometry in real-time to optimize process conditions. Depth-profile XPS confirmed the presence of a Ru film with no oxygen, and the Pt seed layer. SEM and AFM images suggested an island nucleation growth mode. Ru surface roughness measured by AFM showed a systematic decrease with increasing Pt seed layer thickness. The films were also characterized ex-situ by ellipsometry, x-ray reflectometry (XRR), and transmission electron microscopy (TEM) to determine thickness and morphology.

The nucleation delay for film growth could be directly observed by changes in the in-situ ellipsometric data. Without the Pt seed layer, essentially no Ru film growth was observed. Even a 20-cycle Pt seed layer (0.2 nm thick) enabled the growth of a Ru film, though the resulting Ru film thickness and properties were strongly dependent on the Pt seed layer thickness.

Since it is the critical parameter for many applications, the Ru film resistivity was determined by ex-situ four point probe (4pp) measurements. The Ru film resistivity was also estimated from the in-situ ellipsometry data analysis, using a Drude optical model. A linear correlation was observed between the ex-situ 4pp and in-situ ellipsometry resistivity measurements, demonstrating that in-situ ellipsometry measurements could be used to optimize the conductivity properties of thin Ru films.

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AF-TuP-34 Atomic Layer Deposition of Ru Thin Films Using 'Rudense' as a Ru Precursor and Oxygen Gas as a Reactant*, ***Dae Seon Kwon**,* *C An, S Kim,* Seoul National University, Republic of Korea*; H Song,* Seoul National University, Repubic of Korea*; S Cho, S Cha,* Seoul National University, Republic of Korea*; T Furukawa, T Hayakawa,* TOSOH Corporation, Republic of Korea*; K Kawano,* TOSOH Corporation, Repubic of Korea*; C Hwang,* Seoul National University, Republic of Korea

Ru attracts much attention as a potential electrode for the next-generation dynamic random access memory (DRAM) capacitor due to its promising properties such as low resistivity (~7 μΩ·cm) and high work function (~4.7 eV). Atomic layer deposition (ALD) is the most suitable method among numerous thin film growth techniques to grow uniform and conformal film over three-dimensional structures. Upon Ru deposition by ALD, selecting appropriate Ru precursor is crucial, because the film growth behaviors and its properties are highly affected by the Ru precursor used. Currently, metal-organic precursors like $Ru(EtCp)_2$ and $(Ru(EtCp)(\eta^5\text{-}CH_2C(Me)CHC(Me)CH_2))$ (RuDER) are widely used, but problems such as long incubation time and low growth rate still exist. Therefore, it is necessary to develop Ru precursor with improved performance. A new Ru precursor, Rudense $(Ru(EtCp)(\eta^5\text{-}CH_2C(Me)CHC(Me)O))$ (TOSOH Co.), was developed, which was adopted to grow Ru film via an ALD method in this study. The ALD behavior of Ru thin films using Rudense and O_2 as a Ru precursor and a reactant, respectively, was examined at temperatures ranging from 250 to 270^{o}C. At 250^{o}C, the self-limiting growth was confirmed by controlling the Ru precursor and O_2 feeding time. A saturated growth rate of 0.09 nm/cycle and very low incubation cycles (<20) were obtained, which are highly improved results compared with the results from RuDER. Also, well crystallized Ru phases and low resistivity (~ 70 μΩ·cm) were observed from an extremely thin film (< 3 nm). Chemical and structural analysis, such as X-ray photoelectron spectroscopy(XPS), time of flight secondary ion mass spectrometry(ToF-SIMS) and atomic force microscopy(AFM) measurements were conducted to examine the deposited films in more detailed manner. Finally, a high enough step coverage (> 90 %) was also obtained from the Ru thin film on a capacitor hole with a dimension of diameter of 120 nm and depth of 2400 nm.

AF-TuP-35 *In-situ* Half-Cycle Analysis of Atomic Layer Deposited Zinc Oxide as Channel Layer in Thin Film Transistor*, ***Harrison Kim**,* *A Lucero, S Kim, J Kim,* The University of Texas at Dallas

Thin film process monitoring of atomic layer deposition (ALD) has been adopted as the versatile technique to identify both chemical and physical properties of ALD films. However, currently no tool is suitable to monitor the sub-nm device physics even if we are already in the era facing beyond 10 nm node semiconductor processes.

Hence, we have developed an ultra-high vacuum (UHV) cluster tool equipped with thermal processing, plasma surface treatment, thin film deposition, and electrical characterization which can all be performed *in-situ*. With this feasibility, it is possible to witness the genuine changes in interface states without any ambiguity arising from the oxidation or contamination from the atmosphere. Initial results are demonstrated by depositing low temperature ALD zinc oxide (ZnO). Thin film transistors (TFTs) with inverted-coplanar structure were prepared. ALD Al_2O_3 is used as gate insulator with aluminum defined gate and source/drain electrodes. Diethylzinc (DEZ) and water (H_2O) is used as the precursors to grow ALD ZnO at 100°C. DEZ and H_2O half-cycle analysis is carried out to study ALD ZnO behavior which is used as the channel layer in the TFTs. 45 ALD cycles to deposit ZnO was specifically chosen as it is the regime where ALD ZnO shows first switching behavior in vacuum (on/off ratio: ~10^2). Subsequently, one full ALD cycle shifts the threshold voltage (V_{th}) negatively. Additional DEZ half-cycle further results in a negative V_{th} shift along with a simultaneous increase in on and off current. Moreover, H_2O half-cycle decreases off current, making ALD ZnO film more semiconducting (on/off ratio: ~10^4). By using ozone as another oxidant, role of hydrogen as a shallow donor will also be discussed. We believe that our findings support the fundamental understanding on the origination of dominant n-type doping seen in ZnO.

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AF-TuP-36 Investigation of Low Temperature Silicon Nitride Deposition using Hexachlorodisilane and Ultra-High Purity Hydrazine*, **Antonio Lucero**,* The University of Texas at Dallas*; A Kondusamy,* University of Texas at Dallas*; S Hwang, X Meng, H Kim,* The University of Texas at Dallas*; D Alvarez, J Spiegelman,* RASIRC*; J Kim,* The University of Texas at Dallas

Silicon nitride is playing an increasingly important role in the semiconductor industry for use in self-aligned patterning, 3D integration, and memory applications. Conventional silicon nitride deposition relies on either high temperature or plasma to generate reactive species. Both techniques can deliver high quality films in terms of wet etch rate, uniformity, and dielectric properties.[1] However, modern applications demand lower deposition temperatures (< 400°C) and improved conformality over high-aspect ratio structures. Newly available ultra-high purity hydrazine sources have been successfully used to deposit metal nitrides at low temperature.[2] In this work we study the low temperature thermal ALD growth characteristics of silicon nitride using hydrazine and hexachlorodisilane (HCDS) and evaluate the physical properties of the films. Thermal ALD results with hydrazine will be compared to those from films deposited using PEALD with HCDS and ammonia in the same temperature range.

Silicon nitride films are deposited using a thermal ALD reactor from 250-400°C. Hydrazine is supplied from a BRUTE hydrazine source. Growth with hydrazine shows saturation behavior, with growth per cycle (GPC) gradually increasing with hydrazine exposure. GPC from 0.4-0.5 Å/cycle is observed at 400°C with refractive index of 1.813. X-ray photoelectron spectroscopy analysis is used to confirm film stoichiometry: SiN films with low oxygen (< 2%) and chlorine (< 1%) impurities can be achieved. These results are similar to those for films deposited with HCDS and NH_3 using PEALD at 360°C. Film density and wet etch rate results are compared for films deposited at different temperatures. Nucleation behavior on hydrogen terminated silicon, hydroxyl terminated silicon, and hydrazine treated silicon will be discussed.

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AF-TuP-37 Remote Plasma-Enhanced Atomic Layer Deposition of Metallic TiN Films with Low Work Function and High Uniformity*, Y Zhu, F Li, Y Shen, J Zhang, **Xiao Chen**,* Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, China

Thermal stability of metal/*n*-GaN contact is critical for its applications in microelectronic and optoelectronic devices . Metal Ti is generally used to make ohmic contact on *n*-GaN after high temperature annealing, and the key factor is to form TiN at the interface. To reduce the processing temperature and improve the reliability, metallic titanium nitride (TiN) thin film has been proposed to substitute traditional metals (such as Ti) in the contact structures, due to its low work function and high blocking effect. For this novel approach, the first step is to fabricate high quality TiN films. Here we adopted remote plasma-enhanced atomic layer deposition (RPEALD) method to deposit TiN films under well-controlled conditions. Stoichiometric TiN films (Ti: N ~ 1: 1) with low oxygen contamination (<5%) have been deposited uniformly on 2" substrates in a large temperature range of 250 ~ 400 . The work function of TiN films is quite low (~ 3.7 ± 0.1 eV) comparing to metal Ti (~4.33 eV), and almost independent to the growth temperature and substrates. Furthermore, thin TiN film exhibits good blocking effect on metal diffusion. Strong Fermi edge and high conductivity indicate excellent metallic property of the TiN films. This study of TiN film growth paves the way to establish low temperature process and improve the thermal stability of ohmic contacts for wide band gap semiconductor-based devices.

AF-TuP-38 In Situ Surface Reaction Mechanism Studies on ZrO_2 Atomic Layer Deposition from Tetrakis(ethylmethylamino)zirconium*, W Xu,* Colorado School of Mines*; K Sharma, D Hausmann,* Lam Research Corp.*; **Sumit Agarwal**,* Colorado School of Mines

The continued downscaling of modern semiconductor devices has led to the introduction of high-*k* dielectric materials. Atomic layer deposition (ALD) has emerged as a very promising technique for depositing high–*k* thin films. Among the various candidates for the high-*k* dielectric materials, ZrO_2 has been widely investigated for alternative gate dielectric materials because of its high dielectric constant, high breakdown field, excellent thermal stability, and compatibility with Si processing. Understanding the surface reaction mechanisms during the ALD of ZrO_2 will assist in controlling and optimizing the growth process, and therefore, advance the development of new ALD processes and precursors.

Herein, we report on the surface reaction mechanisms during ZrO_2 ALD using tetrakis(ethylmethylamino)zirconium (TEMAZ) as the Zr precursor. TEMAZ was chosen because, unlike $ZrCl_4$, the surface reaction produces no corrosive byproducts. Oxygen plasma, O_2, H_2O, and C_2H_5OH were used as the oxygen sources to grow the ZrO_2 films. The corresponding surface reactions during the ALD process were monitored using in situ attenuated total reflection Fourier transform infrared spectroscopy, which allows us to identify the surface reaction sites and adsorbed surface species that lead to film growth. In addition, the growth per cycle was measured using in situ four–wavelength ellipsometry.

In both O_2-plasma-based ALD and O_2-based ALD, the main reactive sites for TEMAZ are surface carbonates that are formed after exposure of the hydrocarbon terminated surface obtained after the TEMAZ cycle to these oxygen sources. Previously, we had also identified surface carbonates as the reactive sites for O_3- and O_2 plasma-based ALD of TiO_2 and Al_2O_3. In the H_2O-based ALD process, as expected, -OH groups were the reactive sites for TEMAZ (see Figure 1) and there was minimal carbon incorporation in the film. In C_2H_5OH-based ALD, the amide ligand terminated surface obtained after the TEMAZ cycle reacts with C_2H_5OH, forming surface $-OCH_2CH_3$ groups (see Figure 2). However, the ligand-exchange reaction is not complete in the subsequent TEMAZ cycle with net incorporation of $-OCH_2CH_3$ groups. Even up to a temperature of 300°C, we did not observe the decomposition of the $-OCH_2CH_3$ groups via *b*-hydride elimination mechanism.

AF-TuP-39 Wafer-scale Characterization of Atomic Layer Deposited Zinc Oxide Thin Films using a Temperature Gradient Combinatorial Approach*, H Kim, A Lucero, S Kim, **Jiyoung Kim**,* The University of Texas at Dallas

Electrical properties (*e.g.* resistivity or carrier concentration) of atomic layer deposited (ALD) zinc oxide (ZnO) can be easily modulated depending on the process conditions. However, complex transport behavior and insufficient characterizations make it difficult to comprehend the inherent nature of the electrical properties of ALD ZnO clearly. Thus, the combinatorial approach is suggested as one of the possibility to address this challenge. Since various growth conditions can be processed through a single experiment, the combinatorial approach helps to screen large structural or compositional differences rapidly. It provides a high-throughput methodology to develop or optimize material properties as desired.

Therefore, a rapid methodology to correlate electrical properties of ALD ZnO with nanostructures and compositions is developed through combinatorial study. Systematic study on the temperature dependent ALD ZnO is performed by intentionally introduced temperature gradient in the process reactor. A gradual temperature gradient (204°C to 224°C) over the 100-mm wafer is successfully achieved. Then, we acquired comprehensive information on structural, compositional, and electrical properties through a single experiment. X-ray diffraction (XRD) confirmed that ALD ZnO crystallized preferentially along the (002) orientation at a higher process temperature. Based on XRD and using Scherrer equation, we calculated the grain size that gradually varies as a function of process temperature: higher the process temperature, larger is the grain size. E_2 (437 cm^{-1}) peak in Raman spectroscopy is strongly correlated with the ZnO crystallinity as determined by XRD. Lastly, we found that ALD ZnO crystallinity and its grain size determines the film resistivity. This could be attributed to the enlarged conducting zinc oxide domain that increases carrier concentration. Hall mobility effect on conductivity is not considered significantly since its variations over the 100-mm wafer is negligible. An efficient wafer level characterization of ALD deposited material is demonstrated and feasibility of the combinatorial approach, in terms of visualization and interpretation of the material properties, is also shown.

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AF-TuP-40 Study of Hollow Cathode Plasma Enhanced Atomic Layer Deposited Silicon Nitride: Relationship between Film Properties and Wet Etch Rate*, **Harrison Kim**, X Meng, A Lucero, L Cheng, S Kim, Y Byun, S Hwang,* The University of Texas at Dallas*; M Telgenhoff, B Hwang,* Dow Chemicals*; J Kim,* The University of Texas at Dallas

Plasma-enhanced atomic layer deposited (PEALD) silicon nitride (SiN_x) gathered great attention amongst as it can be grown at lower process temperature (< 400°C) with exceptional wet chemical resistance (wet etch rate, WER< 2 nm/min in dilute hydrofluoric acid). However, despite the fundamental difference in growth mechanism between plasma-enhanced chemical vapor deposition (PECVD) and PEALD, study of film properties affecting WER of SiN_x has been primarily limited to the PECVD grown SiN_x. Moreover, irrespective of the type of Si precursor or type of plasma co-reactants used, research have been done mostly to evaluate the effect of hydrogen bonding density on WER.

Herein, we not only highlight the effect of hydrogen bonding concentration on the bulk film densities influencing the WER of PEALD grown SiN_x, but also provide insight on the influence of chemical bonding states of hydrogen or the effect of the residual impurity from the precursor. A customized ALD system installed with hollow cathode plasma source was employed to study SiN_x comprehensively. Hexachlorodisilane (HCDS, Si_2Cl_6) is adopted as Si precursor since it is the most commonly used precursor type for more than a decade owing to its compatibility with both thermal ALD and PEALD. Then, we explore the effect of process temperature (270°C - 360°C) and plasma gas composition (N_2/NH_3 or Ar/NH_3) on WER of SiN_x. Accordingly, we found the changes in hydrogen bonding states and reduction in hydrogen bonding concentration arises from either (1) thermal activation or (2) plasma co-reactant environment. Moreover, we propose mechanisms that affect the WER of SiN_x: hydrogen bonding states and residual impurity content. As a proof of principle, overall correlations are shown. Our findings highlight the significance of designing growth conditions properly through optimizing the process temperature, plasma gas compositions, and choice of Si precursor or type of plasma co-reactants to achieve lower WER.

AF-TuP-41 Investigation of Stability of Boron Oxide and Phosphorus Oxide Thin Films Grown by PALD*, Bodo Kalkofen*, *K Huang, M Silinskas,* Otto von Guericke University, Germany*; S Beljakowa,* Friedrich-Alexander-Universität, Germany*; B Garke,* Otto-von-Guericke University, Germany*; M Lisker,* IHP, Germany*; E Burte,* Otto von Guericke University, Germany

Plasma-assisted atomic layer deposition (PALD) was carried out for growing thin oxide films containing dopants for silicon, germanium, and SiGe. Boron oxide and phosphorus oxide films were deposited as source layers for p type doping and n type doping, respectively. Tris(dimethylamido)borane (TrisDMAB) was used as boron containing precursor and tris(dimethylamido)phosphine (TrisDMAP) as phosphorus containing precursor. The experiments were carried out in a commercial PALD reactor build by Sentech Instruments GmbH, Berlin. Dosing was achieved by "vapor-draw" into a nitrogen carrier flow by fast acting valves. Oxygen radicals in the PALD processes were generated by a remote inductively coupled plasma source.

The boron and phosphorus containing oxide films were highly unstable in ambient air and showed to some extent remarkable degeneration patterns after contact to air (see examples in Fig.1 and Fig.2). The development of the film degradation with time in air was investigated in detail. Films were stabilized by mixing them with stable oxides (e.g. antimony oxide) or by applying capping films of varying thickness. The films and film stacks were measured by spectroscopic ellipsometry and composition of the film stacks was analyzed in detail by x-ray photoelectron spectroscopy (XPS) and secondary-ion mass spectrometry (SIMS).

AF-TuP-42 Effects of Substrate Temperature and Oxygen Deficiency on the Electronic Properties and Optical Dispersion of MgO Thin Films*, Yus Rama Denny,* *T Firmansyah,* University of Sultan Ageng Tirtayasa, Indonesia*; S Lee,* Chungbuk National University*; H Kang,* Chungbuk National University, Republic of Korea

The electronic and optical dispersion of magnesium oxide (MgO) thin films were investigated by means of X-ray photoelectron spectroscopy (XPS), reflection electron energy loss spectroscopy (REELS) and ultra-violet photoelectron spectroscopy (UPS). MgO thin films were prepared on Si substrates by using electron beam evaporation deposited at different substrate temperature and oxygen flow rate. The O 1s peak from XPS spectra showed that the hydrate MgO, Mg(OH)2, was detected in the surface of MgO thin film at room temperature (RT) grown without oxygen partial pressure and it was decreasing at substrate temperature above 300°C. Meanwhile, the hydrate MgO peak was not found in the film deposited under oxygen partial pressure. The UPS results showed that the work functions of the MgO thin films were 4.69, 5.2, 4.65, and 4.29 eV for the films deposited at RT, 300°C, 400°C, and 500°C, respectively. The REELS spectra revealed that the band gaps of MgO thin films were varied with different substrate temperature and oxygen flow rate. The optical properties were also examined REELS data using Tougaard-Yubero model. The dispersion behavior of the refractive index from REELS results was studied in terms of the single-oscillator Wemple-DiDomenico model. The results showed that the different substrate temperature of MgO thin films caused a change in the dispersion parameters in contrast to the static values of refractive indices and dielectric constant which remained the same. Our work demonstrated that the substrate temperature and oxygen deficiency played a crucial role in improving the electronic properties of MgO thin films and REELS is an efficient tool to study the optical properties of a material obtaining the optical parameters.

AF-TuP-43 Design of Hierarchical Metal Oxide Nanowires with Tunable Orientation by Atomic Layer Deposition*, Susanta Bera,* *S Kwon,* Pusan National University, Republic of Korea

Fabrication of metal oxide semiconductors thin films having hierarchical arrangement are the most exciting prospect for optoelectronic application. One of the novel hierarchical nanostructures are branched metal oxide nanowires (NWs) representing a critical building block of the nanomaterials which greatly enhances the optical, electronic and mechanical properties. A variety of fabrication approaches have been investigated to form high-quality hierarchical NWs, including several bottom-up solution or gas-phase processes. However, ability to control the feature size, density, and orientation of the morphology within each level of the hierarchy over large area is a key challenge. However, atomic-scale precision can control the features of the morphology over a macroscopic area. But, attempting the approach can lead to dramatic variations in the morphology during coating on nonplanar surface due to inability to control the parameters of the deposition process. However, atomic layer deposition (ALD) is one of the powerful technique which allows subnanometer precision in film thickness, interfacial composition, morphology, and microstructure of different levels of hierarchy. Herein, we demonstrate the use of ALD to design hierarchical metal oxide nanowires with tunable orientation via controlling each level of hierarchy on wide range of substrates. In this work, some chemical and physical parameters are found to play key role on growth of the hierarchical thin films. In the next step, sol-gel assisted thin layers of $BiVO_4$ was coated on the hierarchical thin films and proposed to use as a photoanodes for photoelectrochemical water splitting. It is found that the hierarchical films show enhanced photoelectrochemical performance. We demonstrate that the hierarchical morphologies are beneficial for efficient light harvesting as well as additional direct conduction pathway to reduce the charge recombination.

AF-TuP-44 Development of High Performance ALD_TiN Process System*, Jinho Jeon,* *J Kang, C Shin, Y Park, S Kim,* Wonik IPS, Republic of Korea

In the past two decades, there has been a significant paradigm shift in Memory Devices. Specifically, (DRAM: Planer -> RCAT -> BCAT, FLASH: Planer -> 3D V-NAND (24nm), and LOGIC: HK/MG -> FinFET (14nm) -> GAA). These new innovations and technologies represent significant improvements from the current systems. Looking at it from the perspective of the Metal Process, we can analyze the ALD_TiN Film used in DRAM Cell Capacitor supporter and 3D NAND W/L barrier metal.

In order to increase the capacities of DRAM Cells, the number of Capacitor Nodes has been increased. In order to prevent bending issues of nodes (high Aspect ratio), ALD_TiN has to be created in high temperature for High Density, Good Step Coverage to be functional. To satisfy these need, the use of different Capacitor materials and innovations around shift from ZAZ to ZAZA….. are being thoroughly researched. In 3D V-NAND, as height of ON Stack increases, W/L (high surface area /Gate W B/M) Gapfill becomes increasingly difficult. The combination of low temperature ALD-TiN / ALD-W is being used to solve the complicated Gate Gapfill Process.

In response to the evolving Device, the research facility has successfully developed a TiCl4 gas base's ALD_TiN Film using the New Platform, achieving greater productivity and stability.

By developing the Low Thickness TiN Film used in 3D-NAND W/L B/M under 430~450 degrees, results of Step coverage above 98%, Film Continuity under 35A, and Density above 4.5g/cc have been successfully achieved. Also, by developing the TiN Film used in DRAM Capacitor (Storage and Plate) in high temperature of above 520~650 degrees, result of Good Step Coverage above 96% has been successfully achieved. This allowed for Cell Capacitor's stability.

Through multiple simulations of Shower Head, Gas Path and chamber designs optimized for ALD Process, system that stabilizes gas purging and pumping was created. The resulting high quality TiN Film has D/R=0.30A~0.45A/cycle and Cl level (SIMS/count) of less than 3xE-3.

AF-TuP-45 Deposition of Thin (0.5 – 42 nm) Alumina Films by ALD to Determine their Optical Constants from 190 – 1688 nm*, **Dhruv Shah, D Patel, D Jacobsen, J Erickson, M Linford,*** Brigham Young University

Atomic layer deposition (ALD) is widely used in the semiconductor industry to provide atomic level control of film thickness and uniformity. Here we report thermal ALD (332 ºC) of thin films of alumina from water and trimethyl aluminum (TMA) precursors. The alumina deposition was optimized by varying the dose and purge times for both precursors with an aim to obtain uniform film thickness and growth per cycle (GPC). Films of varying thickness (0.5 – 42 nm) were characterized by spectroscopic ellipsometry (SE) and X-ray photoelectron spectroscopy (XPS). XPS clearly showed an increase in surface aluminum content with increasing number of ALD cycles. The film thickness was measured by spectroscopic ellipsometry (SE), where film growth was extremely linear over the entire range probed (5 – 500 deposition cycles). The SE data from multiple thin films were used to build an optical model in a multi-sample analysis that included parameterized optical constants for alumina and film roughness. This model yielded a single set of optical constants for alumina over a wide range of thicknesses (0.5 – 42 nm) and wavelengths (190 -1688 nm). Because of the importance and frequency of alumina deposition by ALD, these optical constants should be useful to others in the field.

AF-TuP-46 Investigation of the Si doping effect on the Ga_2O_3 Films Prepared by Atomic Layer Deposition*, **Hong-Ping Ma**, H Lu, T Wang, H Chen, X Li, J Chen,*** Fudan University, China*; J Zhu,* Tongji University, China*; D Zhang,* Fudan University, China

Precise control dopant composition and systematic study the doping effect are critical to the production of functional films with desired properties. In this study, we make the original try to use atomic layer deposition (ALD) to fabricate Si-doped Ga_2O_3 films. Optical spectrometry, Hall measurements, X-ray photoelectron spectroscopy and several other measuring techniques were applied to characterize and analyze the optical, electrical and structural properties of the doped films. The experiment results indicated that the content of the Si has an obvious influence on the photoelectrical properties of Ga_2O_3 films. The refractive index of Ga_2O_3 films was decreased with the increasing of the Si content. The Ga_2O_3 energy gap can be tuned from 4.75 to 4.92 eV through Si doping. The average transmittance was larger than 95% from ultraviolet to visual wavelength for all these Si-doped Ga_2O_3 films although the optical transparency was reduced after the Si doping. These results suggesting that the Ga_2O_3 film-based devices such as transparent electrodes, photodetectors or thin film transistors can be further optimized the structural quality and conductivity by improving ALD process.

AF-TuP-47 Magnetoelectric Properties of Atomic Layer Deposited ZrO_2-HfO_2 Thin Films*, **Kristjan Kalam**, H Seemen, P Ritslaid, A Tamm, K Kukli, M Mikkor,*** University of Tartu, Estonia*; R Stern,* National Institute of Chemical Physics and Biophysics*; S Dueñas, H Castán,* University of Valladolid

ZrO_2 and HfO_2 have been materials of interest due to their several potential applications, for example in microelectronics as a memory material [1]. In this study, ZrO_2-HfO_2 films were grown by atomic layer deposition (ALD) on planar Si(100) and TiN substrates by alternately applying certain amounts of constituent binary oxide growth cycles. $ZrCl_4$ and $HfCl_4$ were used as zirconium and hafnium precursors, respectively. The oxidizer was H_2O.

Films with various compositions were grown, cation ratio Hf/Zr varied from 0.2 to 10 as measured by X-ray fluorescence spectrometer. Some films were grown as solid solutions and some as nanolaminates. The film thicknesses, measured by spectroscopic ellipsometry, varied between 9 and 22 nm. A nanolaminate, where 8 nm of HfO_2 is deposited on Si(100) and 10 nm of ZrO_2 is deposited on top of HfO_2, is ferromagnetic, measured with vibrating sample magnetometer. The same sample deposited on a TiN substrate was subjected to a Sawyer-Tower measurement and exhibited ferroelectric-like behavior.

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AF-TuP-48 Selective Film Stripping Techniques for In-FilmTrace Metal Analysis Using Inductively Coupled Plasma Mass Spectrometry (ICP-MS)*, **Jaya Chowdhury**, J Huang,*** ChemTrace*; K Fu,* Chemtrace*; P Sun, L Shi,* ChemTrace

Atomic layer deposition (ALD) of stacked films often entail thin film deposition based on the sequential use of a gas phase chemical processes[1]. Possibilities for atomic layer depositions to leave some un-reacted precursor elements in the form of impurities can be high. In order to achieve ultra-high purity products, essentially free from trace metals and organic impurities, they need to be fully qualified at the precursor level[2] as well as upon deposition of films[3].These films require full characterization for process optimization to eliminate device critical contaminants in the mature process[4]. The impact of not doing so can be very costly in terms of low yielding and unreliable final product. One of the technical challenges for in-film trace metal contamination analysis is the lack of selective film stripping sample preparation methods.

In this paper, different film surface and in-film trace metal analysis techniques will be described. Results will be discussed as part of a case study for W/TiN/SiOx stacked film wafers. Different stripping chemistries (acid, base, peroxide, etc.) and stripping conditions (etch time, chemical ratios, etc.) studied for target film removal will be elaborated upon. Using the optimized selective film stripping sample preparation recipe and ICP-MS, trace metals in the W film layer have been analyzed with efficient film removal selectivity and satisfactory method detection limits.

Keywords: Selective film stripping, trace metals, device critical contaminants, ICP-MS, wafer films

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AF-TuP-49 Study on Silicon-nitride ALD Process at Low Temperature by a High Density Multiple-ICP Source*, **Ho-Hyun Song**, H Chang,*** 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). Also, we have improved the plasma source to a magnetized-ICP source for generating more high density plasma. 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-TuP-50 Self-Organized Growth of TiO_2 Anatase Nanorods on Graphene Nanoplatelets by Atomic Layer Deposition*, **Damiano La Zara**, F Grillo, M Kreutzer, J van Ommen,*** Delft University of Technology, Netherlands

Understanding the spontaneous organization of atoms on well-defined surfaces promises to enable control over the shape and size of supported nanostructures. Atomic layer deposition (ALD) is an established gas-phase technique for the layer-by-layer deposition of conformal thin films in applications that require atomic-level precision. Given its unparalleled precision and scale-up potential, considerable research effort has been put in expanding its capability to the deposition of nanostructures other than thin films such as nanoparticles (NPs). However, the formation and growth of NPs is mediated not only by ALD surface chemistry but also by non-equilibrium phenomena such as adatom and NP diffusion and aggregation. Since such mechanisms are a strong function of reaction conditions and adlayer-support interactions, control over the NP size can be achieved only under certain system-dependent conditions. Nonetheless, if properly understood, unconventional growth pathways can expand the range of nanostructures that can be synthesized by ALD. After achieving control over the NP size, the natural next step in the advancement of ALD of NPs is the synthesis of shape-controlled NPs and, in particular, of 1D nanocrystals such as nanorods.

Here, we report on the bottom-up formation of TiO_2 anatase nanorods on gram-scale batches of graphene nanoplatelets via $TiCl_4/H_2O$ ALD carried out at temperatures as low as 300 °C. We show that nanorods as large as 200 nm form even after only 5 cycles, indicating that the growth is dominated by diffusive aggregation rather than by a layer-by-layer mechanism. In particular, complex structures such as V-shaped and curved nanorods are observed. Prolonged annealing experiments show that the sequential nature of the ALD process is crucial for the nanorods formation. Statistical analysis of the shape of the nanostructures at different exposure times reveals a competitive process between growth pathways leading to either symmetric growth, and thus NPs, or asymmetric growth, and thus nanorods. In particular, the population of the different observed nanostructures is a non-linear function of the exposure time of $TiCl_4$ and H_2O even at saturation conditions. The number of cycles affects mostly the number rather than the size of the nanorods. Crucially, high-resolution transmission electron microscopy reveals that the TiO_2 nanocrystals can undergo oriented attachment and that the width of the nanorods is bound by {011} facets. Finally, analysis of the relative lattice orientation clearly shows an in-plane rotational alignment between the lattices of the TiO_2 nanocrystals and graphene nanoplatelets.

AF-TuP-51 Surface Reaction Routes of HCDS on SiO_2 using Density Functional Theory*, **Ki-Yung Kim**, D Shin, Y Kim,* Korea University of Technology and Education, Republic of Korea

HCDS (Si_2Cl_6) is still the choice of silicon ALD process in semiconductor industry mainly because of its self-limiting reaction and cost benefit. HCDS, however, does not follow the typical and sequential 'adsorption-reaction' process because of its low surface adsorption energy; the adsorbed molecule would rather desorb from surface than react with it. We try to rationalize its ALD characteristics by considering the kinetic energy of molecules and the succeeding reaction routes. Temperature should be raised to increase the number of molecules with high kinetic energy. This high thermal energy, however, can transform the reaction process from ALD to CVD. We found that the succeeding reaction routes could still be self-limiting at this high temperatures.

AF-TuP-52 Quadrupole Mass Spectrometer for ALD Process Monitoring - Challenges and Solutions*, **Uwe Meissner**,* ALD, Germany

The performance and reliability of Quadrupole Mass Spectrometry (QMS) Systems have been improved significantly over the last few years, and as such employed extensively in a range of semiconductor manufacturing applications as Residual Gas Analyzers (RGA).

Today, RGA systems are widely used to monitor, optimize and control different vacuum-based processes. New innovations in RGA technology and products can provide significant analytical benefit to enable optimization and monitoring for Atomic Layer Deopisition (ALD) and Atomic Layer Etch (ALE) processes.

There are significant developments with respect of improving sensitivity, detection limits and robustness of the QMS (RGA) systems. We will present solutions for improved ion source technology and system robustness. We will discuss specific requirements and solutions for QMS (RGA) applications for Thermal ALD and Plasma Enhanced (PE) ALD processes.

AF-TuP-53 Develop Inhibitor-Utilizing Atomic Layer Deposition for Synthesizing Few-layer Molybdenum Disulfide Thin Films*, **Woojin Jeon**,* Dankook University, Republic of Korea*; Y Cho, S Jo,* Samsung Advanced Institute of Technology*; J Ahn,* Korea Maritime and Ocean University, Republic of Korea*; S Jeong,* Soongsil University, Korea

We present a novel synthesis technique to produce high-quality MoS_2 thin films by utilizing an inhibitor for Mo precursor adsorption in an atomic layer deposition (ALD) process. The spectroscopic and microscopic analysis results revealed the dependence of the crystal and chemical structure of the deposited MoS_2 films on the concentration of the Mo precursor adsorbed on the substrate in the initial stage of the ALD process. The mechanism for this dependence was examined theoretically and experimentally. Based on this, we successfully synthesized highly crystalline few-layer MoS_2 samples on SiO_2.

ALD for Manufacturing
Room Premier Ballroom - Session AM-TuP

ALD for Manufacturing Poster Session

AM-TuP-1 Methods of Precursor Delivery for ALD Process and Studies on Possible By-product Issues Occurred in the Exhaust System and its Solutions*, **Ellis Lee**, C Lee, S Lee,* CSK, Republic of Korea

As the technology in semiconductor manufacturing develops, device characteristics like the density of the pattern and the aspect ratio are changing and according to the change in trends, many changes in the methods for thin films deposition are being required. Especially methods like the ALD(Atomic Layer Deposition) or the PE(Plasma Enhanced) ALD that are able to have more detailed process control are in demand. In order to improve the electrical characteristics of the device as well as the deposition method, various types of precursors used in the ALD method and new precursors are currently being actively pursued.

Currently, liquid precursors used in the ALD method are being used in various mass production processes. For example, TEOS is used in the gap fill, DIPAS is used in the multi patterning, ATARP is used for Low-K process

Generally, the overall concept of the ADL production tool that uses liquid precursors uses the PDS(Precursor Delivery System) to deliver precursors to enhance its tool reliability

The PDS, a liquid precursor delivery system for ALD processes, can be divided into two different types. This is divided according to the vapor Pressure trend of the precursor.

If there are residuals of precursor in the inner side of the tube where the precursor is being delivered, when air flows in, a chemical reaction easily occurs and these reactions will eventually be sources that arouse particles and contamination. Therefore, after all the precursor is used up and the before exchanging the empty canister, the inner sides of the tube must be cleaned due to air exposure.

If it's a precursor that relatively has high vapor pressure trend, the tube can be cleaned with using just inert gas such as Ar or N2. However, if it's a precursor that relatively has low vapor pressure trend, a purge gas and a solvent like N-Hexane will be needed to fully clean the inner sides of the tube.

The excess residuals of the precursor that do not participate in the process after it is flowed into the chamber will be exhausted out through the pump and abatement. During the exhaust process, not only the precursor but also the reactant gas will be exhausted out of the system but through this, various by-products from the reactant of the main precursor occurs in exhaust system.

These various by-products are the main causes for decreasing the up-time of the ALD tool. However, at Edwards, we hold a great history on precursors and the PDS and also, we manufacture pumps and abatement systems of the exhaust system which allowed us to hold various experiences with expected issues regarding by-products that occur in semiconductor process.

*** Keywords: ALD, Precursor Delivery System**

AM-TuP-2 High Purity Hydrazine Delivery System for Low Temperature Thermal ALD of Silicon Nitride*, J Spiegelman, **Daniel Alvarez**, K Andachi,* RASIRC*; A Lucero, A Kondusamy, S Hwang, X Meng, H Kim, J Kim,* University of Texas at Dallas

The demand for faster, smaller and more energy efficient logic devices plus higher density, higher speed and increased reliability for advanced memory devices has led to challenges in Semiconductor device manufacturing. Novel metal materials, 3D architecture and increasing HAR structures are being used to address these challenges, placing additional constraints on film deposition methods. CVD and ALD of SiN is used in several applications including gates spacers, etch stops, liners, encapsulation layers and passivation layers.[1] Recently PEALD of SiN is taking on an increasingly important role due to new temperature constraints of <400C. However several challenges remain on HAR and 3D structures in applications where plasma approaches may not meet conformality requirements. Also, thermal ALD with NH3 may not be feasible due to the high temperature requirement (>500C) of these reactions.[2]

Our approach involves development and use of a novel hydrazine delivery system for thermal ALD of SiN at <400C. A hydrazine delivery system was developed to provide a stable flow of ultra-dry hydrazine gas from a liquid source in a sealed vaporizer. The liquid source combines anhydrous hydrazine and a proprietary solvent that acts as a stabilizer. The solvent is highly non-volatile. High purity hydrazine gas is generated in-situ and delivered to the deposition chamber but the solvent remains in the vaporizer. Testing confirms that hydrazine vapor pressure is maintained at levels viable for ALD (12-14 torr) even in the presence of the solvent. Oxygen contamination has plagued previous hydrazine studies. This study demonstrates high purity hydrazine delivery at <800ppb water contamination in gas phase. Delivery system safety and optimization versus conventional hydrazine will be addressed.

A study of silicon nitride deposition was conducted using hexacholorodisilane (HCDS) and hydrazine on a Si-H substrate. A custom thermal ALD reactor was used to deposit films from 250-400°C. Film growth per cycle (GPC) with hydrazine was 0.4-0.5 Å/cycle at 400°C with refractive index of 1.813. Film stoichiometry was confirmed with XPS. SiN films with low impurities were achieved for oxygen (<2%) and chlorine (<1%). Highly uniform films were obtained across a 4-inch wafer for 200 as well as 400 cycles. Results were similar to films deposited using PEALD at 360°C with HCDS and NH3. The presentation will compare film density and wet etch rate results at different temperatures for hydrogen terminated silicon, hydroxyl terminated silicon, and hydrazine treated silicon. Nucleation behavior comparing surface pre-treated hydrazine versus HCDS will also be discussed.

AM-TuP-3 Spatial ALD for Semiconductor Manufacturing - Expanding the Process Space*, **David Chu**,* Applied Materials

The use of ALD in semiconductor manufacturing has accelerated, growing to nearly a $1.5B market. A number of the new ALD applications challenge the boundaries of conventional ALD processing, often requiring high quality films at reduced thermal budgets. Spatial ALD extends the process space within which the ALD process is viable for volume manufacturing. This presentation will focus on our spatial ALD solution and its advantages over conventional ALD processes.

AM-TuP-4 RT Atomic Layer Deposition System with a 1 m Size Reactor*, **Fumihiko Hirose**,* Yamagata University, Japan

Room temperature (RT) atomic layer deposition has been attracting much attention in the field of coating for electronic parts and micro machines since thermal damages to the coating objects are effectively minimized. In the field of the organic electronics, the RT ALD is applicable for producing the gas barrier flexible films. In our laboratory, RT ALDs of various films [1-3] were developed by using plasma excited humidified Ar[1-3]. Since oxidizing species of O and OH from the plasma excited humidified Ar are delivered at a distance as long as 1m, we developed a mass production system of RT ALD with a 1m size reactor. For the electronic parts with sizes of ~5 mm, the batch processing of thousands of pieces of parts are possible to be treated at one time. In the conference, we introduce the newly developed 1m size reactor of RT ALD and its application for the anticorrosion coating for the metal parts and gas barrier film production.

AM-TuP-5 High Conductance Precursor Delivery and Control Valves*, **Masroor Malik**, Y Jiang,* Swagelok

In today's semiconductor chip manufacturing processes, more low pressure precursors, which are often solid source, are being used. Employing these low pressure precursors requires very high chemical conductance and high temperature systems.

In both the Atomic Layer Deposition (ALD) and Atomic Layer Etch (ALE) processes, control valves are used to precisely meter the chemical dosing. Traditionally, springless diaphragm valves offered the best cleanliness and cycle life in these applications. However, the increased molar chemical delivery demand of low pressure processes requires high conductance delivery systems. Springless diaphragm valves designed to operate under these parameters require very large diameter diaphragms that exceed practical space limitations.

Emerging manufacturing techniques are enabling the design of new control valve solutions to handle these challenging chemistries in the production environment while meeting the required cleanliness and cycle life expectations.

In this paper, we will describe the challenges faced, the solutions considered, and the path chosen to best fulfill the needs for high conductance control valves in low pressure precursors.

AM-TuP-6 Computational Fluid Dynamic Study of Spatial ALD: Mapping the Transition Between Transport, Diffusion, and Reaction Limited Regimes*, **Angel Yanguas-Gil**, J Elam,* Argonne National Laboratory

Spatial ALD provides the advantage of higher throughput compared to conventional ALD by eliminating the need for long purge times. In a recent study, we presented an analytic expression for the saturation curves in spatial ALD in terms of the velocity of the moving substrate, chamber geometry, precursor pressure and input flows, and the surface chemistry.[1]

In this work, we have performed computational fluid dynamic studies of spatial ALD. Momentum, energy, and mass transport equations are solved for a moving surface incorporating both self-limited and non-self limited surface chemistries. The models are solved assuming that ALD precursors are dosed in the presence of a background carrier gas flow. The results show that, at low pressures, the dependence of the surface coverage with the process variables matches extremely well the simple analytic solution. However, with increasing pressure the system reaches a starved, diffusion-limited regime and the validity of the analytic approximation breaks down.

Furthermore, we found that as pressures approached one atmosphere, the flows became unstable, consistent with a transition from laminar flow to a turbulent regime. This transition is not necessarily detrimental for the process: when the timescale of the fluctuations are much smaller than the residence time and the flow becomes fully turbulent, precursor mixing in the chamber is enhanced resulting in a higher effective diffusion.

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AM-TuP-7 Simulation and Measurement of Mass Evaporation Rate of Precursors inside Canister during ALD Process*, **Seung-Ho Seo**, Y Lee, D Kim, H Shin,* GO Element Co.,Ltd, Republic of Korea*; J Kim, W Lee,* Sejong University, Republic of Korea

The precursor for atomic layer deposition (ALD) should have excellent purity, thermal stability, and high evaporation rate to deposit a high-quality thin film with high productivity. In particular, since the evaporation rate of the precursor affects the growth rate of the thin film, a constant amount of precursor should always be supplied to the ALD reactor. Therefore, it is very desirable to predict the evaporation characteristics of the precursor in the real ALD systems depending on the structure and temperature of the precursor delivery system, including the canister, and the temperature and gas flow rate of carrier gas. In this work, we calculated the evaporation rates of precursors as a function of time using computational fluid dynamics (CFD) method and then compared them with the measured rates. The fundamental physical properties of precursors, such as boiling point, vapor pressures at different temperatures, heat capacity, and viscosity, were obtained by either literature survey or measurements. The turbulence model and the evaporation-condensation model were used to predict the evaporation rates, the distributions of temperature and pressure, and the flow streamlines. The evaporation rates were determined using a measurement system equipped with a real-time level sensor to confirm the calculation results. The results of this work are expected to be used to predict the precursor evaporation characteristics or to design the optimal structure of the canister.

Keywords: Mass evaporation rate measurement, computational fluid dynamics simulation, metalorganic precursor, canister

Area Selective ALD
Room Premier Ballroom - Session AS-TuP
Area Selective ALD Poster Session

AS-TuP-1 Use of Low Energy Ion Scattering for the Analysis of Area Selective ALD Processes*, **Thomas Grehl**, P Brüner,* ION-TOF GmbH, Germany*; C Vallee,* LTM-UGA, France*; R Gassilloud,* U Grenoble Alpes, CNRS, LTM*; V Pesce, A Bsiesy, B Pelissier,* Univ. Grenoble Alpes, LTM, France

Low energy ion scattering (LEIS) is a surface analytical technique that enables the characterization of the outermost atomic layer of a sample. The sample is bombarded with noble gas ions with kinetic energies of a few keV, and the energy spectrum of the backscattered ions is recorded. Ions scattered by different atom species in the first atomic layer give rise to distinct elemental peaks in the energy spectrum. As the result of the scattering process is independent of the chemical environment of the target atom, the peak intensities are directly proportional to the surface coverage of the respective element. The elemental composition of the surface can thus be determined in a quantitative way.

In addition to surface scattering events, noble gas ions scattered in deeper atomic layers undergo material-dependent energy losses proportional to their penetration depth. These processes lead to additional sub-surface features in the energy spectra, which can be evaluated to obtain layer thickness values and the depth distribution of elements in the first few nm of a sample.

The extreme surface sensitivity of just a single monolayer is a unique property of LEIS that is not available with other surface analytical techniques like XPS or SIMS, which always integrate over several monolayers. This makes LEIS an ideal tool to study layer growth in ALD processes. The monolayer sensitivity is especially useful to analyze the early stages of film growth, with questions about topics like surface coverage, layer closure, nucleation delay, growth mode, growth rate, or the presence of impurities.

Additional complexities arise in the field of area selective deposition (ASD). A higher number of process steps are involved, and often additional reactants lead to more complex chemical interactions. Growth areas and non-growth areas are present simultaneously, and surface analytical tools become increasingly important to develop, understand, and improve deposition processes.

One example of an ASD process, developed at LTM, includes an atomic layer etching (ALE) step once nucleation sets in on the non-growth area. The area is then passivated to restore its non-growth properties, and deposition is resumed. This cycle is repeated until the desired film thickness is obtained on the growth area. In this study, we apply LEIS to a series of model samples of thin ALD TiO_2 layers, created to improve understanding of this ASD process. The passivation step and the precise point where nucleation re-starts on the passivated area are of special interest. Moreover, the influence of the fluorine-based plasma etching on the deposited TiO_2 layers is investigated.

AS-TuP-2 Area-Selective Atomic Layer Deposition of Zinc Sulfide Based on Inherent Selectivity*, **Chao Zhang**, Z Han, M Vehkamaki, M Leskelä, M Ritala,* University of Helsinki, Finland

The need for simplifying and improving complex electronic device fabrication has motivated the research on area-selective atomic layer deposition (ALD). Area-selective ALD is a bottom-up approach enabling deposition of thin films only on the desired surface areas, thereby accomplishing film patterning more easily as compared with conventional lithography .[1]

It is well known that ALD process involves chemical reactions between precursors and reactive sites existing on substrate surfaces. So, in principle area-selective ALD can be achieved by surface modification including surface passivation and activation. Surface passivation means that reactive sites on the substrate surface are blocked by passivation layers, thus losing their reactivity with ALD precursors. Area-selective ALD by surface passivation has already been studied for years, focusing on using self-assembled monolayers (SAMs) or polymers as resist layers to prevent the film growth.[2]On the contrary, surface activation provides an opposite way to attain selective film growth by patterning of seed layers that can promote ALD film growth catalytically. For example, Färm et al. proved an easy way that used micro contact printed RuO_x films as a seed layer for catalyzing ruthenium ALD process .[3]

Here, a new approach based on inherent selectivity of an ALD process is presented for area-selective ALD. It is found that ALD of ZnS, using elemental zinc and sulfur as precursors at a deposition temperature of 500^{o}C, takes place on Au surfaces but not on Si surfaces with about 2 nm native SiO_2 on top. As a reason for this selectivity, it is suggested that sulfur adsorbs much stronger on Au than on SiO_2. The continuous ZnS growth even after the Au surface is completely covered with ZnS can be similarly explained in terms of strong adsorption of sulfur on ZnS. Alternatively, the selectivity could also arise from Zn alloying with Au, this alloy then reacting with the subsequent sulfur pulse. Patterned Au structures used in our experiment consist of three different size dots (500, 250, 50 µm), prepared by electron beam evaporation (EBE) with a shadow mask. After the deposition of ZnS on this patterned surfaces, ZnS films were detected only on Au dots as confirmed by EDX measurements.

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AS-TuP-3 Selective Etching of Native Silicon Oxide in Preference to Silicon and Silicon Oxide*, C Ahles, **Jong Youn Choi**, A Kummel,* University of California San Diego

The selective removal of native SiO_x in the presence of SiO_2 would be of great importance to the semiconductor industry given the ubiquity of these two materials in electronic devices. Methods of native SiO_x removal have been well studied and typically rely upon HF chemistry. Aqueous HF treatment suffers from an inevitable air exposure of the Si sample and is not selective for native SiO_x versus bulk SiO_2. The Siconi™ process utilizes a NF_3/NH_3 plasma to remove native SiO_x leaving behind a $(NH_4)_2SiF_6$ salt as the etch product. This salt is then removed in a subsequent anneal. While this process is known to work well for removing native SiO_x on Si, the selectivity of this process versus thermal SiO_2 has not been studied. In this study, the etch rates of Si and SiO_2 subjected to a $NF_3/NH_3/Ar$ plasma were examined. Under the optimized conditions of NF_3:NH_3:Ar = 1:10:1.5 at 45°C, 190 mTorr and 100 W no etching of Si is observed with negligible or no etching of SiO_2.

The etch rates of Si and SiO_2 subjected to a $NF_3/NH_3/Ar$ plasma were measured in-situ using a pair of quartz crystal microbalances (QCMs). It was found that the etch rate of Si shows a strong dependence on the temperature, with the Si etching at a rate of 25 nm/min at 50°C while no etching of Si is observed at 40°C. At 45°C, it was found that the native SiO_x on Si is rapidly etched under these conditions, after which there is only deposition (presumably of NH_4F and NH_4FHF salts). X-Ray Photoelectron Spectroscopy (XPS) measurements show that after the dry clean the Si surface has a N:F ratio of 1:3, consistent with $(NH_4)_2SiF_6$ formation. A subsequent anneal at 120°C removes the salt and leaves a very clean Si surface (1% O, 6% C, 1% F and 92% Si^0). Atomic Force Microscopy (AFM) shows that the Si surface has a root mean square (RMS) roughness of 1.1 Å. For comparison, the RMS roughness of a degreased Si sample (containing native SiO_x) which was not subjected to the dry clean was found to be 2.2 Å. This is consistent with no etching of the underlying Si, as etching would be expected to roughen the surface. XPS analysis of SiO_2 after the dry clean showed that on SiO_2 the N:F ratio was closer to 1:2, suggesting the presence of NH_4FHF instead of $(NH_4)_2SiF_6$ (the expected etch product of SiO_2). Annealing at 120°C removed most of the NH_4FHF salt, leaving behind only 4% F and 2% N. AFM measurements show that the degreased SiO_2 has an RMS roughness of 4.3 Å while after the dry clean the RMS roughness is very similar (3.8 Å), consistent with no etching of SiO_2. The reason for this selectivity may be due to the presence of more strained Si-O bonds or undercoordinated Si atoms in native SiO_x than in SiO_2.

Emerging Materials
Room Premier Ballroom - Session EM-TuP
Emerging Materials Poster Session

EM-TuP-1 Structural and Optical Properties of Luminescent Copper (I) Chloride Thin Films Deposited by ALD*, **Tomáš Homola**, R Krumpolec, D Cameron, O Caha, J Humlíček,* Masaryk University, Czech Republic*; R Zazpe, J Přikryl, J Macák,* University of Pardubice, Czech Republic

Zinc blende-structure g-copper (I) chloride is a wide, direct bandgap semiconductor with the potential for applications in UV optoelectronics. We report on the structural, optical and photoluminescent properties of CuCl thin films deposited by atomic layer deposition. The CuCl films were deposited at a reaction temperature of 125 °C from [bis(trimethylsilyl)acetylene] (hexafluoroacetylacetonato)copper(I) and pyridine hydrochloride precursors with pulsing times 2 and 6 s with corresponding purging times 4 and 6 s respectively. The CuCl growth was deposited on various substrates: amorphous soda-lime glass, amorphous quartz glass, crystalline silicon and crystalline sapphire of different orientations. The deposited coatings at 100, 200, 500 and 1000 ALD cycles were studied by XPS, XRD, AFM, optical reflectance and photoluminescence. We also investigated the effectiveness of a thin capping layer of aluminium oxide against degradation of the CuCl by atmospheric. The presence of CuCl was confirmed by the x-ray diffraction and photoluminescence measurement which showed a strong signal at approx. 3.25 eV characteristic of the excitonic emission. The presence of crystalline CuCl was strongly influenced by the substrate and the best crystallinity was found on quartz glass, whereas silicon wafers showed no evidence of CuCl crystals in the deposited films. Moreover we also showed that quick optical reflectance measurement can be used for fast and reliable detection of the presence of CuCl crystals.

EM-TuP-2 Wafer-scale Fabrication and Optoelectrical Application of Organic-inorganic Perovskite Single Crystal Arrays*, **Lynn Lee**, M Sung,* Hanyang University, Republic of Korea

Organic-inorganic hybrid perovskites, especially $CH_3NH_3PbX_3$ (X=Cl, Br, I) have received great attention due to their outstanding light-harvesting properties as well as their low-cost device fabrication process. Their superior optoelectrical properties lead to the exceptional device performances of these materials in various applications such as solar cells, LEDs, and photodetectors. Typically, the quality of the crystal is a well-known factor to decide the efficiency of those optoelectronic applications with long carrier diffusion length and high mobility. However, since a thin film of a single crystal cannot be obtained by a typical film fabrication method, films made by most of the manufacturing methods suffer from low crystallinity issue. For these reasons, fabrication of single crystalline perovskite thin film is required for high-efficiency device applications.

Here, we fabricate the wafer-scale perovskite single crystal arrays in thin film form and characterize the crystallinity of the perovskite thin film by X-ray diffraction (XRD) and selected area electron diffraction (SAED). Also, the morphology of perovskite crystals was observed using optical microscopy (OM) and scanning electron microscopy (SEM). Furthermore, the perovskite patterned thin films are applied in lateral solar cell applications. The average efficiency of the perovskite lateral solar cell in low light intensity is over 4%, which are the world-top efficiency in lateral perovskite solar cell field as far. From this work, the probability of the perovskite single crystal array is successfully demonstrated.

EM-TuP-3 Organic-inorganic Hybrid Optoelectronic Device by Atomic Layer Infiltration*, **Yeongeun Bak**, M Sung,* Hanyang University, Republic of Korea

Hybrid organic-inorganic solar cell have emerged as a remarkable new alternative energy source over the past few years to solve the global energy problems. The sun is sustainable, reliable and long-term supply of energy, in contrast to conventional resources such as fossil fuels. Silicon is the most widely used as material of solar cell because of its high efficiency, but it has limits; expensive manufacturing cost and limitation of application to flexible or transparent devices. So, alternative types of solar cells are also being researched, Sb_2S_3 solar cell is up-rising candidate for next generation solar cells overcoming the above disadvantage of Si solar cell. The problem of commercialization of Sb_2S_3 solar cell is lower efficiency than Si solar cells, so there were previous studies about interfacial engineering have been proceeding for solving the problems.

We studied new organic-inorganic material nickel-4-mercaptophenol (Ni-4MP), as an interfacial engineering material into Sb_2S_3-hole transport material interface. Ni-4MP thin film is deposited using atomic layer deposition method. For infiltrate precursors into FTO/mp-TiO2/Sb_2S_3 structure, exposing procedure is added. The reference cell structure is FTO/mp-TiO2/Sb_2S_3/P3HT/Au. We measured the photo conversion efficiency using solar simulator with source-meter for comparing two samples. And then we observed impedance measurement with variation of voltage for confirming the effect of Ni-4MP on Sb_2S_3 solar cell. As a result, electron lifetime calculated from this measurement proof the longer lifetime of electron after insert Ni-4MP as interfacial engineering material.

EM-TuP-4 A Common Source/Drain Metallization Scheme for (In)GaAs and Ge Channel Materials Featuring Low Contact Resistances*, **Szu-Hung Chen**,* National Nano Device Laboratories (NDL), NARL, Republic of China*; K Chen, Y Chen,* College of Photonics, National Chiao-Tung University, Republic of China*; C Chu, G Luo,* National Nano Device Laboratories (NDL), NARL, Republic of China*; C Lin,* College of Photonics, National Chiao-Tung University, Republic of China

Pursing of the miniaturization of Si-based logic transistors is approaching it's fundamental limits in aspects of geometric scaling, enhancement of intrinsic carrier transport efficiency as well as reduction of parasitic components. Serial extrinsic S/D resistance can seriously degrade the output current of the transistor and constrain it from low-voltage operation. As the transistor channel length (Lg) shrinks, the device's intrinsic channel resistance decreases. Consequently, the parasitic source/drain resistance (R_{sd}) dominates and plays key role in determining the overall device output characteristics, particularly when the technology node is beyond 7 nm and smaller. Despite the stringent challenges in reducing R_{sd}, CMOS technology also requires both n- and p-type transistors in a single chip for various logic functions in integrated circuits. Si is the channel material of current n-/p-type transistors used for industrial mass production. However, due to the potential of incorporating alternative channel materials for future-generation CMOS, n-type and p-type channels may be different materials to maximize the performance. For example, InGaAs, possessing high electron mobility, is used in n-type channel devices and Ge, possessing high hole mobility, is used in p-type channel device, respectively, in an attempt to achieve the best combined performance in CMOS. In such a scheme, the complexity of processing heterogeneous CMOS dramatically increases. From this point of view, it is of great interest and is mandatory to reduce the process complexity, especially in the step of source/drain contact metallization. In this work, targeting the future nano-device application, a single metallization scheme for n-/p-type channel transistors has been developed to reduce the cost of the CMOS manufacturing. W/TiN/Ti multilayer structure is adopted to form metal/$In_{0.53}Ga_{0.47}As$ and metal/Ge contacts. Both contact structures show specific contact resistance of <3E-7 Ωcm^2 by CTLM (circular transmission line model) analysis. However, the interracial relations are distinct as evidenced by material analysis. The promising results show that the developed technology is of great potential for application in future of nano CMOS technology which requires heterogeneous n-/p-channels.

EM-TuP-5 Ruthenium Precursors - Properties and ALD Application*, **Andreas Wilk**, O Briel, D Zeng, A Frey, A Rivas Nass, W Schorn,* Umicore AG & Co. KG, Germany

Umicore has its roots in precious metal chemistry and 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, solid chemical background, purification competence, trace metal analytical capabilities and significant packaging knowhow.

Besides the established cobalt and tungsten precursor portfolio we have established new chemistries for ruthenium based compounds as ruthenium tungsten and cobalt are considered by several chipmakers at 5nm and below for upcoming applications.

Ruthenium is a precious metal with interesting chemical, crystallographic and electronic properties. This makes ruthenium chemistry including the related precursors very interesting for chipmakers for logic as well as memory applications. In our poster we will introduce established and new precursors with a variety of ligands currently considered and review their relevant physical and analytical properties for interesting metal and oxide ALD industry applications including the 5 nm node and below.

EM-TuP-6 Magnetic and Electrical Performance of Atomic Layer Deposited Nanostructures*, **Aile Tamm**, K Kalam, M Mikkor, H Seemen, A Šutka, U Joost, M Rähn, K Kukli,* University of Tartu, Estonia*; J Link, R Stern,* National Institute of Chemical Physics and Biophysics*; H Castán, S Dueñas,* University of Valladolid

The synthesis of multiferroic materials is of relevance while developing the next generation electronic and spintronic devices [1]. Theoretically, several materials could demonstrate saturating and remnant polarization in both electric and magnetic fields, but it is challenging to actually synthesize thin films which demonstrate multiferroic behaviour, because the physical performance of the materials may considerably depend on their synthesis routes. In this study we compare the nanostructures containing nanoparticles $CoFe_2O_4$ or $MnFe_2O_4$ covered by high-k films by ALD with nanolaminate films consisting of high-permittivity oxides (ZrO_2, Er_2O_3) and magnetic materials (Bi_2O_3, Fe_2O_3, Co_3O_4) grown by ALD. Nanolaminate films could be uniformly deposited into three dimensional stacked substrates using the same cycle times otherwise suited to the uniform coverage of planar substrates. The morphology, crystalline phases and composition of nanostructures were described. Those nanostructures promoted both charge polarization and saturative magnetization. Promising results in terms of the simultaneous appearance of the internal magnetization and certain electrical charge polarization were demonstrated in some planar nanostructures. Further electrical and magnetic modelling and analysis will be needed in order to elaborate the phenomenon and optimize the material structure for the magnetoelectric performance.

Acknowledgements

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EM-TuP-7 $HfZrO_2$ Deposited by ALD using TEMAH and ZrCMMM Precursors*, **Ronald Grundbacher,*** IBM Research – Zurich, Switzerland*; Y Ju,* ETH Zurich, Switzerland*; F Eltes,* IBM Research – Zurich, Switzerland*; X Chen,* ETH Zurich, Switzerland

Hafnium zirconium oxide ($HfZrO_2$) with thickness on the order of a few nanometers to tens of nanometers is of interest as a high-k dielectric material that is integrated into compound semiconductor and CMOS devices, nanowire-based devices, and nanostructured devices based upon novel materials. The ferroelectric properties of $HfZrO_2$ are of interest for low-power steep-slope transistor applications and nonvolatile memory. The requirements of the $HfZrO_2$ that is integrated into the above mentioned devices include low concentration of impurities, low interface and bulk trap densities, low leakage current, and often, low temperature deposition due to a limited thermal budget. The characteristics of $HfZrO_2$ deposited by atomic layer deposition (ALD) has been investigated with the above requirements in mind, and deposition parameters have been determined to optimize the Hf/Zr ratio.

Hafnium zirconium oxide thin films were deposited on silicon wafers by atomic layer deposition using tetrakis(ethylmethylamino)hafnium (TEMAH) and bis(methyl-η^5–cyclopentadienyl)methoxymethylzirconium (ZrCMMM) precursors and either oxygen plasma or ozone. Oxygen plasma and ozone conditions, Hf to Zr pulse ratio and sequencing, as well as deposition temperature (250ºC to 350ºC), were varied, and their effects on the $HfZrO_2$ thin films were investigated. The properties of the ALD deposited films were comparatively characterized. The $HfZrO_2$ thin films were characterized by ellipsometry to determine the thickness (growth rate) and dielectric constant, and they were characterized by X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectorscopy (RBS) to determine the hafnium and zirconium content. Atomic force microscopy (AFM) was used to characterize surface roughness and piezoresponse force microscopy (PFM) was used to determine the ferroelectric nature of the $HfZrO_2$ films.

EM-TuP-8 Non-destructive And Precise Control Of Electronic Properties via N-Doping Method with Atomic Layer Deposition.*, **Jong Chan Kim,*** Hanyang University, Repubic of Korea*; M Sung,* Hanyang University, Republic of Korea

For variety of usage, graphene must be under processed its Fermi level and carrier concentration. In this approach introduced n-doping technique with atomic layer deposition(ALD) of Zinc oxide. Precise even quite simple and, the produced ZnO thin film on graphene are uniform, conformal, of good quality with a low pinhole density, besides thickness control of 1 Å resolution available. Evaluation of material properties performed which characterization of graphene transistor at the point of carrier density, doping state and Dirac point as a function of the thin film thickness. Our achievement is not only electronic properties' progress, but also stable device performance has gotten. It is caused from ZnO film did a role of effective barrier against air-borne water and oxygen on the graphene. Additionally, ZnO ALD enhanced too to the other promising 2D materials like MoS_2 and WSe_2 those are candidates to promote electron mobility.

EM-TuP-9 Curvature-Dependent Surface Potentials of Zincone Films Grown by Molecular Layer Deposition*, J Lee, **Yun Yeong Lee,*** Sookmyung Women's University, Republic of Korea

Molecular layer deposition (MLD) is a method for obtaining conformal ultrathin organic films using vapor-phase organic precursors, while their composition and thickness can be controlled at the molecular level. This process is based on self-saturating reactions between the precursors and the substrate surface. Also, in comparison with solution-based technique, it allows epitaxial growth of molecular layer on substrate and is especially good for surface reaction or coating of nanostructures such as nanopore, nanobead, nanowire array and so on.

In this study, we fabricated organic-inorganic zincone polymeric films on surfaces with various curvatures through coupling reactions between diethyl zinc (DEZ) and 2-Butyne-1,4-diol (BYDO) as inorganic and organic precursors, respectively, by molecular layer deposition. Using ellipsometry and transmission electron microscope (TEM), we confirmed the different growth behavior of zincone films grown on curvature substrates with different ratio. And, we investigated their curvature-dependent surface potentials by performing *ex situ* analysis using scanning kelvin probe microscopy (SKPM). Furthermore, their molecular geometries and energies on substrates with various curvatures were predicted by performing density functional theory (DFT) calculations.

EM-TuP-10 Photo-switchable Behavior of Azobenzene-containing Polyamide Films Grown by Molecular Layer Deposition*, J Lee, **Hyemi Lee,*** Sookmyung Women's University, Republic of Korea

Photo-sensitive polymer film has been attracted in the field of material science including biological system and optical devices which are sensitive on the change of surface topology. Recently, azo compound (R-N=N-R'), as one of the photo-induced reversible transformation unit, has been highlighted in the research related photo-sensitive polymer film including surface science, artificial muscle, biological and optical application, because light used as external triggers for inducing surface transformation is manageable to control without modification of nano-structures and environment concerns.

In this study, we fabricated photo-reversible polyamide film based on coupling reactions between azobenzene-4, 4'-dicarbonyl dichloride (Azo) and one of two diamine compounds, which are phenylenediamine (PDA) and hexamethylenediamine (HDA) by molecular layer deposition through self-limiting surface reaction. And, we investigated the photo-induced reversible transformation of azobenzene-containing polyamide thin film. In situ Fourier Transform Infrared (FTIR) measurement was used to monitor the growth of polyamide film, and the light-induced transformation was characterized by UV-vis spectroscopy.

EM-TuP-11 Phase Selective, Low Temperature Growth of TiO_2 by Atomic Layer Epitaxy*, **Virginia Wheeler**, D Boris, S Qadri, J Freitas, S Walton, C Eddy, Jr.,* U.S. Naval Research Laboratory

Atomic layer deposition (ALD) of TiO_2 has been widely explored in recent years due to its promise in non-volatile resistive switches, high-k gate dielectrics, solar cell, and photocatalytic applications. This method has become increasingly useful as device dimensions are reduced and non-planar complexity is increased. Traditionally, the low ALD growth temperature (Tg) yields amorphous films. To facilitate epitaxial films, many have investigated plasma, laser or photon, or electron enhanced ALD processes. Specifically for TiO_2, it would be beneficial to selectively grow epitaxial anatase or rutile phases in order to tailor properties for the required application. Typically, TiO_2 phase selectively is attained by varying the underlying substrate, Ti and/or oxidation precursor, or growth temperature. In this work, we demonstrate high quality epitaxial TiO_2 films at low temperatures and phase selectively by adjusting plasma gas composition, pressure and Tg.

A Veeco Fiji G2 reactor was used to deposit TiO_2 films on different sapphire orientations (c-, m-, a-) with tetrakis(dimethylamido)titanium (TDMAT) and either Ar/O_2 or pure O_2 plasma at 100-350°C. Previous reports indicate that tuning the ion energy, specifically through substrate biasing, can influence TiO_2 film crystallinity and phase [1]. The high pumping speed and large gas flow range available in the system provides a wide variation in operating pressures (7-100's mTorr), which effectively allows tuning of plasma characteristics. Operating at relatively low pressures (9-21mTorr) resulted in a significant flux ($0.5\text{-}1.5\text{x}10^{19}\ m^{-2}s^{-1}$) of very energetic ions (30-50eV); both the flux and energy decrease as the pressure is increased. The low pressure conditions yield high-quality epitaxial films at all temperatures, which differs from previous reports using these specific precursors [2,3] likely due to the plasma conditions.

Gas composition during the plasma step also had a substantial effect on growth rate, TiO_2 phase, and strain. At Tg < 300°C, the growth rate was increased from 0.5 to 0.7 Å /cycle by switching from Ar/O_2 to pure O_2. Additionally, an O_2 plasma produced only rutile TiO_2 films, with less strain, independent of growth temperature or underlying substrate orientation. In contrast, films deposited with an Ar/O_2 plasma show a phase dependence on temperature and substrate. Films on c-plane Al_2O_3 go from anatase at Tg below 200°C to rutile above 300°C. The films on m-plane Al_2O_3 are rutile independent of temperature.

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EM-TuP-12 ALD Deposited Thin Films as Model Electrodes: A Case Study of the Synergistic Effect in Fe_2O_3-SnO_2*, J Kint, F Mattelaer, **Christophe Detavernier,*** Ghent University, Belgium

Li-ion batteries are the current state of the art energy storage devices. They have been around since 1991, yet there still is room for improvement. On the anode side, specific capacities are relatively low. High capacity storage mechanisms (conversion, alloying) are gaining attention. However, these reactions impose strain on the material, leading to pulverization, contact loss, SEI formation and poor kinetics. However, synergistic effects were reported when two of these materials are combined.

Since electrodes are complex systems, we used atomic layer deposition to deposit model electrodes. This approach avoids the need for binders or additives and ensures simple, 1-dimensional Li^+-diffusion pathways. The self-limiting and digital nature of ALD ensures optimal control over the thickness and stoichiometry of the mixed oxides. Furthermore, it enables control of the degree of intermixing of the Fe_2O_3 and SnO_2 at the atomic scale. Here, films of pure Fe_2O_3, pure SnO_2, atomically intermixed Fe_2O_3-SnO_2 and a Fe_2O_3/SnO_2 nanolaminate were deposited with ALD and evaluated as anodes.

Although Li-alloying of SnO_2 delivers a huge capacity, undesirable island formation occurs. During lithiation of the intermixed Fe_2O_3-SnO_2, the conversion of Fe_2O_3 still occurs, yet the conversion and subsequent Li-alloying of SnO_2 is no longer present. Instead, another reaction occurs around 0.9V vs Li^+/Li which has no analogon in either pure SnO_2 or Fe_2O_3. Therefore it is hypothesized that it is a reaction of Li^+ with the $Fe_xSn_yO_z$ ternary oxide. Although the mix of these oxides shows no alloying of Sn, it ensures a better cycle life of the material, as the island formation caused by the alloying is avoided. This can be seen from the cyclability test, as the capacity of the mixed material is more stable than the SnO_2. From a kinetics point of view, the fully intermixed material compares well to the Fe_2O_3, especially at high currents.

For the nanolaminate we can also discern abovementioned reactions, as the interfaces between the oxides give rise to the peaks associated with those for the mixed material. Those corresponding with the conversion and subsequent alloying of SnO_2 are also clearly present. This entails that, although the nanolaminate provides a large capacity, the alloying of Sn still occurs and causes great stress and loss of contact, as can be seen from the SEM image after cycling the nanolaminate for a mere 50 cycles. This results in discrete capacity losses during cycling.

We used ALD to prove that in order to maximize the synergistic effect for Fe_2O_3/SnO_2, an atomically intermixed material is preferred over a nanolaminated system with interfaces between the oxides.

Nanostructure Synthesis and Fabrication
Room Premier Ballroom - Session NS-TuP

Nanostructures Synthesis and Fabrication Poster Session

NS-TuP-1 High Sensitive Strain Sensor with Organic Single-crystal Nanowires by Direct Printing, ***Yoon Kyoung Park***, *M Sung,* Hanyang University, Republic of Korea

Charge transport properties of organic semiconductors critically depend on their molecular packing structures. Controlling the charge transport by varying the molecular packing and understanding their structure−property correlations are essential for developing high-performance organic electronic devices. Here, we demonstrate that the charge carrier mobility in organic single-crystal nanowires can be modulated with respect to the intermolecular center-to-center distance by applying uniaxial strain to the cofacially stacked crystals. Furthermore, the measured values of charge carrier mobility were in good agreement with theoretical calculations based on charge localized hopping theory. These results provide a definitive relationship between intermolecular packing arrangement and charge transports, which enables a huge improvement in charge carrier mobility for organic single-crystal materials.

NS-TuP-2 Charge-transfer Complex Thin Films with Visible-light Absorption by using Molecular Layer Deposition, ***Nguyen Van Long***, Hanyang University, Republic of Korea

A titanium-aryloxide (Ti-Ao) thin films showing high visible-light absorption was fabricated by molecular layer deposition (MLD). The origin of the visible light absorption was ligand-to-metal charge-transfer that is revealed by studying ultraviolet-visible analysis and density functional theory calculations. ZnO/Ti-Ao nano-laminate active channel photo-transistors functioned synergistically with Ti-Ao acting as a visible-light absorber, and ZnO serving as a great semiconductor.

NS-TuP-3 Pretreatment Effect of SnO_2 Layer Coated on Carbon Nanofiber by Atomic Layer Deposition, *D Kim, S Shin,* ***Seok Choi***, *J Han, B Choi,* Seoul National University of Science and Technology, Republic of Korea

Carbon nanofibers (CNF) are used as active materials for electrodes in various energy devices, such as lithium ion secondary batteries, super capacitors and fuel cells. Recent studies have been proved that nanoscale coatings on carbon nanotubes increase the output and lifespan of the devices owing to the improvement of mechanical and chemical properties. Among the various coating methods, atomic layer deposition (ALD) can conformally adjust the thickness of coating layer without any directional growth. Therefore, it has the advantage of coating on the particle with high aspect ratio, such as CNF, even in nanometers thickness.

In this work, we grow SnO_2 layers having two kinds of morphology on CNF. We compare the reactivity and wettability of precursors and reactant gases as follows; trimethylaluminum (TMA), tetrakis(dimethylamino)tin (TDMASn), $Sn(dmamp)_2$, H_2O, O_3. Since the ALD reaction of TMA, $Sn(dmamp)_2$, O_3 with surface functional group requires the smallest activation energy, it is easier to react with surface functional sites. We also use two types of ALD equipment; Flow-type ALD (static ALD), and fluidized bed reactor type ALD (dynamic ALD). Static ALD is processed at 161℃, 5 cycles by TMA and H_2O as Al_2O_3 reactant, and then followed by 105 cycles of TDMASn and H_2O as SnO_2 reactant. Dynamic ALD is processed at 120℃, 5 cycles by TMA and H_2O as Al_2O_3 reactant, and 150℃ 105 cycles by TDMASn and H_2O as SnO_2 reactant.

According to the TEM analysis, static ALD creates an island-shaped SnO_2, but uniform SnO_2 layer is formed by inserting Al_2O_3 layer. On the contrary, dynamic ALD shows formation of uniform SnO_2 layer irrespective of Al_2O_3 layer. In addition, energy dispersive spectroscopy (EDS) analysis showed more intensive elemental Sn and O signal can be detected from Al_2O_3-coated CNF. XPS analysis reveals that both Sn^{4+} and Sn^{2+} are observed in SnO_2 on CNF by static ALD probably due to the formation of an interfacial layer between the SnO_2/CNF interface. Meanwhile, Sn^{4+} spectra are only shown in SnO_2 on CNF by dynamic ALD. Cyclic voltammetry analysis is performed to characterize the electrochemical properties of SnO_2 coated CNF as an electrode on fuel cell.

NS-TuP-4 Plasma-enhanced Atomic Layer Deposition of Molybdenum Compounds Thin Films Using $Mo(CO)_6$ with Various Plasma Gases, ***Jeong-Hun Choi***, *S Lee, C Hyun, J Ahn,* Korea Maritime and Ocean University, Republic of Korea

In recent years, transition metal oxides and dichalcogenides have received much attention due to its attractive properties for a wide range of applications. Among these materials molybdenum compounds were studied most initiatively and achieved considerable progress. Meanwhile, metallic molybdenum is also widely used as conducting materials in many electronic applications. In this study, therefore, optical, structural and electronic properties of metallic molybdenum and its compounds thin films have been investigated. Plasma-enhanced atomic layer deposition (PEALD) was employed to form the uniform Mo, MoO_3, MoS_2 thin films. Especially, When $Mo(CO)_6$ was used as the precursor, different kinds of plasma gases such as O_2, H_2, H_2S and their mixtures for reactant resulted in selective growth of Mo, MoO_3, MoS_2, respectively. Basically, the ALD characteristics with each reactant were studied. The ellipsometry, raman spectroscopy, photo luminescence, X-ray photoelectron spectroscopy, scanning electron microscopy were used to examine film characteristics according to the different precursor combinations and growth conditions. Furthermore, the potential of metallic Mo as well as Mo compounds for device component was investigated.

NS-TuP-5 Fabrication and Characterization of Titanium Disulfide Thin Films by Atomic Layer Deposition, ***Gyuhyeon Park***, *N Kornelius, A Thomas,* IFW-Dresden, Germany

Titanium disulfide (TiS_2) is part of the family of layered transition metal dichalcogenides, where each layer consists of edge-sharing TiS_6 octahedra, which leads to strong covalent bonds in plane and weak van der Waals forces out of plane. Because of the uniqueness of the layered structure,TiS_2 enables the formation of various intercalation compounds with guest species such as Na, Li, Mg, and Bi. Therefore, it has potential to adopt to numerous applications, such as thermoelectrics, Lithium ion battery (LIB) or field effect transistor (FET) devices to name a few. In this study, we fabricate TiS_2 by either ALD with H_2S and $TiCl_4$ as precursors or employ sulfurization methods with pre-deposited TiO_2 thin films on various substrates. We will investigate the thermoelectric and electrical properties with a custom setup. This was developed at the IFW in cooperation with Linseis Meßgeräte GmbH in the last years and can simultaneously measure the in-plane electrical and thermal conductivity, the Seebeck coefficient as well as the Hall constant of thin films. Moreover, the result is compared to our previous results of TiS_2 preparation by using CS_2 gas.

NS-TuP-6 Single-Crystal Poly(3-hexylthiophene) (P3HT) Organic Field Effect Transistor which was used to Fabricate Ammonia Gas Sensor*, **Jihee Hwang**, M Sung,* Hanyang University, Republic of Korea

An ammonia gas sensor which was fabricated based on the P3HT organic field-effect transistor (OFET) in the range of 0.01 to 25ppm. Single-crystal poly(3-hexylthiophene) (P3HT) nanowires (100 nm wide 150 nm high nanowires that were separated a 600nm space) were used as the organic semiconductor (OSC) layer of an OFET with a top-contact geometry. This ammonia gas sensor showed outstanding results such as electrical and sensitivity characteristics. First, electrical properties (high mobility, output signal and on/off ratio) of single crystal P3HT nanowire OFET were around two orders of magnitude higher than those of P3HT thin film OFET. Second, it showed enhanced ammonia sensitivity, around three times higher than conventional P3HT thin film OFET with same geometry. In addition, the reversibility of ammonia response was presented on this OFET, and constant results were obtained in the changes of humidity from 45% to 100%. These excellent performances of P3HT nanowire were presented due to high surface/volume ratio and single crystal characteristics of the P3HT nano wires.

NS-TuP-7 Synthesis of Layered TiTe Thin Films by Atomic Layer Deposition*, **Chan Young Yoo**, C Hwang,* Seoul National University, Republic of Korea

Due to increased research interest in 2-dimensional nanomaterials, single- and multi-layer transition metal dichalcogenide (TMD) nanosheets have attracted considerable attention for their potential use in the fields of catalysis, electronic switching devices, and gas sensors. [1] The key technology for utilizing TMD in various applications is a reliable fabrication of the nanosheets over a large area. Chemical vapor deposition and sulfurization have been introduced for large-area synthesis, but the high-temperature conditions adopted in these methods are not compatible with many of the device fabrication processes, especially on flexible substrates. Therefore, low-temperature atomic layer deposition (ALD) process using highly reactive precursors has been suggested as an alternative to overcome the thermal limit and to enable the practical use of TMD for electronic devices. [2]

In this report, $TiTe_2$ thin films were deposited by ALD, adopting $TiCl_4$ and $[(CH_3)_3Si]_2Te$ as the Ti- and Te-precursors, respectively. Thermally activated ligand exchange occurred at a substrate temperature of 60~200 C, and the saturated growth rate (at 180ºC) was ~15 ng·cm^{-2}cy^{-1} as shown in Figure 1. T he ALD $TiTe_2$ films grown over 180ºC showed extraordinary plate-shaped hexagonal $TiTe_2$ grains, parallel to the substrate surface, on Si substrate. They were aligned along the (001) plane, showing sharp (001) family peaks in theta-two theta X-ray diffraction (XRD) as shown in figure 2. Further confirmations of layered growth of the deposited $TiTe_2$ are analyzed by scanning electron microscopy (SEM) and Raman spectroscopy . Tilted and vertically grown plate-shaped grains were confirmed in SEM, but the amount was small, showing no peak in grazing-angle X-ray diffraction (GAXRD). This preference was more pronounced for those deposited on sapphire (0001) substrates, which is attributed to the low atomic mismatch of the same hexagonal crystal structure of sapphire and $TiTe_2$. A bottom-gate thin film transistor (TFT) structure was used to characterize the electrical properties of $TiTe_2$ TFTs. Figure 3 displays the transfer curves of the TFT, showing a typical *p*-type conduction behavior. Although the demonstrated device performance is quite low compared to other *p*-type oxide TFTs, these results demonstrate the feasibility of the atomic layer deposited TMD TFT. Further detailed discussions on such ALD deposition will be made in the presentation.

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NS-TuP-8 Effects of Vacancies on Electronic and Optical Properties of BiOCl Nanosheets*, **Yoon Myung**,* Sejong University, Republic of Korea*; W Song,* Washington University, St. Louis*; L Mehdi, N Browning,* Pacific Northwest National Laboratory*; A Krayev,* AIST-NT Inc.*; J Park,* Korea University, Republic of Korea*; L Yang, P Banerjee,* Washington University, St. Louis

In this study, we report conductivity switches from p-type of BiOCl to n-type of black BiOCl with generated oxygen vacancies by UV illumination at the exposed (001) surface. This n-type conductivity occurs by formation of oxygen vacancy at the surface of BiOCl nanosheets, confirmed by XPS spectra that oxygen vacancy gradually increasing as a function of UV illumination time. The raman spectra shows oxygen vacancy related vibration mode was rising under 2 mtorr and low temperature PL, the result reveals decreasing band edge emission of BiOCl due to high density oxygen vacancies placed under conduction band edge of black BiOCl. The oxygen partial pressure dependent electrical conductivity shows$\sigma=pO_2^{1/4.05}$ with a positive slope under low pressure region for the BiOCl and $\sigma=pO_2^{1/5}$ with a negative slope under atmospheric region for the black BiOCl.

NS-TuP-9 Novel ZnO Nanorod Ethanol Sensor using ALD Delta Doping with Al_2O_3 for Nested AZO Wrap-around Coatings*, P Lin, X Chen, K Zhang, **Helmut Baumgart**,* Old Dominion University

Metal Oxide Semiconductor (MOS) gas sensors have received significantly attentions as electronic devices for the specifics identification and concentration detection of combustible and hazardous gases. Among various semiconductor materials used in MOS gas sensors, ZnO has been widely used for gas sensor applications due to its good electrical conductivity, wide band gape of 3.37 eV, ~60 meV exciton binding energy, low cost, and high mechanical stability. Currently ZnO ethanol sensors based on nanorod structures have been extensively investigated due to their high electrochemical stability, suitable doping, nontoxicity, and high surface-to-volume ratio. ZnO gas sensors with one-dimensional nanostructures have good performance in terms of their sensing response, response time and recovery time.

In this project, Aluminum doped ZnO (AZO) thin films coated by Atomic Layer Deposition (ALD) was deposited on the surface of the ZnO nanostructure to further enhance its sensing performance. The ZnO seed layers were deposited on Si wafer by ALD with $(C_2H_5)_2Zn$ and DI water as precursors of zinc and oxygen. Hydrothermal method was carried out to grow aligned ZnO nanorods. There was a layer of Al_2O_3 as sacrificial spacer deposited on the surface of ZnO nanorods by ALD with $Al_2(CH_3)_6$ and DI water as precursors followed by an additional layer of ZnO thin film synthesized by ALD. To expose the Al_2O_3 sacrificial spacer layer, Precision Ion Polishing System was employed to remove the top cover of synthesized ZnO nanorods. Then Sodium hydroxide was applied to etch the Al_2O_3 layer to form ZnO nanorod/nanotube structure. Finally, Al doped ZnO thin films were deposited on the surface of ZnO nanorod/nanotube by ALD to further enhance its sensing performance to ethanol vapors.

The sensing performance of ZnO nanorod/nanotube to ethanol vapor was investigated by a gas sensor testing system which was home-made with a sealed reaction chamber, ethanol vapor generator, testing circuit, and controlled heating system. The gas sensor testing system interface is operated in LabVIEW program and CompactRio system from National Instruments. The resistant variances of ZnO nanorod/nanotube were measured by the home-made sensor testing system. The demonstrated sensing performance results include the sensing response comparison between ZnO nanorods and ZnO nanorod/nanotube structures before and after ALD coatings with nested AZO films at different temperatures and with various concentrations of input ethanol vapor. The response times and recovery times of ZnO nanorod/ nanotube samples before and after ALD coatings with nested AZO thin films were analyzed to investigate the sensing enhancement.

NS-TuP-10 Crystallization of Nanoparticle Shells Grown by Rotary ALD*, **Benjamin Greenberg**, J Wollmershauser, B Feigelson,* U.S. Naval Research Laboratory

Rotary ALD, wherein oxide and nitride shells are grown by ALD on nanoparticles agitated in a rotating drum, is an emerging technique for scalable production of a wide variety of core/shell nanoparticles. Due to deposition temperature limitations, the shells are typically grown in the amorphous phase. However, many applications of these particles, including batteries and structural nanocomposites, require crystalline shells. In this work we study the crystallization of ALD-grown shells by post-deposition thermal annealing, an approach rarely examined in detail in the nanoparticle ALD literature, despite the technological potential of fully crystalline core/shell nanoparticles. The crystallization temperature of nanoshells is difficult to predict due to a variety of competing effects of spheroidal geometry. For example, compared to a planar film of the same thickness, a nanoshell has more atoms at the surface but fewer atoms at the film/substrate interface. Using Al_2O_3 shells as a prototype, we investigate the dependence of crystallization behavior on shell thickness as well as underlying nanoparticle material and size. We characterize shell composition, structure, and morphology by XPS, XRD, and TEM.

NS-TuP-11 Multi-walled Carbon Nanotubes Coated by Atomic Layer Deposition of TiO_2*, Lenka Zajickova,* Masaryk University, Czech Republic*; M Elias,* CEITEC, Brno University of Technology, Czech Republic*; P Kaushik,* Masaryk University, Czech Republic*; J Michalicka,* CEITEC, Brno University of Technology, Czech Republic*; L Michal, M Michlicek,* Masaryk University, Czech Republic*; D Hegemann,* EMPA, Swiss Federal Laboratories for Materials Science and Technology

Carbon nanotubes (CNTs) coated with titanium dioxide (TiO_2) have become a promising hybrid nanomaterial for a wide range of applications, e.g. photocatalysis, gas sensors, dye-sensitized solar cells and energy storage. These nanostructures combine the high surface area and excellent thermal and electrical conductivity of the CNTs with the high photoactivity and chemical stability of TiO_2. In this study multi-walled carbon nanotubes (MWCNTs) were grown by catalytic chemical vapor deposition on Si and Si/SiO_2 substrates using Fe catalyst. They were subsequently coated by atomic layer deposition (ALD) of TiO_2 from tetrakis(dimethylamido)titanium. Since the ALD is a self-limiting surface process it is important to understand how it proceeds on the inert and nanostructured surface of carbon nanotube forest. Therefore, we tested different plasma modifications of MWCNTs surface (oxygen plasma treatment, carboxyl or amine plasma enhanced chemical vapor deposition) prior to the ALD and also compared thermal and plasma enhanced ALD of TiO_2. Pristine and modified MWCNTs were characterized by scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

NS-TuP-12 ALD on DNA Nanostructures: Application in the Synthesis of Programmably Shaped Carbon Nanostructures*, Haitao Liu,* University of Pittsburgh

DNA nanostructures are versatile templates for low cost nanofabrication. However, their applications in nanofabrication have long been limited to low temperature processes. We show that a thin film of Al_2O_3, grown by ALD, enables the high temperature cabonization of DNA into carbon nanostructures. Atomic force microscopy (AFM) data showed that carbon nanostructures preserved the shape of the DNA nanostructure. Conductive AFM measurement shows that the carbon nanostructures are electrically conductive.

NS-TuP-13 Multifunctional Ultrathin Coating Layers on Nanoparticles via Atomic Layer Deposition*, Eunyong Jang*, *T Park,* Hanyang University, Republic of Korea

Industrial applications of nanoparticles have surged recently. In most cases, however, there are difficulties in utilizing nanoparticles itself without any further processing. For example, protective layer coating on metal nanoparticles should be processed to circumvent explosive combustion reaction. Thus, need for development of multipurpose nanoparticles coating techniques, has brought great enthusiasm among researchers. Atomic layer deposition (ALD), a vapor deposition technique, has potential to produce conformal and uniform ultrathin-film on nanoparticles due to sequential self-limiting surface chemical reactions. Being capable of these unique merits, ALD can be introduced to applications including photocatalysts, cosmetics, optical quantum dots and protective layers for various nanoparticles/nanostructures. Herein, we used specially-designed ALD rotary reactor in order to address critical issues in cosmetics and photocatalysis applications. Particularly, in photocatalysis, we deposited TiO_2 and ZnS on g-C_3N_4 to reduce recombination rate of charge carriers. In addition, we studied anti-photocorrosion effect of TiO_2 passivation layer on ZnO nanoparticles. In cosmetics application, study on Al_2O_3 blocking barrier for phototoxicity of TiO_2 particles as a sunscreen ingredient was carried out. It was demonstrated that all the nanoparticles with ALD coating layer showed superior properties. Details in each work will be discussed.

NS-TuP-14 Fabrication of Hierarchically Ordered Optically Active Nanocrystal Solids by Surface Passivation using Atomic Layer Deposition of Metal Oxides*, Riya Bose,* University of Texas at Dallas

In order to achieve high efficiency in harvesting solar energy, several types of architectures and active materials have been suggested for photovoltaic devices that may surpass the Shockley-Queisser limit for single p-n junction solar cells. Nanostructured energy transfer (ET) hybrids involving quantum dots (QDs) in conjunction with Si substrate provides an attractive alternative, as excitonic ET and sensitization of Si layer by spectrally tunable QDs with high absorption coefficient eliminates the weak absorption factor in indirect bandgap Si, whereas the high carrier mobility Si component can be used for charge separation and transport. Also, ET instead of charge transfer in quantum dot media revokes the necessity of high charge carrier transport in QDs. Use of a multilayer of different sized quantum dots may further enhance the efficiency of the device by increasing the spectral absorption window. However, the bottleneck for fabrication of multilayer QD films remains the use of solution phase deposition methods, where the solvent in the subsequent step of deposition dissolves the initial layer, until each QD layer is rendered insoluble by means of any surface passivation technique. Again, surface passivation techniques also play a critical role to protect the deposited QD layers from oxidation and deterioration during long-term use. An attractive method to passivate the QD films during the deposition as well as from environmental exposure is to coat them with various metal oxides grown using atomic layer deposition (ALD). Though there are few reports of ALD encapsulation of QD films, they mostly focus on use of the same for charge transfer based devices, as well as few of them report a significant quenching of the photoluminescence intensity after encapsulation. For an efficient ET based QD-Si photovoltaic device however, removal of energy loss channels and preservation of the photoluminescence is necessary. So, we aim to investigate the exact growth mechanism of metal oxide layers by ALD on the surface of QDs and how it, along with the ALD parameters, affect their photoluminescence properties. We start with well-developed QD systems like CdSe-ZnS core-shell nanocrystals and Al_2O_3/ZnO as the metal oxide layers to study the interaction of the ALD precursors with the surface ligands of the QDs with the aid of in-situ FTIR and ex-situ XPS measurements along with the study of the photoluminescence properties of the same. We further aim to extend our study for new generation of multiexciton-bearing QDs, two-dimensional transition metal dichalcogenides and organic-inorganic perovskites, which may provide unique optoelectronic opportunities.

ALD Applications
Room 116-118 - Session AA1-WeM

Display Device and Material

Moderators: Kwang Soo Lim, LG Display, Chang-Yong Nam, Brookhaven National Laboratory

8:00am **AA1-WeM-1 Growth Of Indium Oxide Thin Films Based On A Plasma Enhanced Atomic Layer Deposition Technique***, **Joaquin Alvarado,** L Martinez,* University of Puebla, Mexico*; M Chavez,* CINVESTAV-IPN, Mexico*; S Alcantara, D Cortes,* University of Puebla, Mexico*; S Gallardo,* CINVESTAV-IPN, Mexico

Indium oxide is a wide band-gap transparent n-type semiconductor with a body centered cubic structure (a=1.012 nm) and relatively high electrical conductivity, in its non-stoichiometric form it has been widely used in the microelectronic field for gas sensors, window heaters, solar cells, memory devices, transistors, chemical and biosensors, transparent conducting electrodes, some types of batteries, hot mirrors, and also for transparent electronics [1].

It is expected that lowering the film dimensions or increasing the surface-to-volume ratio of the material can improve the performance of those applications; thus, several researchers worldwide have dedicated considerable efforts to the synthesis of In_2O_3 nanostructures such as nanowires, nanoparticles and thin films with a few nanometers of thickness [2].

Considering a homogeneous deposition, in this work we present a comparison of the growth of In_2O_3 thin films by thermal ALD and plasma enhanced atomic layer deposition PEALD at different temperatures, where we expect to get optical and/or electrically favorable layers to improve the performance of solar cells as well as a capacitor in order to use it as the base of a cost effective thin film transistor (TFT) suitable for radiation sensors (x-rays, alpha and gamma radiation) at low temperatures.

Figure 1 left shows that quite similar transmittance is obtained between In_2O_3 layers deposited by both ALD methods at the same temperature, where the ones deposited at 150ºC shows high transparent layers. Also, Figure 1 right depicts the absorbance of these layers as well as its band-gap, which is close to 3.2eV. Furthermore, Tauc plot calculation allows extracting a correct band-gap for each sample, being the layers grown by thermal ALD the ones that present higher band-gap that the ones grown by plasma. We will also present optical, electrical and elemental characterizations such as XRD, SEM, Transmittance, Reflectance, SIMS, AFM, Profilometry, C-V Curves and I-V Curves to explain the characteristics and applications of the material.

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8:15am **AA1-WeM-2 Large-Area Atmospheric Pressure Spatial ALD for Display Applications***, C Frijters, F van den Bruele, A Illiberi,* ***Paul Poodt,*** Holst Centre - TNO, Netherlands **INVITED**

Atmospheric pressure Spatial ALD (sALD) is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. First industrial applications of Spatial ALD include passivation of c-Si solar cells and roll-to-roll manufacturing of flexible barrier foils. An emerging application for Spatial ALD is flat panel (OLED) displays. Examples include semiconducting and dielectric layers for use in thin-film transistors, and thin-film encapsulation for flexible OLED displays. As today's displays are fabricated using glass panels in the order of several square meters, a remaining challenge is the development of large-area Spatial ALD deposition technology that is able to combine high throughput with uniform performance across very large areas.

We are developing large-area Spatial ALD technology, and as a first step between the lab and the display fab, we have installed a large area Spatial ALD sheet-to-sheet tool which can handle up to 400x325 mm^2 sized substrates. With this tool we are able to deposit uniform films across a deposition width of 400 mm. The whole tool is operated under an atmospheric pressure but inert N_2 environment. The tool can be used to deposit a variety of materials using both thermal and plasma-enhanced Spatial ALD.

We will present the basic deposition performance of the tool in terms of thickness- and compositional uniformity. Large-area thickness non-uniformities of less than 1% are achieved for several oxide materials. Next, we will focus on two display-related applications: thin-film encapsulation of OLED devices, and high mobility InZnO and InGaZnO semiconductors for thin-film transistors. We will explain the requirements, the deposition process and the performance of the deposited films. Finally, the challenges in up-scaling Spatial ALD to plate sizes of 1.5 m and beyond will be discussed.

8:45am **AA1-WeM-4 Amorphous Indium Zinc Tin Oxide (IZTO) Semiconductor Materials and the Associated Thin Film Transistor Properties Deposited by Atomic Layer Deposition***, **Jiazhen Sheng,** T Hong,* Hanyang University, Republic of Korea*; J Lim,* Samsung, Republic of Korea*; J Park,* Hanyang University, Republic of Korea

Oxide semiconductor thin film transistors (TFTs) have been extensively researched as a backplane technology in display industry. Comparing to the indium gallium zinc oxide (IGZO) which has been widely used as TFT active layer ma terial, indium zinc tin oxide (IZTO) has been suggested as a promising material due to its attractive performance, including relatively high mobility (>25cm^2/Vs) and superior stability. Relying on the self-limiting reaction, the atomic layer deposition (ALD) takes advantage of uniformly depositing the films over large areas with precisely controlled thickness that makes ALD become a promising technology to apply in thin film transistor, including of active layer fabrication. In this research, the ALD Sn doped IZO thin film was first investigated, which was deposited using the concept of "super-cycle" – IZO (1 cycle InOx – 1 cycle ZnO), IZTO111 (1 cycle InOx – 1 cycle ZnO – 1cycle SnOx) and IZTO112 (InOx 1 cycle – 1 cycle ZnO – 2cycle SnOx). It is found, by doping with SnOx, the band gap structure, micro-structure as well as the electrical characteristics were changed. Then, the bottom gate top contact IZO, IZTO111 and IZTO112 thin film transistors were fabricated by ALD process. The devices with Sn doped IZO active layer exhibited increased mobility (27.8cm^2/Vs for IZTO111 and 22.7cm^2/Vs for IZTO112) and stability under positive bias temperature stress (threshold voltage shift of 1.8V and 0.7V) than IZO TFTs (mobility of 18.0cm^2/Vs and threshold voltage shift of 2.2V). The flexible ALD IZTO TFT also fabricated on the PI substrate, and 200,000 cycles bending test was processed to investigate the degradation mechanism of flexible ALD TFT under mechanical stress.

9:00am **AA1-WeM-5 Evaluation of Si precursor for SiO_2 OLED Encapsulation by PEALD***, **GunJoo Park,** J Park, B Yang, S Kim, J Park, S Jang, S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

OLED devices are made up of organic compounds, which are excited to emit light due to the nature of the material. In this excited state with high energy, it easily reacts with moisture and oxygen. When the OLED element reacts with moisture and oxygen, problems such as decrease in luminance, increase in voltage, and poor emission occur.

Recently, TFE (Thin Film Encapsulation) technology has been used to overcome this problem. The OLED encapsulation technology using a thin film can provide the display flexibility and effectively prevent the infiltration of air and moisture into the organic layer of the OLED device, which is suitable as a next generation display encapsulation film.

In this paper, NSi-01 and 1N5 precursors were applied to thin film encapsulation technology for next generation OLED devices, and low-temperature SiO_2 deposition process by PEALD method was developed. In both precursors, SiO_2 deposition conditions were similar, and RF dosage experiments confirmed their suitability as ALD precursors.

High growth rate of 1.95 Å / cycle and 2.65 Å / cycle (Fig.2) and formation of pure silicon oxide film free of impurities were confirmed (Table.1).

The density of the SiO_2 thin film was 2.23 g / cm^3 (Table.2) for both precursors, and the bulk SiO_2 density was 2.6 g / cm^3, indicating that an amorphous SiO_2 thin film was formed. The encapsulation layer affects the image quality and brightness of the display when the visible light transmittance is decreased. In the case of the precursor used in this experiment, the visible light transmittance was 99% at a thickness of 700Å (Table.2). It can be seen that there is no difference in image quality or brightness after applying the encapsulation layer .

The moisture permeability, which is the core of the encapsulation layer, varies with RF time and thickness. In case of NSi-01 with a thickness of 700Å, the RF time was 0.9 seconds at 4.6×10^{-3} g / m^2-day. In case of 1N5, the RF time was 1.5 seconds at 5.0×10^{-3} g / m^2-day Sufficient RF dosage is required compared to NSi-01. However, in case of 1N5, high film growth rate was confirmed compared to NSi-01, and the actual process time was confirmed to be similar. We also confirmed the excellent WVTR characteristics of 5.5×10^{-3} g / m^2-day even at a thin thickness 500Å (Fig.6), thus confirming the possibility of the next generation OLED element encapsulation film precursor.

9:15am **AA1-WeM-6 Hydrogen Barrier Properties of ALD Al_2O_3 with Different Oxidants***, H Kim,* ***Yujin Lee****, T Nam, S Seo, C Lee,* Yonsei University, Republic of Korea*; J Yang, D Choi, C Yoo, H Kim,* LG Display

Amorphous In-Ga-Zn-O (a-IGZO) semiconductors have been used as an active channel material in high mobility, flexible, and transparent thin film transistors (TFTs), but it is highly influenced by the external environment. To protect from it, plasma-enhanced chemical vapor deposition (PECVD) SiN_x deposited using SiH_4/N_2O is commonly used as the encapsulation film. In this process, however, the amount of hydrogen was introduced to backchannel.[1] It is well known that the hydrogen in an oxide semiconductor acts as a shallow donor by ionizing and bonding with oxygen to form hydroxyl bonds. It makes the oxide TFT very conductive and causes it not to show an on/off property.[2] Therefore, appropriate hydrogen barrier is required to prevent hydrogen incorporation into the IGZO channel, but there is a lack of systematic research on it.

In this study, Al_2O_3 was deposited on the a-IGZO TFT by atomic layer deposition (ALD) using trimethylaluminum(TMA) with water or O_3, as the precursor and oxidant, respectively, at low temperature (about 60°C). First, we fundamentally investigated the characteristics of Al_2O_3 according to the oxidant. The composition of the Al_2O_3 was different depending on the oxidant used in the ALD process. Based on this, we analyzed the effect of these characteristics on hydrogen barrier properties by using transfer curve and stress test of device. As a result, the device in which the Al_2O_3 was deposited exhibited excellent hydrogen barrier properties as compared with the bare device. There was no device degradation after the hydrogen treatment, which suggested the possibility of enhancing the device reliability in mass production in the future.

Reference

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[2] S. I. Oh, G. Choi, H. Hwang, W. Lu, and J. H. Jang, “Hydrogenated IGZO thin-film transistors using high-pressure hydrogen annealing,” *IEEE Trans. Electron Devices*, vol. 60, no. 8, pp. 2537–2541, 2013.

9:30am **AA1-WeM-7 Flexible Al_2O_3/Organic Multilayer Moisture Barrier Films Deposited by Spatially Resolved ALD Processes in a Single Chamber***,* ***Sang Heon Yong****, S Kim, Y Choi, H Hwangbo, H Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Thin film encapsulation (TFE) is one of essential technologies required for flexible organic light emitting diode (OLED) display devices. It is well known that organic materials are easily damaged by moisture and oxygen when plastic films are adopted for substrates. Atomic layer deposition (ALD) processes on plastic films demonstrated superior moisture barrier property to other inorganic barrier deposition processes.[1] However, extremely low throughput of ALD processes is a big huddle for commercialization and active research on ‘spatial ALD’ process is underway to enhance throughput. [2] To improve the barrier property further and to increase flexibility of barrier films simultaneously, various multilayer structures have been reported with various inorganic and organic layers. Since the multilayer structure consists of several thin films, the diffusion path of the barrier film can be increased and flexibility can be increased by reducing the bending stress of thin films. [3]

In this study, we deposited Al_2O_3 and organic layers in a single spatially-resolved processing chamber and demonstrated multilayer structures to achieve high barrier property and flexibility. The water vapor transmission rate (WVTR) of Al_2O_3 single thin films decreases significantly above 10nm thickness as shown in Figure 1. Organic layers were also deposited in the same chamber by plasma-enhanced chemical vapor deposition. About 20nm or thicker organic layers are required to improve the barrier film flexibility in this experiment. The total of 21 layers of Al_2O_3 and organic layers are deposited alternately and WVTR of 8.5 10^{-5} g/m^2·day was achieved. The WVTR increases by 10%, 21% and 32% in 3cm, 1.5cm and 1cm bending radius, respectively.

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9:45am **AA1-WeM-8 Optimization of Film Structure by Stress Engineering for Flexible Thin Film Encapsulation***,* ***Ju-Hwan Han****, D Choi, J Lee, K Han, J Park,* Hanyang University, Republic of Korea

Flexible electronics are focused recently as future-oriented devices such as light emitting device, sensing device and photoelectric cell. One of critical issues is a rapid degradation by oxygen and water vapor in flexible organic light emitting diodes (OLEDs) devices. Thus, thin film encapsulation (TFE) process is highly recommended to protect the OLEDs from water vapor and also preserve their flexibility. The inkjet printing and PECVD methods have been comerciallized to make orgniac/inorganic hybride layer. Unfortunately, they have some limits on flexible OLEDs; not only poor step coverage and particle issues but also cracking films under mechanical stress conditons. Atomic Layer Deposition (ALD) can be a promising candidate to solve the above issues.

In this study, we optimized the TFE layer via the stress engineering using organic/Al_2O_3 ALD hybrid films. In order to suggest optimized structure for flexible gas diffusion barrier layer, we investigated water vapor transmission ratio (WVTR) of the layer under the bending stress as a function of thickness of substrate, thin film and additional layer on the thin film. With additional layer of similar thickness to the substrate, the degradation of TFE layer is minimum (W/W_0 ~ 1.08, bending radius of 2.5mm). And there was almost no degradation of TFE layer with more than 2 dyads of organic/Al_2O_3 layer (W/W_0 ~ 1.01, bending radius of 2.5mm). As a result, optimized TFE layer structure using inorganic/organic layer showed not only improved moisture barrier property, but mechanically robust behavior after bending stress.

ALD Applications
Room 116-118 - Session AA2-WeM
Flexible Application

Moderator: Jin-Seong Park, Hanyang University

10:45am **AA2-WeM-12 A Condense Polymer-inorganic Hybrid Nanolayer with Extremely Low Gas Transmission Rate Behavior and Ultra-flexible Nature***,* ***Myung Mo Sung****,* Hanyang University, Republic of Korea

Hermetic sealing is an important technology to isolate and protect air-sensitive materials, and a key issue to develop foldable and stretchable electronic devices. We reported an ultrahigh gas-proof polymer hybrid nanolayer, prepared by filling the free volume of the polymer with Al O by using gas-phase atomic layer infiltration. The free-volume-free polymer-inorganic hybrid shows extremely low gas transmission rate behavior, which is below the detection limit of the Ca corrosion test (< 10 g m day). Furthermore, due to the ultra-thin complete hybrid of polymer-inorganic materials, the polymer hybrid nanolayer has ultra-flexible nature, which is useful as hermetic sealing for stretchable and foldable electronic devices.

11:00am **AA2-WeM-13 SiN-Al_2O_3 Nano-laminates Fabricated with Combination of CVD-ALD Method for Encapsulation of Highly Stable Flexible OLED Electronics***,* ***Huizhi Yang****, Y Li, Y Liu, K Cao,* Huazhong University of Science and Technology, China*; H Hsu, J Huang,* Wuhan China Star Optoelectronics Technology Co., Ltd (CSOT), China*; R Chen,* Huazhong University of Science and Technology, China

The expansion demand for wearable and flexible electronics based on organic light emitting diode (OLED) displays have attracted great attention. Flexible OLED displays, however, widely utilize materials that are sensitive to oxygen and water which causes performance degradation or failure during usage. It is imperative to develop reliable and efficient thin film encapsulation methods to improve the stability and meet the requirements of miniaturization, flexibility and low cost.

This work focuses on the design and fabrication of nano-laminates SiN-Al_2O_3 encapsulation films for high stable flexible OLED electronics with the combination of plasma enhanced chemical vapor deposition (PECVD) and spatial separated atomic layer deposition (S-ALD) methods. SiN layer is deposited on OLED devices with ~1 um thickness via PECVD, after which ~20 nm Al_2O_3 is deposited on the SiN layer with S-ALD. The service life of encapsulated devices is tested under heat/humid environment. The failure time of nano-laminates SiN-Al_2O_3 encapsulated device is enhanced ~10 times compared with SiN or Al_2O_3 coating alone. The coating layers configurations play an important role in determining the encapsulation ability. It is found that the SiN layer fabricated by PECVD contains large amount of pinholes and defects. After very thin layer of Al_2O_3 deposited, most of defects are passivated and the water-oxygen resistance ability is enhanced significantly.

11:15am **AA2-WeM-14 Thermoelectric Device Based on ALD/MLD-grown ZnO and ZnO:benzene Thin Films on Flexible and Textile Substrates***, **Giovanni Marin**, M Karppinen,* Aalto University, Finland

We have fabricated simple flexible thermoelectric devices on different substrates, such as plastics, flexible glass and different textiles, using ALD-grown ZnO and ALD/MLD-grown coatings as the active thermoelectric materials. In the hybrid ZnO:benzene superlattice thin films monomolecular benzene layers are inserted in between ZnO blocks of varying thicknesses to block the thermal conductivity.[1], [2]

The thermoelectric performance of the devices with the different ZnO and ZnO:benzene layer structures were tested with an applied (cross plane) temperature varying between 30 and 100°C at the bottom side of the substrate. The voltage generated by the device with the varying temperature was measured for both open-circuit and with a load of 1.4 Ω. The hybrid ZnO:benzene devices exhibited enhanced performances compared to those based on plane ZnO.

The final goal of our work is in wearable devices fabricated on textile. Such devices would enable energy harvesting from human body heat to power small sensors (constant medical monitoring) without the need of changing batteries. The current results based on simple model device architectures have provided us useful knowledge and guidelines towards this final goal.

11:30am **AA2-WeM-15 Transparent Graphene Heater Improved by Defect Healing of Metal Atomic Layer Deposition***, **Hyun Gu Kim**, W Kwon, T Im, M Khan,* Incheon National University, Republic of Korea*; H Choi,* Yonsei University, Republic of Korea*; W Kim,* Chonbuk National University, Republic of Korea*; J Chung,* Soongsil University, Republic of Korea*; H Lee,* Incheon National University, Republic of Korea

Graphene has been widely applied for various applications, such as flexible display, energy device, and transparent electrode due to its superior properties over bulk materials in transparency, flexibility, and electrical conductivity. Until now, many methods to synthesize graphene have been reported, such as physical exfoliation, epitaxy, chemical vapor deposition (CVD), and chemical reduction of graphene oxide (GO). Since the chemical reduction of GO has a high rate of obtaining graphene as a single layer, it can be used in a wide variety of applications through the formation of a complex with other materials as well as high compatibility with mass production. In many cases, however, the reduced GO (RGO) is not completely reduced and many defects are left, so there is a disadvantage that reliability such as electrical properties is deteriorated. When the GO is reduced to RGO, the functional groups of the graphene surface remain or are not restored to the original structure of the graphene. In order to avoid such problem, researches for improving the conductivity by healing defects of RGO have been reported in recent years. In this study, a selective metal deposition process by atomic layer deposition (ALD) was applied on the surface of RGO to study the defect healing of RGO. Since the ALD process involves deposition only through a surface reaction, it is able to perform selective deposition at defective sites that have a relatively high energy. The surface coverage of Pt deposited on RGO was analyzed by using various analytical methods, including field emission electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS), and THz spectroscopy. In order to confirm the defect healing effect, the thermal characteristics of the heater were prepared by using a transparent graphene heater before and after healing the defect. In addition, the self-healing of damaged self-healing polymers was studied suing the thermal properties of the heater.

11:45am **AA2-WeM-16 Surface Modification Studies and Stabilization of Perovskite Quantum Dots with Atomic Layer Deposition***, **Binze Zhou**, Q Xiang, K Cao, R Chen,* Huazhong University of Science and Technology, China

Perovskite quantum dots (QDs) have received extensive attention for potential display applications, due to their excel lent prop erties for high photoluminescence, tunable wavelength, and narrow emission wavelength [1]. However, perovskite QDs are very sensitive to air, and hot/humid atmosphere which tend to failure in practical applications.[2,3] In this work, atomic layer deposition (ALD) is applied to modify and encapsulate the surface of perovskite QDs with thin layers of oxides to enhance the stability during usage. To study the surface interaction mechanisms of ALD precursors with the ligands of perovskite QDs, in-situ characterizations such as quartz crystal microbalance (QCM), infrared spectrometer (IR) are applied to monitor the ALD process. It is found that process parameters, such as deposition temperature, precursors and pulse time are critical to its surface modification behavior. Higher temperatures resulted in etching or replacing the surface ligands of perovskite QDs by ALD precursors. At room temperature, the perovskite QDs films can be stabilized effectively with just few cycles of oxide passivation, and the light emitting diode's performance has also enhanced.

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ALD Applications
Room 107-109 - Session AA3+AF+EM-WeM
AA+AF+EM

Moderator: Iian Buchanan, Versum Materials, UK

8:00am **AA3+AF+EM-WeM-1 Fabrication of TiO_2 Interconnected Nanotubes by ALD and Synthesis of g-C_3N_4/Au/TiO_2 Heterostructure for Photocatalytic Water Splitting***, **Li-Chen Wang**, L Tsai, C Liu, T Perng,* National Tsing Hua University, Republic of China

Recently, the catalysis science has ascended to a new horizon due to the advent of novel nanotechnologies such as atomic layer deposition (ALD) with the capability of fabricating a marvelous panoply of nanomaterials. The sequential and self-limiting gas-solid surface reactions of the ALD process enable to deposit extremely conformal and ultrathin film on a wide variety of templates, favoring the innovative design of various nanostructured photocatalysts. Herein, we report a controllable fabrication of a hybrid photocatalyst comprising graphitic carbon nitride (g-C_3N_4), Au nanoparticles, and TiO_2 hollow fibers for photocatalytic water splitting. Titanium tetrachloride ($TiCl_4$) and H_2O were used as precursors for the ALD process to uniformly deposit a thickness-controllable TiO_2 thin film on hollow polysulfone fibers (PSFs). In order to minimize the e^--h^+ pair recombination, the TiO_2 hollow fibers were further decorated with Au nanoparticles by chemical reduction and then coated with a g-C_3N_4 nanolayer by pyrolysis of urea at a certain elevated temperature. For comparison, Au/TiO_2 hollow fibers and Au/g-C_3N_4 nanosheets were also prepared and individually used as photocatalysts for water splitting. It was demonstrated that the photocatalytic efficiency of the g-C_3N_4/Au/TiO_2 heterostructure could be influenced by the thickness of the TiO_2 thin film which can be tailored by the ALD cycle number. TiO_2 with perfect conformality on the porous PSF template also offers a large surface area of the hybrid catalyst and efficient trapping of the reflected photons within the interconnected nanotubes of the hollow fibers. More importantly, the surface plasmon resonance (SPR) effect of Au nanoparticles and the g-C_3N_4/Au/TiO_2 heterostructure that could effectively increase the separation of e^--h^+ pairs further enhance the photocatalytic efficiency of g-C_3N_4/Au/TiO_2 for water splitting when compared to those of Au/TiO_2 and Au/g-C_3N_4.

8:15am **AA3+AF+EM-WeM-2 Nano-energetic Materials Fabricated by Atomic/Molecular Layer Deposition***, **Hao Feng**,* Xi'an Modern Chemsitry Research Institute, China

As key components to improve energy densities, metal nanoparticle based energetic materials are widely used in many energetic systems, for example, as additives for propellants and explosives. Metal nanoparticle based energetic materials have fairly large surface areas and are extremely reactive. Proper surface modification improves the safety and stability of these materials and may also enhance their energy releases. By applying atomic layer deposition (ALD) or molecular layer deposition (MLD), surfaces properties of the metal nanoparticles can be dramatically changed and their energy release patterns can be effectively tuned at minimum losses of the energy densities.

Zr nanopowder is a very promising high energy metal fuel. However, this material is extremely sensitive to electrostatic discharges, which greatly jeopardizes its applications. By applying ALD/MLD surface modification, metallic Zr nanoparticles can be encapsulated by uniform layers of metal oxides, polymers, or carbon. The thicknesses of the encapsulation layers can be precisely controlled. The electrostatic sensitivity of Zr nanoparticles can be tuned in a wide range by varying the type and thickness of the ALD coating, which significantly enhances the safety in handling, storage, and utilization of this high energy material.

Metal nanoparticle based thermite materials feature very exothermic solid-state redox reactions. However, reaction rates of traditional thermite mixtures are limited by reactant diffusion velocities. Core-shell structured nanothermite materials can be synthesized by depositing certain types of metal oxides (oxidizers) on Al nanoparticles. The oxidizer layers deposited on the Al nanoparticles are conformal and their thicknesses can be precisely controlled by adjusting the number of ALD cycle. Reaction rates of the core–shell structured nanothermites synthesized by ALD are several times faster than the mixture of nanopowders. The enhanced reaction rate is ascribed to the intimate fuel-oxidizer contact as a result of the exquisite core–shell nanostructure and excellent conformity of the oxidizer shells.

8:30am **AA3+AF+EM-WeM-3 Atomic Layer Deposition of Alumina on Lactose Particles for Modified Release: Effect of Co-reactants and Substrate Crystallinity***, **Damiano La Zara,*** Delft University of Technology, Netherlands*; D Zhang, M Quayle, G Petersson, S Folestad,* AstraZeneca, Sweden*; J van Ommen,* Delft University of Technology, Netherlands

Atomic layer deposition (ALD) is an established technique for the synthesis of thin films for various applications ranging from semiconductors to energy storage devices. Recently, it has been gaining attention in the pharmaceutical field to modify the particle properties, for example the drug release. Compared to the conventional methods of drug particle coating, ALD has a number of advantages: control over the amount of deposited material, conformality, and its solventless nature. A few studies about ALD of metal oxides, including Al_2O_3, TiO_2 and ZnO, on acetaminophen, lactose and budesonide particles showed that the deposition of nanoshells can effectively slow down the drug release. However, the dependence of the film growth on pharmaceutical particles on the ALD operating conditions has not yet been investigated. Furthermore, the relationship between the properties of the coating (e.g, uniformity, conformality) and the dissolution behaviour of the resulting core-shell structures is not clear. Therefore, as the dissolution profile strongly depends on the coating quality, understanding how process parameters (e.g., number of cycles, co-reactants and substrate surface) affect the coating uniformity and conformality is crucial.

In this work, we study the effect of co-reactants, namely H_2O and O_3, on the Al_2O_3 growth on two kinds of lactose particles (i.e., fully crystalline lactose and crystalline lactose with micronization-induced amorphous surfaces) and evaluate the dissolution behaviour. The ALD process is carried out at ambient conditions in a fluidized bed reactor for a low number of cycles (i.e., from 4 to 14) using trimethylaluminum (TMA) as a metal precursor. Time-of-flight secondary ion mass spectrometry and Transmission Electron Microscopy (TEM) show that TMA/O_3 ALD on crystalline lactose particles offers greatly improved control over the coating uniformity and conformality compared to TMA/H_2O ALD. In fact, by causing severe agglomeration of the particles, water deteriorates the fluidization quality and thus the homogeneity of the coating process. In-vitro dissolution tests reveal more sustained release for the O_3-based process than for the H_2O-based one, thus underlining the benefit of O_3 in providing uniform and conformal coatings. However, little to no difference between TMA/O_3 and TMA/H_2O ALD is observed on lactose particles with amorphous surfaces. In fact, such amorphous surfaces firstly are inherently inhomogenous across the particles and secondly present micropores, as suggested by BET measurements. This inevitably leads to non-conformal films regardless of the co-reactant and moreover results in both surface and subsurface growth.

8:45am **AA3+AF+EM-WeM-4 A High Vacuum Plasma Enhanced Atomic Layer Deposition System for Depositing Very Reactive Metals***, **Feng Niu,*** SVT Associates, Inc.

Most of metal elementals deposited by ALD or PEALD so far are less electropositive or relatively stable. Very reactive metals which are defined as highly electropositive elements(electronegativity c <1.8) including alkaline, alkaline earth, group III, some transition and rare earth metals are needed for applications such as batteries, improved adhesion, barriers, etc.. However they have been proved very difficult to deposit in a conventional thermal ALD or PEALD reactor due to thermodynamic limitation, impurity requirements and unavailability of proper precursors and reducing agents.

A new high vacuum PEALD system achieving base pressure at level of 10^{-8} Torr range with a high efficiency hydrogen plasma source was developed and applied to deposit highly reactive metals. The system has demonstrated deposition of pure Mg metal using commercially available Bis(ethylcyclopentadienyl) magnesium ($Mg(CpEt)_2$).[1] Self-limiting performances of Mg was evaluated(Figure1).Results for film characterizations such as surface morphology by atomic force microscopy (AFM), and film composition especially O impurity by x-ray photon-electronic spectrometer (XPS) (Figure2) will also be presented. A binary sequence surface chemistry is suggested that the hydrogen radicals serve to strip the ligands from the metal precursor according to the general overall reaction scheme: $Mg(CpEt)_2+H_2$*--Mg+2HCpEt.

This system should also be excellent for deposition of many other very reactive metals such as Sr, Ba, Ti, Nb, Zr, Hf, Li, Na, etc., and for borides, carbides and nitrides where the materials are extremely sensitive to contaminants such as oxygen, moisture, carbon oxides, etc…

[1] US patent # US 9828673 B2.

9:00am **AA3+AF+EM-WeM-5 Plasma Properties of High Pressure ALD***, C Qu,* University of Michigan*; **Pulkit Agarwal**, Y Sakiyama, A LaVoie,* Lam Research Corp.*; M Kushner,* University of Michigan

Plasma enhanced atomic layer deposition (ALD) of high quality dielectric films ultimately depends on controlling the fluxes of plasma produced reactive species onto the substrate and into features. In a typical plasma enhanced ALD cycle of SiO_2, the Si-containing precursor is usually deposited in a non-plasma environment. The oxidation step is then conducted by an oxygen containing plasma such as Ar/O_2. In order to produce high fluxes of the oxidizing radicals, which requires high power deposition, while having ion energies onto the wafer with below-damaging energies, the capacitively coupled plasmas are typically operated at pressures of many Torr. Theses pressures with high power produce high radical fluxes, while the collisional nature of the sheath results in low ion energies. There are several challenges in optimizing this system, including uniformity of reactant fluxes, controlling ion energies and minimizing damaging UV/VUV fluxes.

Results from a computational investigation of high pressure capacitively coupled plasmas designed for plasma enhanced ALD of SiO_2 will be discussed, with the goal of providing insights to the tradeoffs to simultaneously optimizing deposition conditions. Consequences of varying fluxes on uniformity of deposition in moderate aspect ratio features will also be discussed. The modeling platforms used in this study are the Hybrid Plasma Equipment Model (HPEM) and the Monte Carlo Feature Profile Model (MCFPM). The example system uses Ar/O_2 mixtures at pressures of 1-5 Torr, with power deposition of up to a few kW. The fundamental plasma properties of this operating regime (e.g., plasma and radical densities, electron temperature, reactive fluxes to the substrate, sources of ionization), ion energy and angular distributions (IEADs) to the substrate will be discussed. Feature scale modeling will correlate the reactive fluxes to deposition uniformity.

* Work supported by LAM Research Corp. and the DOE Office of Fusion Energy Science.

9:15am **AA3+AF+EM-WeM-6 Remote Plasma Atomic Layer Deposition of Gallium Oxide Thin Films using Trimethylgallium and Oxygen Plasma***, H Hao, Y Shen, J Zhang, **Xiao Chen,*** Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, China

Because of its large band gap and many other excellent properties, gallium oxide (Ga_2O_3) is being considered as an important oxide semiconductor for large power transistors, UV optoelectronics and solar cells, etc. Particularly, amorphous Ga_2O_3 is now attracting great interest as gate dielectric and surface passivation layer in transistors. In this work, we have deposited high quality Ga_2O_3 thin films by remote plasma atomic layer deposition (RP-ALD) with trimethylgallium (TMGa) and oxygen plasma. The deposition rate was constant at 0.36Å/cycle within a wide process window from 100 to 400 ℃. X-ray photoelectron spectroscopy (XPS) indicates the presence of gallium, oxygen, and carbon elements with content of ~37.4, ~54.5 and ~8.1 at % respectively in the Ga_2O_3 thin films deposited on silicon substrate at 250℃. The carbon impurity in the film was reduced by ~ 34% comparing with previous reported results[1]. Atomic force microscopy shows smooth surface morphology with a small root-mean-square roughness of 0.156nm. Furthermore, Ga_2O_3 films were successfully deposited on silicon, sapphire and GaN surfaces, indicating the low substrate selectivity that is beneficial to the III-V device fabrication . X-ray diffraction reveals no any crystallization happened in the amorphous Ga_2O_3 films after annealed at a high temperature up to 900℃, under O_2 atmosphere for 90 sec in a rapid thermal annealing system. The excellent thermal stability and high uniformity of Ga_2O_3 thin films deposited by RPALD are very critical to further improve the stability of III-V devices.

Reference:

1. Donmez, I.; Ozgit-Akgun, C.; Biyikli, N. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2013,** 31, (1), 01A110.

9:30am **AA3+AF+EM-WeM-7 Impact of Substrate Biasing during Plasma-enhanced Atomic Layer Deposition on Dielectric Breakdown of Al_2O_3 Thin Film*, Hyun Soo Han*,** *M Winterkorn, Y Kim, K Lee, T Yong, K Bae, W Park, P Schindler, F Prinz,* Stanford University

The plasma as reactants in atomic layer deposition process enables a great flexibility in processing conditions and a wide spectrum of material properties. In this study, we demonstrate the tunable electrical property of Al_2O_3 thin film through the substrate biasing during the plasma-enhanced atomic layer deposition. We modulate the substrate bias voltage from 0 to 150 V and evaluate its impact on growth per cycle, mass density and electrical breakdown strength. By applying substrate bias of ~ 20 V during the deposition, an impressive breakdown strength of 0.96 V/nm is achieved, which is approximately 11% higher value than that of the film prepared without substrate bias. Our results demonstrate that the plasma energy control via substrate biasing in the plasma-enhanced atomic layer deposition process is able to be a promising technique in optimizing materials' properties for various electronic or optoelectronic devices.

9:45am **AA3+AF+EM-WeM-8 Growth Mechanism of High-k Y_2O_3 on GaAs(001)-4×6 using *in-situ* Cycle-by-Cycle ALD and Synchrotron Radiation Photoelectron Spectroscopy***, C Cheng,* National Chia-Yi University, Republic of China*; **Wan-Sin Chen**, Y Cheng, L Young, H Wan,* National Taiwan University, Republic of China*; C Yang,* National Tsing Hua University, Republic of China*; K Lin,* National Taiwan University, Republic of China*; T Pi,* National Synchrotron Radiation Research Center, Republic of China*; J Kwo,* National Tsing Hua University, Republic of China*; M Hong,* National Taiwan University, Republic of China

Atomic layer deposited (ALD) high-k dielectrics on semiconductors with thickness from sub-monolayer (ML) to nano-meter (nm) has become a norm in the fabrication of metal-oxide-semiconductor field-effect transistors (MOSFETs).[1,2] The high-performance nano-electronic devices demand scaled-down nm thick oxide layers. Moreover, a low interfacial trap density (D_{it}), the most critical property for the device, depends on the initial oxide growth on semiconductor. Literature contains many studies on ALD oxide films on semiconductors, but few studies have investigated the oxide growth mode in the embryo stage. Thus, the present investigation is motivated to reach the fine region of a single precursor molecule in contact with a single surface atom of a semiconductor substrate. We specifically selected the system of ALD-Y_2O_3 on freshly molecular beam epitaxy (MBE) grown pristine GaAs(001)-4x6. The oxide film is a single-domain single-crystalline cubic phase with a surface normal (110).[3,4] The D_{it} is low of mid 10^{11} $cm^{-2}eV^{-1}$, having a flat D_{it} distribution within the GaAs band gap without a peak bulge in the mid-gap.[5] We have studied the interfacial electronic structure with the film sub-ML to nanometers thick using *in-situ* synchrotron radiation photoelectron spectroscopy (SRPES). In this talk, we will present the growth mechanism of ALD-Y_2O_3 adsorption on GaAs(001)-4×6 with different cycles of deposition in an atomic scale. The pristine p-type MBE-GaAs(001)-4×6 surface was grown in an integrated ultra-high vacuum (UHV) growth/analysis system.[6] After each MBE and ALD deposition, the sample was *in-situ* transferred to National Synchrotron Radiation Research Center (NSRRC) for SRPES measurements with a UHV portable chamber, in which the vacuum is maintained below 5×10^{-10} torr. In the embryo stage, we found that $Y(EtCp)_3$ precursors mainly undergo a charge transfer to the faulted As atoms on the GaAs(001)-4x6 surface. Upon H_2O co-reactant deposition, followed N_2 purge, the footed As atoms are readily removed. Moreover, the oxygen atoms in H_2O take over the bonding role with the underneath Ga atoms and lines of Ga-O-Y bonds stabilize the Y_2O_3 film on the GaAs substrate. After one-monolayer Y_2O_3 formed, the coordinatively unsaturated Y-O pairs of Y_2O_3 open the next ALD cycle of alternated $Y(EtCp)_3$ and H_2O process.

[1] J. W. Elam *et al*., *Chem. Mater.*15, 3507 (2003).

[2] M. Retala and Markku Leskelä, *Handbook of Thin Films* Volume 1, 103 (2002).

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

[4] S. Y. Wu *et al*., *Microelectron. Eng.***147**, 310 (2015).

[5] T. W. Chang *et al*., *Microelectron. Eng.***178**, 199 (2017).

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

ALD Fundamentals
Room 113-115 - Session AF1-WeM
Plasma ALD I

Moderators: Dennis Hausmann, Lam Research, Jonas Sundqvist, Fraunhofer Institute for Ceramic Technologies and Systems IKTS

8:00am **AF1-WeM-1 Role of Low and Medium Energy Ions in PEALD Processes*, Marceline Bonvalot*,** *C Vallée, S Belahcen, V Pesce, A Chaket,* LTM-UGA, France*; R Gassilloud,* CEA-Leti, France*; P Gonon, A Bsiesy,* LTM-UGA, France

Plasma assistance in ALD has proven to be of primary importance for the production of materials with improved properties as compared to standard ALD. Indeed, Plasma Enhanced ALD (PE-ALD) enables efficient impurity removal, improved control of film stoechiometry, higher deposition rates through reduction of purge time, lower substate temperatures and a wider choice of precursors. Moreover, ionic or radical species produced in the plasma can induce reactions which cannot occur under standard thermal ALD conditions. The plasma step in PEALD can also be used as a method for in-situ surface treatment to modulate the nucleation time of precursors on different substrates. This last point has proven to be attractive for the direct selective growth on patterned surfaces [1].

But high energy ion bombardment from the plasma may also induce damages on materials properties and make it difficult to obtain conformal films in high aspect ratio features, thus loosing a key ALD asset. This can be limited with remote plasma sources or by using an intermediate grid between the two electrodes of a capacitive discharge. However, medium/low energy ions and associated fluxes are thereby significantly reduced, even if they may positively contribute to materials properties.

In PECVD, this problem is solved with ICP sources and substrate biasing, but a similar set-up in PEALD has been seldom reported: Profjit et al [2] have shown that substrate biasing in PEALD helps tailor metal oxide properties. Here, we have investigated the specific impact of low/medium energy ions (10-100 eV) on 15 nm TiN and TiO_2 properties for microelectronic applications. These investigations have been carried out in a FlexAL PEALD tool equipped with an ALE (Atomic Layer Etching) bias system developed by Oxford. A very low power (1-10 W) can be applied on the substrate to allow low DC self-bias voltage determining ion energies. Plasma active species are identified by in-situ Optical Emission Spectrometry and growth is monitored by in-situ spectroscopic ellipsometry. The impact of ion assistance on TiO_2 insulating or TiN conducting properties (measured by 4 point probe) is discussed and related to film microstructural properties (density, crystallinity). Finally, the advantages of ion assistance for conformal thin film processing (mainly metallic) in high aspect ratio structures is presented.

[1] : R. Vallat et al.*Journal of Vacuum Science & Technology* A 35, 01B104 (2017); doi: 10.1116/1.4965966

[2] : H.B. Profijt et al. *ECS Trans*. 50 (2013) 23-34

8:15am **AF1-WeM-2 Energetic Ions during Plasma ALD and their Role in Tailoring Material Properties*, Tahsin Faraz*,** *K Arts,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, UK*; S Karwal, E Kessels,* Eindhoven University of Technology, Netherlands

The contribution of highly reactive radicals towards film growth is a well-known feature of plasma-enhanced ALD (PEALD). On the other hand, the ions generated by the plasma can also play a significant role in PEALD which has been relatively less explored. The extent to which ions can influence the deposition process depends on a variety of ion characteristics. Recently, we demonstrated how material properties of oxides and nitrides grown using PEALD at fixed temperatures can be tailored by controlling ion energies with RF substrate biasing.[1] In this contribution, we report on the measurements of ion energy characteristics to investigate their role in tailoring material properties.

We analyzed ion energy distributions (IEDs) of plasmas typically used for PEALD (e.g. O_2, H_2, N_2, etc.) in a commercial 200-mm remote inductively-coupled-plasma (ICP) ALD system equipped with RF substrate biasing. IEDs were measured using a gridded retarding field energy analyzer (RFEA) for plasma exposures without and with substrate biasing. Performing such measurements is essential towards understanding how a given PEALD process can be influenced by energetic ions. PEALD with substrate biasing yielded relatively broad IEDs with low and high energy peaks centered at high energies in contrast to narrow single peaks centered at ≤30 eV observed for PEALD without any biasing. This showed how a growing film surface in RF-biased plasmas is subject to a range of ion energies, ΔE, where the maximum ion energy, $E_{i,max}$, can significantly exceed the mean ion energy, $<E_i>$. On the basis of such studies, we determine the ion energy regimes that induce changes in material properties at a constant deposition temperature. Furthermore, varying the duration of RF substrate biasing applied during plasma exposure can alter the total energy dose of ions per cycle, $E_{i,dose}$, which was also demonstrated to be a factor influencing the deposition process.

Analyzing growth rate and properties (e.g., density, refractive index, resistivity, etc.) of several materials as a function of the aforementioned parameters derived from IEDs has provided more insight on the relation between ion characteristics and the ensuing properties, e.g., identifying ion energy thresholds between property improvement and degradation. Datasets will be presented for relevant material examples illustrating how controlling ion energy characteristics during PEALD provides a platform for synthesizing thin-films with desired properties.

[1] Faraz *et al.*, Tuning Material Properties of Oxides and Nitrides by Substrate Biasing during Plasma-Enhanced ALD on Planar and 3D Substrate Topographies, *ACS Appl. Mater. Interfaces* **10**, 13158 (2018)

8:30am **AF1-WeM-3 Role of Plasma Chemistry on Structure and Properties of Low Resistivity PEALD TiN Films**, ***Igor Krylov***, *D Ritter, M Eizenberg,* Technion - Israel Institute of Technology, Israel

Titanium nitride (TiN) is probably the most popular metal grown by atomic layer deposition (ALD). The commonly used titanium precursors for TiN ALD growth are metalorganic compounds and volatile halides. Halide precursors (e.g. $TiCl_4$) allow deposition of highly crystalline TiN films with low resistivity at both thermal activated (~200 µOhm·cm) and plasma-enhanced (~150 µOhm·cm) regimes. However, the deposited films suffer from halide contamination leading to degradation of microelectronic devices. At the same time, halide contamination isn't present in TiN films deposited by metalorganic precursors. However, these films are often amorphous (or with poor crystallinity) and exhibit high oxygen contamination. Consequently, such films result in higher electrical resistivity, compared to the films deposited using the halide precursors.[1]

Recently, we reported plasma enchased (PE) ALD process resulting in low resistivity (~100 µOhm·cm) TiN film. These films were deposited from the TDMAT precursor and $N\text{-}_2$/Ar plasma mixture.[2] Such resistivity is comparable or even lower than that reported for PEALD processes using halogen based precursors.[1]

Here, we will report the effect of reactive gas (N_2, NH_3, H_2 or N_2/H_2) on the structure and properties of PEALD TiN films, grown from the TDMAT precursor. We will show that grain orientation of TiN can be tuned by both plasma chemistry and substrate choice. Consequently, deposition of either (001) or (111) single oriented TiN films may be obtained (Fig. 1 and 2). Such single oriented TiN films serve as effective "seed" layers for subsequently grown ALD films (Fig. 3). Effect of substrate (Al_2O_3, HfO_2, TiO_2, Ta_2O_5, MoO_x, WO_3, SiO_2) and plasma chemistry on the preferential orientation of TiN films will be discussed (Fig. 4). Based on experimental data, a qualitative model of TiN nucleation and growth will be presented for the PEALD process.

Plasma gas has a strong effect on TiN film quality (Fig. 5). The lowest resistivity of ~80 µOhm·cm was obtained for TiN films deposited from NH_3 plasma. In addition, NH_3 plasma results in the highest TiN deposition rate. The superior characteristics achieved by NH_3 plasma will be discussed.

References:

[1] V. Miikkulainen, M. Leskela, M. Ritala and R.L. Puurunen, J. Appl. Phys. **113**, 021301 (2013)

[2] I. Krylov, E. Zoubenko, K. Weinfeld, Y. Kauffman, D. Ritter, and M. Eizenberg, J. Vac. Soc. Technol. A (in preparation, 2018)

8:45am **AF1-WeM-4 Effect of Oxygen Plasma and Growth Temperature on the Densification of Plasma-Enhanced Atomic Layer Deposited Silicon Dioxide Film**, ***Donghyuk Shin***, *H Song, H Park, D Ko,* Yonsei University, Republic of Korea

Silicon dioxide (SiO_2) has been widely used in silicon-based electronics for various applications. In particular, plasma-enhanced atomic layer deposition (PE-ALD) technology for SiO_2 film has attracted attention due to its high film uniformity, conformality and excellent step coverage compared to conventional thermal oxidation process. In addition, plasma exposure step in PE-ALD cycle enabled a low-temperature process by promoting the chemical reaction between the reactant gas and precursor. However, film properties of plasma-enhanced atomic layer deposited low-temperature SiO_2 such as wet etch rate (WER) differs from high-temperature thermal oxide. Several researchers have proposed post thermal annealing or plasma treatment to improve the quality of PE-ALD SiO_2 film [1,2]. Nevertheless, it is not clear yet how oxygen plasma treatment or growth temperature affects the densification of the PE-ALD SiO_2 films, especially at low temperatures of 200°C or below.

In our experiments, PE-ALD SiO_2 films, using Di-isopropylaminosilane ($SiH_3N(C_3H_7)_2$), namely DIPAS) as a Si source, were deposited on Si (100) substrates at various temperature of 50, 100 and 200°C with different in-cycle O_2 plasma (RF, 27.12MHz) time. O_2 plasma power was 400W and reactor pressure was maintained at 2 torr. Post plasma treatment was also executed to examine the film densification effect.

The thickness of SiO_2 films were measured by Spectroscopic ellipsometry (alpha-SE model, J. A. Woollam Co. Ltd.) to evaluate growth per cycle (GPC) and WER. Wet etch test was carried out using 100:1 dilute hydrofluoric (DHF) solution maintained at 22°C and a WER of a thermal oxide was found to be 1.0 Å/sec. As shown in Fig. 1, GPC of the SiO_2 film decreases as with the process temperature and in-cycle O_2 plasma time. WER also decreased with increasing process temperature and in-cycle plasma time, showing much greater decrease along with in-cycle plasma time. In addition, X-ray reflectivity (XRR) analysis was conducted to confirm the film thickness measured with Ellip sometry, and to further obtain the film density. As the wet etch rate decreased with increasing growth temperature or plasma treatment time, the density of PE-ALD SiO_2 film increased slightly from 2.20, generally similar to the film density value of silicon dioxide, to 2.34. Our study discusses the impact of oxygen plasma treatment and growth temperature on PE-ALD SiO_2 film properties such as GPC, WER, and density.

Reference

[1] D. Hiller et al., J. Appl. Phys. 107, 064314 (2010).

[2] Kim et al., J. Vac. Sci. Technol. A 33, 1 (2015).

Fig 1. WER and GPC of PE-ALD SiO_2 films along with varying in-cycle plasma time and growth temperature.

9:00am **AF1-WeM-5 On the Co-reactant for Atomic Layer Deposition of Metals: Hydrogen/Nitrogen-based Plasmas for Cobalt ALD**, ***Martijn Vos***, *E Kessels, A Mackus,* Eindhoven University of Technology, Netherlands

The choice of the co-reactant used in an ALD process is critical, since it greatly affects the properties of the deposited material as well as the technological feasibility of the process. For metal ALD, a wide range of gases and chemicals have been explored as co-reactants, with O_2, H_2, and NH_3 being the most common choices (both in thermal and plasma ALD). In this work, it is investigated in detail what the effect of the co-reactant is on the ALD behavior, material properties and reaction mechanism for Co ALD. A connection is made between the plasma composition and the properties of the deposited layers, thereby gaining detailed insight in the influence of the various plasma species.

Cobalt is a transition metal which is receiving increasing interest, mainly for applications in metal interconnects. Co is used as liner, thereby replacing the conventional Ta, while it is also being explored as local interconnect or contact material (replacing Cu or W). Here, we address ALD of Co using the $CoCp_2$ precursor and different hydrogen- and nitrogen-based plasmas.[1,2] In particular, an AB (i.e. two-step) process with NH_3 plasma, an AB process with H_2/N_2 plasma and an ABC process with sequential H_2 plasma and N_2 plasma are compared.

Using quadrupole mass spectroscopy (QMS), H_2, N_2 and NH_x are identified as the main species in both the NH_3 and H_2/N_2 plasma, used for the AB processes. In addition, the release of HCp (C_5H_6) is observed during the plasma exposure of both AB processes. This is in contrast to the ABC process, where fragments of the Cp ring are detected. Furthermore, it has been found that both the NH_3 plasma and the H_2/N_2 plasma result in high-purity Co films. On the other hand, films deposited using the ABC process contain considerable amounts of C, O and N contamination (5-8 at.%). This difference in material properties suggests that the presence of NH_xspecies in the plasma is required for effective impurity removal. Moreover, variation of the H_2/N_2 ratio in the H_2/N_2 gas mixture shows that the film purity and resistivity are correlated to the amount of NH_x in the plasma. Overall, the results indicate that the choice of co-reactant is important for obtaining high-quality Co films and that NH_x species play a crucial role in the ALD growth.

9:15am **AF1-WeM-6 Plasma-enhanced Atomic Layer Deposition of Tungsten Films using Tungsten Chloride Precursor**, *H Kim,* ***Seunggi Seo,*** *Y Lee, I Oh,* Yonsei University, Republic of Korea*; B Shong,* Hongik University, Korea, Republic of Korea

Tungsten (W) is a hard, refractory, and relatively inert metal, with widespread applications such as making filaments, filling contact holes and vias in microelectronic circuits, high-temperature technology, medicine, aviation, military uses, sport equipments. Atomic layer deposition (ALD) is a vapor phase thin film deposition technique based on sequential, self-limited surface reaction between chemical species. ALD enables deposition of thin films with high material quality, good uniformity, high conformality, and sub-nanometer thickness controllability. Furthermore, plasma-enhanced ALD (PE-ALD) which uses radicals as a reactant has been investigated as an attractive deposition method in terms of processing temperature and film quality. The most commonly used precursor for vapor deposition of W is WF_6, a highly reactive gas that often produces toxic hydrofluoric acid (HF) as a byproduct. WF_6 is also reactive toward common semiconductor device materials such as Si, Al, or Ti, and thus can lead to spontaneous etching during device fabrication. Therefore, fluorine-free tungsten precursors have recently received attention. In this work, we fundamentally investigated PE-ALD process of W on SiO_2 substrate, using tungsten chloride (WCl_x) precursor and hydrogen plasma. Various analytic techniques such as X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), rutherford backscattering spectrometry (RBS), 4-point probe, and field emission scanning electron microscopy (FE-SEM) were utilized, as well as density functional theory (DFT) calculations. Our PE-ALD W process showed typical ALD growth characteristics with a growth rate of 0.24 Å/cycle. W thin film deposited by our process showed low Cl impurity (< 1%) and low resistivity (~ 5.22×10^{-4} Ωcm).

9:30am **AF1-WeM-7 Tailoring Molybdenum Carbide Properties by Plasma and Ion Energy Control during Plasma Enhanced ALD**, *A Bol,* ***Eldad Grady,*** *M Verheijen, T Faraz, S Karwal, W Kessels,* Eindhoven University of Technology, Netherlands

Molybdenum carbide (MoC_x) exhibits a high mechanical and thermal stability together with a metallic like electrical conductivity, making it attractive for various applications. As an IC diffusion barrier MoC_x is ideally amorphous and dense, while for superconductivity the cubic δ-$MoC_{0.75}$ shows the highest transition temperature (14.3 K) for MoC_x films.[1] The ability to separately control the crystallinity and density of MoC_x allows for tailoring film properties to the specific application. In this work, we present the first extensive study on how film density and crystallinity of MoC_x can be tailored independently during plasma-enhanced ALD (PEALD) by controlling either the plasma exposure time or the ion energy.[2] We investigated MoC_x films grown using $(^tBuN)_2(NMe_2)_2Mo$ as the precursor and H_2/Ar plasma as the co-reactant at temperatures between 150°C and 300°C.

PEALD of MoC_x at 300°C using a plasma time of 20s yielded a mass density of 7.0 g/cm^3, which increased to 8.0 g/cm^3 upon increasing plasma time to 80s, while film crystallinity remained relatively unchanged. The trend in mass density was reflected by a significant decrease in film porosity and resistivity (272 to 143 μΩ−cm) which was also accompanied by a corresponding change in material composition owing to a decrease in C/Mo ratio (0.96 to 0.78) and film [N] content. In order to investigate the effects of varying the energy of ions impinging on the substrate, a radio-frequency bias voltage was applied to the substrate in the 20s plasma exposure step at 300°C. The measured mean ion energy increased from 25 eV for non-biased plasma to 125 eV with -100V bias. The elevated ion energy resulted in a higher mass density of 8.2 g/cm^3 together with an increase in film crystallinity, with crystallite size doubling in comparison to non biased deposition. The increase in density and crystallinity was reflected by a decrease in film porosity, resistivity (272 to 143 μΩ−cm) and C/Mo ratio (0.96 to 0.79). The effects of varying temperature and ion energies at 300°C on the film chemical and physical properties will be discussed.

From these and other results to be reported, it can be concluded that longer plasma time densifies the film but has little effect on crystallinity, while substrate bias densifies and crystallises the MoC_x film. Both longer plasma exposure and bias are successful in mitigating impurities in the film and lowering the film resistivity. This work opens new processing opportunities at low temperatures for the integration of tailor-made MoC_x thin films into a wide range of applications.

[1] Sathish et al., Solid State Comm. 177, 33 (2014)

[2] Profijt et al., JVSTA, 31, 01A106 (2013)

9:45am **AF1-WeM-8 Atmospheric-Pressure Plasma-Enhanced Spatial ALD of In_2O_3:H**, ***Yves Creyghton,*** *A Varanasi, F Roozeboom, P Bolt, P Poodt,* Holst Centre - TNO, Netherlands

Hydrogen-doped indium oxide (In_2O_3:H), a transparent conductive oxide first developed in 2007, has recently attracted strong attention as a replacement for tin doped indium oxide because of its high mobility (>100 cm^2/Vs) and high transparency (>90%) in the visible region of the spectrum. Sputtered In_2O_3:H has been demonstrated successfully but one of the challenges remaining is the damage induced by energetic ion-bombardment which may give rise to point defects [1]. High-quality In_2O_3:H layers were obtained previously using time-sequenced ALD at 100°C with cyclopentadienyl indium and a mixture of H_2O and O_2 followed by solid phase crystallization at 150-200°C in N_2 [2].

In the scope of large-area and high-throughput applications at low temperature we developed a plasma enhanced spatial ALD process for In_2O_3:H using tri-methyl indium (TMI) as precursor and a new type of Dielectric Barrier Discharge (DBD) plasma source for the supply of reactive co-reactants. The DBD plasma is generated very proximate (<200 µm) to the substrate without interacting electrically with the substrate. The highly uniform line-shaped plasma provides high concentrations of radicals while neutral gas and ion temperatures remain low. Depositions have been realized using a rotary spatial ALD reactor. Layer growth, electrical, optical and structural properties were investigated as a function of gas composition (H_2, H_2O, O_2 and N_2), gas flow rate and temperature in the range 100-200°C.

Best results without post-annealing were obtained in H_2O-H_2-N_2 plasma at temperatures above 140°C which is just above the transition temperature from amorphous to polycrystalline growth. The thickness of ~140 nm (1600 cycles) as determined by spectroscopic ellipsometry has less than 3% non-uniformity for films deposited at 150°C. Carrier mobility values as high as 85 cm^2/V.s for films grown at 150°C and 110 cm^2/V.s at 175°C with resistivity values of only 10^{-3} Ω.cm have been determined by Hall measurements. A transparency of ~90% in the visible region of the spectrum and ~85% on average was observed in the spectral range of 300-1800 nm for temperatures in the 150-175°C range. XRD and SEM analysis of the thin films showed that the layers deposited are polycrystalline. The average size of the crystals increases from ~35 nm to ~70 nm with increasing temperature. Current research is focused on the optimization of the thermal budget including options offered by solid-phase crystallization of amorphous layers.

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ALD Fundamentals
Room 113-115 - Session AF2-WeM
Plasma ALD II

Moderators: Markku Leskela, University of Helsinki, Finland, Jihwan Ahn, Seoul National University of Science and Technology

10:45am **AF2-WeM-12 Low-Temperature Plasma-Enhanced ALD of Highly Conductive Niobium Nitride Thin Films with RF Substrate Biasing**, ***Yi Shu,*** *A O'Mahony,* Oxford Instruments Plasma Technology*; H Knoops,* Oxford Instruments Plasma Technology, UK*; A Kurek,* Oxford Instruments Plasma Technology*; T Miller,* Oxford Instruments Plasma Technology, UK*; O Thomas, C Hodson,* Oxford Instruments Plasma Technology

Low-temperature superconductivity of Niobium Nitride (NbN) enables the utilization of NbN thin films in numerous quantum information applications. Recently, plasma-enhanced ALD (PEALD) of NbN thin films has been studied extensively[1,2,3], aiming for high quality NbN thin films deposition with precise thickness control at low process temperature (e.g. <400°C). These processes still require a long plasma exposure time (>40 s) and relatively-high deposition temperatures (>300°C) to eliminate impurities for the optimum film properties, such as high superconducting transition temperature (T_c) and low normal-state resistivity. On the other hand, it has been shown that RF substrate biasing applied during PEALD deposition can increase ion energy and influence film properties including stress[4], crystallinity[5], density[6], and resistivity[7]. Following above results, bias-enhanced PEALD of NbN thin films deposition with (t-butylimido)-tris(diethylamido) niobium (TBTDEN) and remote H_2/Ar plasma is investigated in this work.

This study was carried out in an Oxford Instruments Plasma Technology FlexAL ALD tool equipped with an RF-biased table (13.56 MHz, substrate biasing up to 100 W power, -350 V resulting DC bias voltage), where independently controlled RF substrate biasing was applied along with mixed H_2/Ar plasma generated by inductively-coupled plasma (ICP) RF power. Coupons of silica samples were used as substrates. Film quality was evaluated by film resistivity at room temperature (RT), which was calculated from sheet resistance measured by the four-point probe method (FPP), and film thickness measured by ex situ spectroscopic ellipsometry (SE).

Different plasma parameters were investigated, e.g. RF bias power ranged from 0-75 W, and plasma duration ranged from 10-50 s. Benefit from the RF biasing, RT resistivity as low as 142 μΩ*cm was observed with NbN thin films deposited at 250°C, by PEALD process with a 20 s plasma exposure time. Moreover, such conductivity, which is corresponding to high superconducting transition temperature (T_c) [1], was found to remain with films grown at lower process temperatures down to 120°C.

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11:00am **AF2-WeM-13 Low-temperature Plasma Assisted Atomic Layer Deposition of Cadmium Telluride*, James Pattison,*** University of Maryland*; B VanMil, A Hewitt,* U.S. Army Research Laboratory*; N Strnad,* University of Maryland*; Y Chen, P Wijewarnasuriya,* U.S. Army Research Laboratory

Cadmium telluride (CdTe) is an important group II-VI semiconductor that can be alloyed with the semi-metal HgTe to create $Hg_{1-x}Cd_xTe$ (MCT) based semiconductor materials, with a band gap tunable from 0 to 1.5 eV. MCT is the incumbent technology used in long-wave infrared (IR) imaging. Surface passivation is critical for the next generation of infrared focal plane arrays (FPAs) used for imaging in the long-wave infrared (8-12 mm band). As device dimensions decrease in newer FPA designs, the surface area to bulk volume ratio increase, and the surface recombination of charge carriers in MCT photodiodes can limit the performance of FPAs, ultimately degrading the diode signal-to-noise ratio. CdTe is an ideal passivation material for MCT due to being very close in lattice match to $Hg_{0.78}Cd_{0.22}Te$ (band gap of 115 meV equal to 10.6 mm), having similar thermal expansion coefficient, and being transparent to long wave infrared. The high-aspect ratio features present in next-generation FPAs present a challenge to current state of the art CdTe passivation by molecular beam epitaxy, which deposits material in a line-of-sight fashion. Atomic layer deposition of CdTe provides conformal coverage of these features with atomic-level thickness control, overcoming this challenge. The temperature of any MCT processing step, including passivation, must occur at low enough temperatures to avoid outgassing of mercury from the MCT device, which is catastrophic to performance. Past work on CdTe ALD and CdTe MOCVD has relied upon thermal deposition processes (> 220°C) that are incompatible with MCT device processing. Here we present preliminary results from our novel plasma-assisted ALD process for deposition of CdTe on silicon and MCT device substrates at a variety of temperatures (from 50 to 200°C) compatible with MCT device processing. Optical characterization by dynamic in-situ spectroscopic ellipsometry (iSE) during growth provides growth-per-cycle and insight into the nucleation and deposition mechanisms. X-ray photoelectron spectroscopy (XPS) confirms the presence of CdTe and examination of other contaminants within the ALD film. X-ray diffraction was used to study the orientation of ALD films on both HgCdTe and silicon substrates. Transmission electron microscopy was used to characterize the film thickness, orientation, and chemistry.

11:15am **AF2-WeM-14 Improved Deposition Rate of Low T PEALD Silicon Nitride Using Amines*, Sungsil Cho,*** *S Chang, J Park,* Entegris Inc., Republic of Korea*; B Hendrix, T Baum, J Giolitto,* Entegris Inc.

Plasma-enhanced atomic layer deposition (PEALD) of silicon nitride (SiNx) films using silicon-halide precursors and plasma-activated ammonia (NH_3) is well-known and characterized. In this presentation, we dramatically improved the efficiency of the process by catalyzing the precursor dose with an amine. Specifically, hexachlorodisilane (Si_2Cl_6) and tetrabromosilane ($SiBr_4$) were used to deposit SiN films via plasma-activated NH_3 at a deposition temperatures from 250-450°C. The deposition rate was increased 2-3X by modifying the pulse sequence, as shown in Figure 1.

The results of amine catalyzed PEALD-SiNx films were compared to conventional PEALD-SiN films. Figure 2-A shows that the growth rate of the NH_3 catalyzed PEALD-SiN film from Si_2Cl_6 saturated at 2.8~3.0 Å/cycle; this was 2~3 times higher growth rate than the normal PEALD-SiN film (~1Å/cycle) process. This increase may be attributed to the amine catalyst leading to a lower activation energy, influencing the surface reaction of the Si compound. A similar 2X enhancement in growth rate was observed for $SiBr_4$.

In terms of the characterization of the amine catalyzed PEALD-SiN film, we found that the wet etch rate (WER) of the amine catalyzed PEALD-SiN film was generally higher than that of the normal PEALD-SiN film process. The WER of the SiN film was improved as plasma exposure time or plasma power was increased. Furthermore, the amine catalyzed PEALD-SiN film showed excellent conformality on silicon oxide trench structures with high aspect ratios (AR~11:1), as shown in Figure 3-A. We also observed that the SiN film was uniformly etched down the sidewall and at the bottom of the via structure.

11:30am **AF2-WeM-15 Improved Adhesion and Electrical Properties of Plasma-Enhanced ALD Platinum through Cycle-by-Cycle Hydrogen Plasma Treatment*, Martin Winterkorn,*** *J Provine, H Kim, P Schindler, T Kenny, F Prinz,* Stanford University

Insufficient adhesion of platinum thin films to their underlying substrates is a cause of concern in many applications such as biomedical and MEMS devices. We report on significantly improved adhesion of plasma-enhanced ALD platinum films on multiple substrates through in-situ cycle-by-cycle hydrogen plasma treatment. Further, we demonstrate a novel method for quantifying adhesion, which involves the deposition of a highly stressed overlayer and a subsequent liftoff procedure. The effect of the hydrogen plasma treatment on film resistivity and uniformity have also been characterized, and an extreme substrate dependence has been observed, with the most extensive treatment condition resulting in a 8% decrease in resistivity compared to no treatment on Al_2O_3 substrates, but a 78% increase on SiO_2 substrates.

All films were deposited at 270°C in an Ultratech / Cambridge Nanotech Fiji ALD reactor, using trimethyl(methylcyclopentadienyl)platinum(IV) as the precursor and remote O_2 plasma as the oxidant, with 400 cycles resulting in approximately 20 nm thick films as confirmed by X-ray reflectivity measurements. The plasma treatment consisted of an additional 10 seconds of H_2 plasma and 10 seconds of O_2 plasma after each cycle, with purge times of 5 seconds. Various conditions were investigated, performing the treatment during all 400 cycles, only the first 200 cycles, only the first 50 cycles, or not at all (numbers 4 through 1, respectively).

Adhesion was evaluated using tape lift-off, and a novel method that mimics real application in MEMS fabrication processes: Two-layer photoresist is patterned with arrays of squares of various sizes on top of the platinum film, followed by e-beam evaporation of a 200 nm thick Pt layer which has a high tensile stress of 640 Mpa. A lift-off procedure is then carried out on the sample, which includes submerging it in solvents and ultrasonic agitation. In case of insufficient adhesion, individual patterned squares delaminate at the interface between the ALD platinum layer and the substrate. The fraction of delaminated squares at various sizes, as observed by optical microscopy, can then be used as a quantitative indication for adhesion strength.

11:45am **AF2-WeM-16 Low Temperature SiNx Film Deposition by Plasma Enhanced Atomic Layer Deposition with Trisilylamine*, Sun Jung Kim,*** *S Yong, Y Choi, H Hwangbo, H Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Recently, the degree of integration density of semiconductor devices is continuously increasing and critical dimension (CD) also is reduced to less than 20nm. In the nanoscale devices, silicon nitride (SiN_x) layers are essential and critical for the fabrication of nanoscale devices and it is important to control SiN_x film thickness at atomic level. Atomic layer deposition (ALD) processes are applied for the atomic layer thickness control. It is also known that the low process temperature for SiN_x film deposition less than 400^{o}C is becoming an issue in ALD processes maintaining growth per cycle (GPC) of 1.0Å/cycle or above [1].

In this study, we developed SiN_x plasma-enhanced atomic layer deposition (PEALD) films with trisilylamine (TSA) as a Si precursor and NH_3 in inductively coupled plasma (ICP) reactor for low temperature deposition high GPC. Reactive radicals and ions are generated in ICP environment and make low temperature processing possible. The GPC was measured as high as 1.2Å/cycle at 350℃ of substrate temperature. The ratio of nitrogen and silicon (N/Si) was determined as high as 1.33 at an optimized condition. We also investigated chemisorption path of TSA on SiN_x film during first-half reaction of PEALD process with a reference of adsorption analysis of TSA on Si (100) surface [2].

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Emerging Materials
Room 104-106 - Session EM1-WeM
Battery and Energy Storage I

Moderators: Seungmin Hyun, Korea Institute of Machinery and Materials, Dongping Lu, Pacific Northwest National Laboratory

8:00am **EM1-WeM-1 Enhanced Thermal Stability of LTO Electrode by Atomic-Layer-Deposited Al_2O_3***, J Yoon,* ***Seunghoon Nam,*** Korea Institute of Machinery and Materials, Republic of Korea*; K Park, T Yoon,* ISAC Research Inc.*; H Park,* ISAC Research Inc., Republic of Korea*; S Hyun,* Korea Institute of Machinery and Materials, Republic of Korea

Despite of several inherent advantages as high-rate capability and cycling stability of $Li_4Ti_5O_{12}$ (LTO), the gas generation, as a result of the undesired reactions with commercial electrolytes, has been a challenge for the electric-vehicle (EV) application of the material as a negative electrode for Li-ion batteries. Since the gas generation from LTO tends to be accelerated under high temperature (~40 - 60˚C), the thermal stability of LTO should be guaranteed during discharge of the batteries for EVs. In order to mitigate such technical issue, a thin layer of Al_2O_3 (~1 nm) was deposited on the LTO electrode by an atomic layer deposition (ALD), and the resulting electrochemical stability was accessed by cycling cells under 60˚C. The retention of capacity after 500 cycles clearly shows that Al_2O_3-coated LTO outperforms the bare one, with the discharge capacity retained 98% of the initial value. Analysis by TEM with XPS corroborates suppressed surface reaction of the coated LTO, while the uncoated one exhibits the phase transformation of (111) to (222) plane, as indicated by earlier literatures.

8:15am **EM1-WeM-2 Electrochemical Performance of Atomic Layer Deposited Zinc Oxysulfide Thin Film in Li-ion Battery***,* ***Soumyadeep Sinha,*** *J Heo,* Chonnam National University, Republic of Korea

In the recent time, the sustainable and eco-friendly rechargeable energy sources are in high demand to obtain the global environmental pollution free energy storage. Therefore, the choice of Li-ion batteries is not only the power source of the portable electronic gadgets but also for the next-generation electric vehicles. This factor eventually leads to the investigation of new electrode materials to maximize the energy/power density per unit mass as well as per unit area or volume of the active materials. Therefore, the 3D-porous conducting scaffolds coated with active electrode materials or the free-standing electrode materials are the need for the hour. In this regard, zinc (Zn) based materials always have a great importance in any field of energy applications due to its earth abundance, low cost, eco-friendly nature with an easy synthesis process by a variety of deposition techniques. On the other hand, atomic layer deposition (ALD) technique is a great tool for the conformal deposition of a thin film with a precise thickness and desired stoichiometry on any randomly oriented 2D/3D substrates.

In this study, zinc oxysulfide ($ZnO_{1-x}S_x$) thin films on stainless steel (SS) current collector were deposited by ALD which were directly used as an anode material in Li-ion battery without any carbon and binder. The electrochemical performance of the anode material was investigated by cyclic voltammetry (CV) measurements against Li in a half cell configuration which showed prominent redox-peaks during both cathodic and anodic process. A stable discharge capacity of above 500 mAh g^{-1} was obtained at 100th cycle during the charge-discharge cycling performance of this electrode at a high current density of 1 A g^{-1} which was significantly higher than the pristine ZnO and ZnS. Thus, this work can be presented as a typical approach to study the electrochemical responses of a double-anion compound active material which can be easily obtained with a desired stoichiometry with high precision by ALD.

8:30am **EM1-WeM-3 Interfacial and Surface Design of Electrode by ALD and MLD for Next-generation Batteries***,* ***Xueliang (Andy) Sun,*** University of Western Ontario, Canada **INVITED**

The interface of electrode-electrolyte in Li batteries is root for poor cell lifetimes mainly due to various side reactions. The use of surface coatings to control of the electrode-electrolyte interface is an important strategy to design new electrodes. Atomic layer deposition (ALD) and molecular layer deposition (MLD) are ideal coating techniques to control the interface and surface of the electrodes in various battery systems [1]. This talk will include three parts:

In the first part, I will report our work on the applications of atomic layer deposition (ALD) in Li ion batteries including synthesis of coating materials such as Al_2O_3, ZrO_2, TiO_2, $AlPO_4$ and $LiTaO_3$ and $LiNbO_3$ as well as the ALD coating materials to modify cathode (NMC) [2].

In the second part, we will discuss MLD alucone coating on Li-S batteries operating at 55C [3].

In the third part, we will discuss our recent results on ALD Al_2O_3 and MLD alucone coatings on Na metal for Na ion batteries and Na-Air batteries [4,5,6].

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9:00am **EM1-WeM-5 Biodegradable ALD Materials for the Packaging of Thin Film Batteries for Implantable Medical Devices***,* ***Messaoud Bedjaoui,*** *S Poulet,* Univ. Grenoble Alpes, CEA, LETI,, France

Nowadays, biodegradable electronics are highly expected to play an important role to achieve a variety of medical applications and more particularly for transient medical devices. In fact, the implantable biodegradable electronic devices provide shorter-term therapeutic function for predetermined periods without any recourse to secondary surgical removal. In the meantime, the power supply of biodegradable electronics must be adapted by providing compatible energy sources. Thin Film Batteries (TFB) offer a unique combination of energy densities and safety properties that are attractive as an energy-storage. In practice, the ideal solid TFB should be biocompatible, and comprise biodegradable materials that would satisfy device power requirements and benignly degrade thereafter.

The purpose of this work is to evaluate the potential biodegradable materials obtained by ALD (Atomic Layer Deposition)/MLD (Molecular Layer Deposition) techniques for the packaging of TFB. The packaging materials can gradually degrade in an in vivo environment within an expected timeframe, during which the TFB is protected before fully dissolving. A judicious design of the packaging strategies can ensure an equilibrium between TFB lifetime and bioapbsorption timelines that therefore conditioning the TFB effectiveness.

First, we explore the biodegradability properties of Al_2O_3, TiO_2 and alucone materials obtained as single layers as well as multilayers at low temperature range (80°C-150°C). In vitro degradation tests employ the exposition to Phosphate Buffer Saline (PBS) and Hank's Balanced Salt Solution (HBSS) for several weeks at different temperatures (37°C-67°C). In order to establish the biodegradation kinetics, the different structures have been characterized using infrared spectroscopy, scanning electron microscopy (SEM) and complementary analysis (spectroscopic ellipsometry, X-ray photoelectron spectroscopy) before and after exposition to PBS and HBSS saline solutions. The first results seem to prove the biodegradability characteristic of the selected materials. However, the degradation kinetic (from few hours to 4 weeks) may perform very differently depending on the exposition conditions (temperature, PBS, HBSS). It is quite clear for alumina layers in comparison to other materials (Figure 1 and Figure 2). On the other way, we demonstrate in this work that the introduction of multilayer structures (Al_2O_3-Alucone; Al_2O_3-TiO_2) permits the monitoring of this degradation. Finally, the developed structures transferred on TFB devices shown that the electrochemical performances is prolonged by using ALD/MLD materials but it instantaneously damaged without packaging.

9:15am **EM1-WeM-6 Enhanced Conductivity in Thin-Film Solid-Composite Electrolytes for Lithium-Ion Batteries by Combining Molecular and Atomic Layer Deposition***, **Simon Hollevoet**, K Gandrud,* IMEC, Belgium*; A Patil,* KU Leuven, Belgium*; B Put, P Vereecken,* IMEC, Belgium

Improvements in energy storage are a critical aspect to enable future applications, such as the Internet of Things (IoT), which will lead to an exponential growth in wireless sensors and autonomous microsystems. Currently, planar solid-state thin-film lithium and Li-ion batteries are commercially available but have limited capacity (<0.3mAh/cm2). To meet the future demands in microelectronics in terms of safety, power and energy density the need for all-solid-state 3D thin-film Li-ion batteries arises [1], i.e. there is a need for batteries consisting of thin-films deposited conformally on high aspect ratio substrates.

Here, we present thin-film solid-state composite electrolytes (SCEs), manufactured by combining molecular layer deposition (MLD) with atomic layer deposition (ALD). The SCEs consist of a nanoporous oxide that provides both mechanical stability and a high internal surface area. This nanoporous oxide is coated with a nanometer thin Li-compound layer to exploit the enhanced ion transport at the interface between oxides and lithium salts, as first reported by Liang [2].

In this work, the SCE showed an enhancement in ionic conductivity of up to a few orders of magnitude compared to the pure Li-compound. Moreover, different enhancements were obtained based on different Li-compound/alumina matrix combinations. The nanoporous alumina matrices were obtained through several post-treatments of alucone deposited by MLD. Subsequently the alumina matrix was coated with lithium-compounds (e.g. Li_2CO_3) by ALD. Thus, this is a novel approach to open up new paths regarding design and development of thin-film solid-state electrolytes. Moreover, the SCEs can be deposited on high aspect ratio features, required for e.g. 3D thin-film batteries, and on conventional particle-based electrodes as protective coating.

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9:30am **EM1-WeM-7 Resolving the Mutual Contradiction between Porosity and Toughness of Carbon Textile for Flexible Supercapacitors***, **Do Van Lam**, J Kim, S Lee,* Korea Institute of Machinery and Materials

Activated carbons, which are highly porous materials prepared from carbonization of carbon-rich precursors with chemical reagents, have numerous advantages in the current energy storage technologies, but could realize further gains in flexible electronics if their mechanical properties were highly improved. However, so far, the mutual contradiction between porosity and toughness in activated carbons still remains unsolved. By coating a nanothin film via atomic layer deposition on cotton prior to the conventional chemical activation, we prepared a flexibly activated carbon textile with high specific surface area (1065 m^2/g) and greatly enhanced toughness of over 40 folds, thus can be directly used for fabricating high-performance flexible supercapacitors. Our results open a general strategy for resolving the contradiction between porosity and toughness in carbon materials and thus hold great promise towards flexible/wearable electronics.

Emerging Materials
Room 104-106 - Session EM2-WeM

Battery and Energy Storage II

Moderators: Parag Banerjee, Washington University, St. Louis, Neil P. Dasgupta, University of Michigan

10:45am **EM2-WeM-12 Atomically-Precise Interfacial Engineering of Energy Conversion and Storage Materials by ALD***, **Neil P. Dasgupta**,* University of Michigan **INVITED**

There has been a dramatic increase in research of nanoscale materials for energy conversion and storage devices due to several advantageous features such as high surface areas, short transport distances, and tunable material properties. However, with these benefits come challenges. In particular, the ability to precisely control the properties of surfaces and heterogeneous interfaces limits the performance of many of these devices, and requires novel approaches. Additionally, the ability to manufacture materials with precise control of heterogeneous features in three dimensions and at length scales spanning from atoms to meters is challenging, requiring complementary processing techniques. To bridge this gap requires novel approaches to design material systems across these length scales, allowing us to fabricate hierarchical structures with deterministic control of geometric and chemical properties.

To address this challenge, the Dasgupta Research Group at University of Michigan focuses on the atomically-precise modification of surfacesandinterfaces to control material assembly and transport phenomena across physical and chemical boundaries. Examples include surface passivation against undesirable reactions at electrode-electrolyte interfaces in batteries, integration of co-catalysts on semiconductor surfaces for solar-to-fuel conversion, and charge transport layers in photovoltaics. The key enabling technology that is used for surface modification is Atomic Layer Deposition (ALD). This atomic-scale modification of surfaces allows for precise control of interactions at heterogeneous interfaces, which can be used to direct self-assembly processes, provide tunability of the optical, electronic, thermal, and mass transport properties of integrated material systems, and encapsulate structures to promote their stability in a wide range of environments. In this talk, I will demonstrate examples of the ALD process for modification of electrode-electrolyte interfaces with an emphasis on "beyond Li-ion" batteries and solar-to-fuel conversion, and provide a perspective on how this versatile approach can lead to the design and manufacturing of hierarchical material systems with "designer" interfaces and interphases.

11:15am **EM2-WeM-14 Minimizing Polysulfide Shuttle Effect in Lithium-Ion Sulfur Batteries by Anode Surface Passivation via Atomic Layer Deposition***, **Jian Liu**,* The University of British Columbia, Canada*; D Lu, J Zheng, P Yang,* Pacific Northwest National Laboratory*; B Wang, X Sun,* University of Western Ontario, Canada*; Y Shao, C Wang, J Zhang, J Liu,* Pacific Northwest National Laboratory

Lithium-sulfur (Li-S) batteries have grained increasing attentions as competitive power supply system for electric vehicles, due to their high energy density and low cost of sulfur [1,2]. During the past few years, encouraging progresses have been made to develop novel cathode structure to address the polysulfide shuttle effect and poor conductivity of sulfur. However, the problems associated with Li metal, such as Li dendrite and polysulfide corrosion, remain unresolved. To circumvent the problem, one promising route is to pair a non-Li anode with the sulfur cathode to develop Li-ion sulfur batteries [3,4]. Nevertheless, polysulfide shuttle reactions still occur when using non-Li anodes, leading to limited cycling life and low CE in Li-ion sulfur batteries.

In this work, we developed a surface passivation strategy to minimize polysulfide shuttle effect on those alternative anodes, in order to enable high-performance practical Li-ion sulfur batteries. We used an ultra-thin electron-insulating layer (Al_2O_3), deposited by atomic layer deposition (ALD), to passivate the surface of the non-Li anodes (graphite as an example), with the aim of blocking the electron transfer pathway and alleviating polysulfide shuttle (Figure 1). We found that with the optimal thickness of 2 nm Al_2O_3 coated on graphite anode, the Coulombic efficiency of the sulfur cathode was improved from 84% to 96% in the first cycle, and from 94% to 97% in the subsequent cycles (Figure 2). As a result, the discharge capacity of the sulfur cathode was increased to 550 mAh g^{-1} in the 100th cycle, as compared with 440 mAh g^{-1} when the pristine graphite anode was used. Mechanism study disclosed that the Al_2O_3 passivation layer minimized the formation of insoluble polysulfide (Li_2S_2, Li_2S) on the surface of graphite anode and improved the efficiency and capacity retention of the graphite-sulfur batteries. It is expected that this surface passivation strategy could be also applied to other sulfur based battery systems (with Li, Si, and Sn anodes), to reduce side reactions and enable high-performance sulfur batteries.

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11:30am **EM2-WeM-15 A Facial Way to Prepare Large Areal 3D Porous Carbon via Molecular Layer Deposition and its Application for Lithium Sulfur Batteries***, **Yan-Qiang Cao**, W Zhang, A Li,* Nanjing University, China

Nowadays, rechargeable batteries with a high energy density and long life are needed in many applications, ranging from portable electronic devices to electric vehicles. Unfortunately, the state-of-the-art lithium ion batteries (LIBs) cannot satisfy these requirements now. Therefore, tremendous efforts are being dedicated toward developing "beyond-lithium-ion" batteries. Lithium sulfur (Li-S) batteries are one of the most promising next-generation energy storage systems with a high capacity of 1675 mAh/g and energy density of 2600 Wh/kg. However, significant issue must be overcome before Li-S batteries can be implemented, such as the highly insulating nature of sulfur and the high solubility/diffusivity of lithium polysulfides in the electrolyte. A great deal of scientific and technological innovations have been proposed to solve these problems, such as optimizing the electrolyte and fabricating composite electrodes of sulfur/polymer, sulfur/metal organic framework (MOF) or sulfur/carbon.

In this work, a novel and facial approach was proposed to synthesis the large areal three-dimensional (3-D) porous carbon. Inorganic-organic hybrid film via molecular layer deposition (MLD) was used as carbon precursor, while metal foam or metal oxide fiber was utilized as sacrifice template. Inorganic-organic hybrid films would be transformed into carbon/oxide by pyrolysis in inert atmosphere. After etching the oxide in carbon and template, 3D porous carbon of various shapes can be achieved. We can gain a large porous carbon of 10*10 cm at present. In addition, as-prepared porous carbon exhibits well flexibility.

Further, a composite cathode system for Li-S batteries was synthesized by loading sulfur onto 3D network of porous carbon via a sulfur melt infiltration method. The 3D porous carbon can offer excellent electrical conductivity, and an appropriate hierarchical pore structure containing the electro-active sulfur facilitates rapid electron/ion transport. More importantly, this cathode system does not require any additional binding agents or conductive additive. A Li-S battery with the sulfur-3D porous carbon cathode shows good electrochemical stability and high rate discharge capacity retention, which delivers a reversible capacity of about 930 mAh/g at the current density of 100 mA/g. Our results indicate the great potentials of MLD derived 3D porous carbon for high-performance batteries.

11:45am **EM2-WeM-16 Enhanced Metal-support Interaction of Ceria Supported Platinum Single Atoms and Subnanoclusters for Room Temperature CO Oxidation***, **Xiao Liu**, Y Tang, B Shan, R Chen,* Huazhong University of Science and Technology, China

The CO poisoning effect is one of the critical problems plaguing platinum (Pt) catalyst, which can limit its activity by blockage of surface active sites and subsequent reaction steps under low temperatures.[1] Such phenomena is quite general considering that CO will be used as reactants or generated as reaction intermediates in many catalytic processes such as CO oxidation, water-gas shift reactions, and fuel cells.[2-3] In view of the high dispersion (smaller Pt nanoparticles) required for catalyst applications, CO poisoning will be only more pronounced, wherein large fraction of coordinately unsaturated edge and vertex sites over-bind CO molecules.[4] Here, we report a method to tackle the CO poisoning effect on high dispersed Pt clusters by enhancing the metal-support interaction. The Pt single atoms and subnanoclusters have been prepared on ceria (CeO_2) nanorods by optimizing the atomic layer deposition recipe and post-treatment annealing process. The copper doping at the interface of Pt/CeO_2 has been performed to enhance the low temperature CO oxidation activity. The as-prepared copper-doped CeO_2 supported Pt subnanoclusters show excellent CO oxidation activity, which is significantly better than that of the reported subnanocluster and single atom catalysts in previous studies. The results of X-ray photoelectron spectroscopy, *in-situ* CO diffuse reflectance infrared absorption spectroscopy and density functional theory calculations show that the enhanced catalytic activity is due to the activation of lattice oxygen and the decrease of CO binding strength.

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Nanostructure Synthesis and Fabrication
Room 107-109 - Session NS-WeM

Nanostructures III

Moderator: Mike McSwiney, Intel, USA

10:45am **NS-WeM-12 DBD Plasma Assisted Atomic Layer Deposition Alumina Barrier Layer and its Applications***, H Wei,* Beijing Institute of Graphic Communication, China*; H Guo,* Qilu University of Technology, China*; L Yang, Z Liu, **Qiang Chen**,* Beijing Institute of Graphic Communication, China

In this paper, the plasma generated by dielectric barrier discharge (DBD) is utilized to assist atomic layer deposition. We compare the discharge properties in low pressure and atmospheric pressure. By optical emission spectroscope (OES) we find the oxide species in two kinds of plasma are different, the atomic oxygen is the major radicals for oxidization reaction in low pressure condition rather than ozone as the oxidant in atmospheric pressure. With these DBD plasma assisted ALD alumina coatings on polyethylene terephthalate (PET) and polylatic acid (PLA) webs as barrier layers are carried out. The Al O component and the surface morphology in two plasmas are compared. The influence of Al O thickness on barrier, mechanical, optical and degradation properties is investigated. It is obtained that the growth rate of Al O coating are 0.12 and 0.23 nm/cycle respectively in low pressure and atmospheric pressure DBD. For same water vapor transmission rate (WVTR) the alumina thickness is thicker in atmospheric pressure deposition Al_2O_3 than that in low pressure deposition Al_2O_3. Atomic force microscope (AFM) and screening electron microscope (SEM) analysis confirm that alumina deposition in atmospheric assisted ALD is loose, as a result, the moisture permeates the barrier layer at a large magnitude.

11:00am **NS-WeM-13 Sequential Infiltration Synthesis for sub 20 nm Thermal Scanning Probe Lithography Patterns***, **Tero Kulmala**, M Spieser,* SwissLitho AG, Switzerland*; B Chan, J de Marneffe,* Imec Vzw, Belgium*; A Knoll,* IBM Research-Zurich, Switzerland

As feature sizes of emerging device concepts in for example nanoelectronics and nanophotonics continuously shrink, a high demand for novel lithography and pattern transfer processes exists. Recently, thermal scanning probe lithography (t-SPL) [1] which relies on the thermal decomposition of thermally sensitive polymer resists, such as polyphthalaldehyde (PPA) has entered the market. Using this technique, single-digit nanometer patterning and pattern transfer [2] as well as superior alignment accuracy [3] and sub-nanometer accurate 3D patterning [4] have been demonstrated. The patterning speed is comparable to high-resolution electron beam lithography [5].

As in all lithographic processes, patterning sub-10 nm features with t-SPL requires use of ultra-thin resist layers which complicates the pattern transfer process. So far, a few nm PVD silicon dioxide layer has been used as a hard mask to enable transferring the PPA patterns into a ~50 nm thick layer of amorphous carbon [6] for further amplification of the shallow t-SPL patterns.

Here, we show how sequential infiltration synthesis (SIS) [7,8] can be used to infiltrate t-SPL patterned PPA with aluminum oxide. We employed a pattern transfer stack consisting of ~10 nm PPA, 6 nm cross-linkable Polystyrene (x-PS) and 13 nm silicon nitride for transferring patterns into silicon. The amount of aluminum oxide infiltration in PPA increases with the number of SIS cycles as verified by energy dispersive spectroscopy carried out in a transmission electron microscope and results in an increase in etching resistance of the material. The resulting patterns were analyzed by atomic force microscopy and cross-section transmission electron microscopy. With an optimized process, patterns with sub-20 nm critical dimension were successfully transferred into Si.

In conclusion, SIS offers an interesting alternative for transferring high resolution patterns written by t-SPL. Furthermore, it eliminates the need for a hard mask layer in the transfer stack, thereby simplifying the process. Moreover, it was shown that such a "soft" transfer stack enhances the resolution of t-SPL patterning to the sub 10 nm range [2].

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11:15am **NS-WeM-14 Fabrication of BN Coated Carbon Nanostructures using ALD Based on Polymer Derived Ceramics Route***, **Catherine Marichy**,* Univ Lyon, France*; W Hao,* LMI - UMR CNRS/Univ Lyon 5615, France*; C Journet, A Brioude,* LMI - UMR CNRS/Univ Lyon 5615

Development of sustainable energy as well as environment issues are two of the most important current concerns. In particular, applications in corrosive and/or high temperature treatment such as in heterogeneous catalysis need support with excellent thermal stability and chemical inertness. Boron Nitride (BN) seems thus an excellent candidate; however it is an electrical insulator. Carbon nanotubes, despite their excellent electric properties, suffer of instability under reaction condition at high temperature (>300°C) especially, if the targeted reactions are partial oxidations. Deposition of a very thin BN coating appears an elegant approach to prevent the CNT oxidation while preserving its electric properties [1,2] and access to a support allowing for instance heterogeneous catalysis/electrocatalysis even at high temperature (e.g. 400-700°C). Nevertheless, fabrication of such hetero-structures requires a synthetic approach capable of controlling the size and morphology of the desired materials. Atomic Layer Deposition (ALD) has demonstrated to be an effective approach for surface modification and fabrication of carbon based heterostructures.[3] Currently, BN coating of carbon material by ALD has been poorly investigated. Based on polymer derived ceramic chemistry, a novel two-step ALD approach for BN has been recently reported.[4] Due to its low deposition temperature and non-corrosive precursors, it has been successfully use for BN deposition onto various substrates such as inorganic and polymer nanostructures.[5]

Herein coating of various carbon nanostructures is reported using this new ALD process. As inertness of highly graphitic carbon inhibits the initiation of ALD growth, use of amorphous and graphitized carbon substrates allows studying the impacts of the crystalline nature of the substrate on the coating in term of growth and structure. The obtained BN coated carbon materials are characterized by advanced electron microscopy and related techniques. As a function of the degree of graphitization, nucleation delay and impact on the crystalline quality (amorphous, turbostratic, hexagonal phase) of BN films are observed. Finally, potential of such coating to improve the oxidation resistance of carbon material is demonstrated.

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11:30am **NS-WeM-15 Atomic Layer Deposition of Lead(II) Iodide***, **Georgi Popov**, M Mattinen, T Hatanpää, M Vehkamäki, M Kemell, M Ritala, M Leskelä,* University of Helsinki, Finland

Over the years of ALD process development, metal halides have attained the role of classic metal precursors. Lead(II) iodide for instance, was studied as a lead precursor for ALD of PbS.[1] An attempt to deposit these typical precursor compounds might seem as a questionable endeavor at best. However, this is not theoretically impossible, provided that technical challenges, such as the relatively high vapor pressure of the target compound, are addressed. Therefore, it is tempting to explore whether the library of materials that can be deposited by ALD, can be expanded to metal iodides. Our interest in lead(II) iodide has also practical motivation. Lead(II) iodide possesses a two-dimensional structure and a band-gap in the visible range. The material is suitable for photodetectors[2] and lead(II) iodide thin films are an established starting point for preparation of hybrid halide perovskite thin films employed in perovskite solar cells[3].

The ALD process we developed for lead(II) iodide relies on lead(II) bis[bis(trimethylsilyl)amide] as the lead precursor and tin(IV) iodide as the iodine precursor. The process works at low temperatures (< 100°C) and is compatible with a variety of starting surfaces ranging from oxides to metal thin films. We observed saturative film growth with respect to both precursors on substrates selected for detailed study, namely silicon and fluorine doped tin dioxide coated glass. We also noticed a linear relation between the film thickness and the number of deposition cycles. The process yields crystalline films that show different crystalline textures depending on the nature of the starting surface. We also demonstrate that lead(II) iodide films deposited with this process, when treated with methyl ammonium iodide vapors, convert into a methyl ammonium lead triiodide. Methyl ammonium lead triiodide is a hybrid halide perovskite commonly employed as a light absorber in perovskite solar cells.

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11:45am **NS-WeM-16 Crystalline High-k Dielectric Films on Atmospheric Plasma Treated Graphene by Atomic Layer Deposition***, **Jeong Woo Shin**,* Seoul National University of Science and Technology, Republic of Korea*; M Kang,* Kwangwoon University, Republic of Korea*; S Oh, B Yang, K Seong, H Ahn,* Seoul National University of Science and Technology, Republic of Korea*; T Lee,* Kwangwoon University*; J An,* Seoul National University of Science and Technology, Republic of Korea

Graphene has excellent electrical and mechanical properties such as high carrier mobility (~200,000cm^2/Vs), high surface-to-volume ratio, high flexibility and high mechanical property (Young's modulus: ~0.1TPa). Due to these excellent properties, graphene has been extensively studied for flexible electronics and sensors.

However, the basal plane of graphene is known to be chemically inert because of its strong sp^2 carbon bonding. For the fabrication of graphene-based field-effect transistors (GFETs) with high sensitivity and stability, it is important to deposit thin and uniform dielectric films on the graphene surface. Among various dielectric deposition method, atomic layer deposition (ALD) has the advantage of being able to deposit ultra-thin and uniform films. However, the inertness of the graphene basal plane prevents the facile nucleation of ALD dielectric materials on the graphene surface.

In this paper, we demonstrate the deposition of high-quality ALD dielectric films without additional seed layer on the atmospheric oxygen plasma treated graphene while minimizing the structure and electrical degradation. Optical microscope, raman spectroscopy, water contact angle analysis and X-ray photoelectron spectroscopy show that the atmospheric oxygen plasma treated graphene surface become super-hydrophilic. Also, it is confirmed that the uniform and highly crystalline ALD dielectric films deposited at a relatively low temperature (150℃) on the functionalized graphene surface through the atomic force microscopy, field-emission scanning electron microscope and X-ray diffraction analysis. ALD dielectric films on the plasma-treated graphene result in negative shift in the Dirac voltage and the enhanced air stability.

ALD Applications
Room 116-118 - Session AA1-WeA
Energy: Catalysis and Fuel Cells

Moderators: Myung Mo Sung, Hanyang University, Yongfeng Mei, Fudan University, China

1:30pm **AA1-WeA-1 Oleo Sponge: Reusable Sorbent for Oil Spill Cleanup Fabricated using Sequential Infiltration Synthesis***, **Jeffrey W. Elam**, A Mane, E Barry, S Darling, J Avila, J Libera,* Argonne National Laboratory

Crude oil spills in the ocean can be devastating to the environment and extremely expensive to mitigate. Furthermore, while oil on the surface can be removed by skimming or burning, there are currently no technologies for the cleanup of subsurface oil droplets in the ocean. To address this need, we have developed a reusable sorbent material, Oleo Sponge. To synthesize this material, we begin with commercial polyurethane foam, and first treat the foam using sequential infiltration synthesis (SIS). SIS is similar to ALD in that it uses alternating, self-limiting exposures between gaseous precursors and a substrate. However, whereas the ALD substrate is a solid surface, in SIS the substrate is a polymer, and the precursors react on organic functional groups within the polymer to seed the nucleation of metal oxide clusters. We performed in situ infrared spectroscopy and mass spectrometry to elucidate the mechanism for metal oxide SIS within the polyurethane foam, and we have studied the effects of temperature, time, and partial pressure on the resulting SIS deposits. The next step is to graft an oleophilic monolayer onto the SIS-treated foam, either through gas-phase or solution phase treatment. The resulting material is simultaneously hydrophobic and oleophilic, and is able to rapidly extract oil from water. We have performed extensive bench-scale testing using 1" cubes of the Oleo Sponge and found that it absorbs >40x its weight in oil, and can be simply squeezed out and used again. Next, we performed a 10,000 scale up, and tested the material at the Ohmsett facility in Leonardo, New Jersey, using the largest outdoor saltwater tank facility in North America. The Oleo Sponge performed very well in extracting subsurface crude oil and diesel fuel from seawater under realistic conditions.

1:45pm **AA1-WeA-2 Evaluation of Zinc Oxide Fabricated by Atomic Layer Deposition as an Antibacterial Coating under UV Light***, **Gwon Deok Han**, K Park, M Kim, H Choi, J Koo, H Park, J Shim,* Korea University, Republic of Korea

Zinc oxide (ZnO) is widely used as a promising antibacterial agent in environmental remediation processes such as water disinfection and air purification [1]. This is because ZnO has a wide band gap energy (approximately 3.3 eV) which is favorable for photocatalytic reaction. In aquatic environments, ZnO produces reactive oxygen species (ROS) such as superoxide anion, hydroxyl radical, and singlet oxygen based on photocatalytic reaction promoted under UV irradiation. The photo-generated ROS exhibits antibacterial activity against microorganisms such as gram-negative bacteria and gram-positive bacteria. Recently, the improvement of the antimicrobial effect through application of nanoparticle ZnO having a high active surface area has been verified [2]. However, the ZnO nanoparticles have a problem in that the antibacterial ability is lowered due to agglomeration between nanoparticles and weak adhesion to the continuous flow-through reactor in wastewater treatment. Accordingly, immobilization of ZnO on reactor surface is essential.

In this study, we successfully demonstrated that thin-film ZnO fabricated by atomic layer deposition (ALD) exhibits comparable levels of antibacterial activity to commercially available ZnO nanoparticles [3]. We observed that the as-deposited ZnO consisted of closely packed nano-sized grains and firmly attached to the underlying substrate. As an alternative to the particulate photocatalysts, it was confirmed that the thin-film ZnO efficiently adsorbed UV light of 380 nm or less and continuously generated ROS even in repeated use in an aqueous environment. *Staphylococcus aureus* (*S. aureus*) was used as a gram-positive model bacterium for antimicrobial activity evaluation. Finally, we demonstrated that the photo-generated ROS from the thin-film ZnO damage cellular membrane and contribute to the death of *S. aureus*.

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2:00pm **AA1-WeA-3 ALD Enabled Non-linear Optical Properties at Substrate-film Interfaces***, Z Gao,* Washington University, St. Louis*; M Hussain,* University of Dayton*; D Ceglia,* Aegis Technology Group Inc.*; M Vincenti,* University of Brescia, Italy*; A Sarangan, I Agha,* University of Dayton*; M Scalora,* US Army AMRDEC*; J Haus,* University of Dayton*; **Parag Banerjee**,* Washington University, St. Louis

Metal-insulator and metal-semiconductor interfaces are a technologically important class of interfaces, given their ubiquitous presence in advanced materials and devices. ALD is an enabling synthesis tool for studying such materials systems as the first few monolayers deposited during ALD provide superb control over film thickness and nuclei morphology. Together with theoretical calculations and experimental nonlinear optical measurements, interfacial electronic properties at the nanoscale can be unraveled.

In this talk, the unique nonlinear optical signals generated from Au-Al_2O_3 and Au-ZnO systems will be described and correlated with predictions from hydrodynamic model for free electrons, incorporating quantum tunneling effects. Al_2O_3 and ZnO provide vastly differing nucleation behavior on Au substrates. Further, whereas Al_2O_3 is not known to be a nonlinear optical material, ZnO is strongly non-linear. The nucleation and growth of Al_2O_3 and ZnO on Au are studied using x-ray photoelectron spectroscopy (XPS) and Kelvin-Probe Force Microscopy (KPFM). The results show a clear nucleation followed by growth mechanism for ALD Al_2O_3 on Au, whereas for ALD ZnO on Au, a conformal layer-by layer growth is observed.

Second harmonic (SH) generation and third harmonic (TH) generation of incident light were measured on metal/insulator (MI): Au/Al_2O_3 & Au/ZnO; and metal/insulator/metal (MIM): Au/Al2O_3/Au & Au/ZnO/Au. The MIM was fabricated by coating the surface with gold nanoparticles. Both Al_2O_3 and ZnO films show a common feature for the SH signal in both MI and MIM structures. SH signals monotonically decreases and saturate once the Au surface is fully covered by the ALD film. In the case of Au/Al_2O_3, this allows us to develop a new phenomenological model[1] that estimates the occupancy of delocalized electrons in metal-induced-gap-states (MIGS) at 44%. On the other hand, the TH signal for the MIM case has a maximum that reaches a peak when the ALD film has a sub-nanometer thickness and is fully consistent with the electron quantum tunneling theory. Thus, ALD enables us to measure and understand interfacial electronic properties at the nanoscale for designing and fabricating future nonlinear optoelectronic devices.

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2:15pm **AA1-WeA-4 Bottom-up Fabrication of X-ray Optics using ALD***, **Umut Tunca Sanli**,* Max Planck Institute for Intelligent Systems, Germany*; C Jiao,* Thermo Fisher Scientific, Netherlands*; M Baluktsian, G Schütz, K Keskinbora,* Max Planck Institute for Intelligent Systems, Germany

The interest in X-ray microscopy has gained a rapid momentum especially in the last decade with the emergence of third- and fourth-generation synchrotrons, free electron lasers and new laboratory size X-ray sources. These new advanced X-ray sources require high-performance X-ray optics to study nano-scale structures. One of the most popular X-ray optic is the Fresnel zone plate (FZP), owing to its high-performance, monolithic structure and versatility. A FZP consists of alternating opaque and transparent co-axial annuli, which are the zones of the FZP. The resolution of the FZP is defined by the width of the outermost zone. Fabrication of the FZPs have been mostly relied on e-beam lithography, achieving resolutions down to 20 nm. However, efficient focusing of hard X-rays and resolutions beyond 20 nm requires structures that are extremely challenging to achieve *via* e-beam lithography or any other top-down subtractive method.

In this study, we follow a bottom-up approach and exploit the conformality and precision of ALD to manufacture the extremely challenging FZPs to achieve ultra-high resolution, highly efficient FZPs. Our method consists of three-steps: i) the fabrication of a micro-pillar array using a Plasma Focused Ion beam milling (PFIB), ii) the deposition of the multilayer zones of the FZP *via* ALD on the micro-pillar array and iii) the lift-out of individual FZPs using a FIB lift-out technique. The fabrication of FZPs requires using the ALD at the extreme. We deposit several hundred layers of ceramic materials, with thicknesses of 20-40 nm. The total deposition thickness reaches 6 µm. Due to its conformality, ALD allows multiple pillars to be deposited simultaneously. Hence, virtually unlimited number of FZPs can be fabricated out of one successful deposition. ALD is essential here as it provides the needed precision in zone positions through sequential, self-limiting reactions.

ALD-FZPs resolved 15 nm structures, the best resolution ever obtained via a multilayer FZP. For even higher resolutions, a better control of the interface sharpness, the microstructure, the volumetric mass density, and the chemical composition of the deposited layers become essential. In this study, characterization of the ALD layers via High-resolution Transmission Electron Microscopy (HR-TEM), Electron Energy Loss Spectroscopy (EELS), Energy dispersive X-ray Spectroscopy (EDX) Wavelength-Dispersive X-ray spectroscopy (WDX), X-ray Photoelectron Spectroscopy (XPS) and X-ray reflectometry (XRR) will be presented. Our results confirm that high-quality layers and interfaces are achieved through our ALD processes, required for sub-10 nm resolutions.

2:30pm **AA1-WeA-5 Thickness Optimization of Aluminum Oxide for High Secondary Electron Emission Deposited via Atomic Layer Deposition***, **Baojun Yan,*** Institute of High Energy Physics, Chinese Academy of Sciences, China

The performance of traditional electron multipliers, such as microchannel plate and channel electron multipliers, can be improved by coating high secondary electron emission (SEE) layers such as aluminum oxide via atomic layer deposition (ALD). The gain, peak to valley ratio and energy resolution of coated electron multipliers have been greatly improved by our previous study. As we all know, the SEE coefficient is depend on the material thickness if other conditions are fixed. In this study, the thickness optimization of aluminum oxide have been investigated. The aluminum oxide with varied thickness were deposited by ALD, and by comparing the performance of MCPs without and with aluminum oxide, the optimal range of SEE thickness can be obtained.

2:45pm **AA1-WeA-6 Effect of Deposition and Annealing Condition on Atomic Layer Deposited SnO_2 for Environmental Ozone Monitoring***, S Mills, V Misra, **Bongmook Lee,*** North Carolina State University

Portable and wearable systems to continuously monitor environment pollutants over long periods of time is great interest to correlate an individual's exposure levels to personal health. For example, Asthma is a lifelong respiratory ailment causing wheezing, breathlessness, chest tightness, coughing and degrades the quality of life for the patient. The impact of certain environmental exposures such as ozone and particulate matter are also known to be critical triggers in asthma attacks. Solid-state based thin film sensors are favorable for real-time and long-term environmental monitoring. Among various types of gas sensors, metal-oxide based thin film sensors are widely used but detection of gases relies on high temperatures (>300°C) for sensitivity and selectivity to various gases at the cost of many mW of power. Development of nanoscale metal oxide gas sensors which operate at room temperature is a promising strategy that leads to improved performance and reduced power consumption in the µW range. We have demonstrated that the high sensitivity and room temperature operated an ozone sensor based on atomic layer deposited (ALD) tin oxide (SnO_2). This work investigates the processing parameters such as deposition temperature and annealing time and its effects on tin dioxide sensor characteristics. Hall measurements were conducted on the SnO_2 films to evaluate the electrical properties as deposition and annealing conditions changed. It was found that the carrier concentration is generally increased with deposition temperature due to carbon impurities in the film at lower deposition temperatures. The electron mobility also increases strongly with deposition or annealing temperature resulting in lower resistivity of the film. It was also found that the SnO_2 deposited at 250°C has a crystalline structure confirmed by the XRD but the orientation was not preferable for sensor application. Transient sensor response was conducted for different ozone concentrations varying from 25 parts per billions (ppb) to 100 ppb. Decreasing deposition temperature was found to be associated with decreasing film conductivity, increased ozone response, and increased carbon content. The carbon content was a result of steric hindrance during the deposition process and that the carbon is a substitutional impurity for oxygen in the crystal lattice. This results in the decreased electron concentration and increased ozone response. The effect of annealing temperature was also evaluated. 600C air anneal shows a maximum ozone response. By optimizing deposition temperature and annealing condition, a highly sensitive, selective and room temperature operated ozone sensor is realized.

3:00pm **AA1-WeA-7 Etch Behavior of Ti-based Oxide Grown by Atomic Layer Deposition for Spacer Application***, H Kim, **Sanghun Lee**,* Yonsei University, Republic of Korea*; W Lee,* Pusan National University, Republic of Korea*; W Noh, S Gatineau,* Air Liquide Laboratories Korea*; S Kwon,* Pusan National University, Republic of Korea

Thin film grown by Atomic Layer Deposition has been enabled advanced nanopatterning technology such as spacer defined multiple patterning. The main scheme of this patterning technology is using sidewall spacer deposited by ALD as a hardmask.[1] However, usually the high aspect ratio and poor mechanical strength of spacers often causes its collapse problem and this phenomenon was also identified during multiple patterning process.[2] Therefore, the studies for spacer materials that have high etch selectivity and good mechanical properties are required, but there is lack of research on it. In this respect, TiO_2 is one of good candidate for spacer materials.[3,4]

Here, we studied on film properties of TiO_2 grown by ALD for spacer materials and further investigations for mixture with SiO_2 were followed. We observed growth of $Ti_xSi_{1-x}O_2$ (x=0~1) using $Ti(CpMe_5)(OMe)_3$, $Ti(O^iPr)_4$ and $H_2Si[N(C_2H_5)_2]_2$ and O_2 gas using PE-ALD at low temperature (100 °C). The chemical composition and carbon impurities of the films were analyzed by x-ray photoelectron spectroscopy (XPS), and the nanostructures of the films were analyzed by x-ray diffraction (XRD). And mechanical property of $Ti_xSi_{1-x}O_2$ films was investigated by nanoindentation. We compared the etch rate of $Ti_xSi_{1-x}O_2$ films using both dry and wet etching process. As a result, we obtained $Ti_xSi_{1-x}O_2$ films with various Ti/(Ti+Si) compositions and there was no Ti precursor dependency on dry etch rate which decreases as Ti composition increases. However, both pure TiO_2 films were not strippable by diluted HF solution due to its anatase phase. Furthermore, wet etch rate of mixtures were higher than even pure SiO_2 film when the films deposited by using $Ti(CpMe_5)(OMe)_3$.

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3:15pm **AA1-WeA-8 Scaling Atomic Layer Deposition to Astronomical Sizes: Low-temperature Aluminum Oxide Deposited in a Meter-sized Chamber***, **David Fryauf,*** University of California Santa Cruz*; A Phillips,* University of California Observatories*; G Tompa,* Structured Materials Industries Inc.*; N Kobayashi,* University of California Santa Cruz

Atomic Layer Deposition (ALD) is attractive for producing transparent barrier films on metal-coated astronomical mirrors, but to date has been limited to relatively small-sized substrates. A new ALD tool has been designed, constructed, and tested to apply uniform protective coatings over a substrate with 0.9 m diameter. The new tool, nicknamed the Big ALD , employs a novel chamber design which isolates a large substrate surface to be coated by utilizing the substrate as a wall of the reaction chamber. Conceptual design and implementation of this new tool are discussed with potential applications to large astronomical telescope optics, specifically protective coatings for silver mirrors, and other future large structures. To demonstrate the potential of this new design, aluminum oxide was deposited by thermal ALD using trimethylaluminum and water at a low reaction temperature of 60°C. Growth rates, dependent on precursor pulse times and chamber purge times, show that the two half-reactions occur in a saturated regime, which demonstrates typical characteristics of ideal ALD behavior. It is found that uniformity in growth across the chamber, rather than growth rate at a single chamber position, must be studied and optimized to identify saturated growth mode in the Big ALD. Thickness uniformity across a 0.9 m substrate is within 3% of the average film thickness. Aluminum oxide deposition process parameters of the Big ALD are compared with those of a conventional 100 mm wafer-scale ALD tool, and saturated ALD growth over the 0.9 m substrate is realized with a simple scaling factor applied to precursor pulse and purge times. The results show promising application of transparent robust dielectric films as uniform barriers across large optical components scaled to meter-sized and potentially larger substrates.

ALD Applications

Room 104-106 - Session AA2-WeA

Catalytic Application

Moderators: Yongbeom Kim, Hanyang University, Min Hwan Lee, University of California Merced

1:30pm **AA2-WeA-1 Surface Treatment of Solid Oxide Fuel Cell Cathodes by Atomic Layer Deposition***, **Min Hwan Lee**,* University of California Merced **INVITED**

The high operating temperature of solid oxide fuel cells (SOFCs) has limited their lifetime, cost competitiveness, start-up/shut-down speed and applicability to small-scale devices. Reduction of operating temperature, however, results in a dramatic loss of kinetics in both ionic transport and electrode reaction. In particular, sluggish electrode kinetics of oxygen reduction reaction (ORR) at the cathode side has been the main issue to resolve for a decent performance. As ORR of conventional intermediate-temperature SOFCs is often limited by dissociative adsorption and/or transport of electroactive species, an enlargement of catalytically active surface area while minimizing the transport distance is expected to improve the overall ORR kinetics significantly. For this end, a well-dispersed coating of nanoparticle-like catalysts on a cathodic backbone is achieved by e.g. infiltration of proper nitrate solution. The choice of infiltrated material can be mostly based upon catalytic activity and chemical inertness in the given environment, not limited by other criteria such as thermal expansion matching with underlying electrolyte and charge conductivity, which makes the material choice quite flexible. However, the merits of these high surface area structures come with susceptibility to thermal instability caused by particle agglomeration (by ripening and coarsening) during high-temperature operation. In this talk, we will present the application of atomic layer deposition (ALD) to form nanoscale oxide interfaces with platinum or lanthanum nickel ferrite (LNF or $LaNi_{0.6}$ $Fe_{0.4}O_{3-\Delta}$)-based cathodic backbones to tackle the concomitant issue of thermal instability. The impact of ALD treatments on the ORR kinetics, thermal degradation rate and changes in bottleneck process will be also discussed.

2:00pm **AA2-WeA-3 Bottom-Up ALD Engineering of FexCo1-xSy for Electrocatalytic Hydrogen Evolution***, **Wei Xiong**,* Peking University, China

The development of low-cost, efficient electrocatalyst for hydrogen generation from water (HER) is currently a core task for the hydrogen clean-energy technology. Generally speaking, an efficient electrocatalyst requires its bonding strengths with the reaction intermediates to be neither too high nor too low. Accordingly, the specific activity of a catalyst can be optimized by tuning the elemental composition of the catalyst. Experimentally, the tuning of the catalyst composition can be achieved by atomic layer deposition (ALD). Also, ALD allows for highly conformal loading of the catalyst as a thin coating layer onto a mesoscopically rough electrode support, which has a high surface area and therefore can further boost the overall electrocatalytic activity.

In this presentation, we will show a bottom-up strategy for designing an efficient ternary electrocatalyst by ALD.[1] The strategy involves two separate optimization steps: one is to optimize the specific activity of the catalyst material by ALD, and the other is to optimize the geometric structure of the catalyst support by fabricating a carbon nanotube (CNT) network on mesoscopically rough carbon cloth (CC). As an example, we optimize the composition of a promising ternary electrocatalyst of $Fe_xCo_{1-x}S_y$ via ALD, and the optimized $Fe_{0.54}Co_{0.46}S_{0.92}$/CNTs/CC electrode exhibits a fairly low HER overpotential of −70 mV for achieving −10 mA/cm^2 in current density in alkaline solution, which demonstrates the effectiveness of this ALD-based engineering strategy.

Reference

[1] Wei Xiong, Zheng Guo, Hao Li, Ran Zhao, Xinwei Wang,* "Rational Bottom-Up Engineering of Electrocatalysts by Atomic Layer Deposition: A Case Study of $Fe_xCo_{1-x}S_y$-Based Catalysts for Electrochemical Hydrogen Evolution", ACS Energy Lett., **2017**, *2* (12), pp 2778–2785 .

2:15pm **AA2-WeA-4 Plasma Enhanced Atomic Layer Deposition of Iron Carbide for Electrocatalytic Hydrogen Evolution***, Z Liu, **Yulian Hu**, Q Chen,* Beijing Institute of Graphic Communication, China

A plasma enhanced atomic layer deposition process for depositing iron carbide (Fe_3C) thin films is reported, using bis(N,N'-di-tert-butylacetamidinato)iron(II) and H_2 plasma. The process shows an ideal self-limiting ALD growth fashion with a saturated film growth rate of 0.041 nm/cycle for a fairly wide process temperature window from 80 to 200°C. The surface morphology of iron carbide film is investigated by atomic force microscopy and scanning electron microscopy. X - ray diffraction, X - ray photoelectron spectroscopy and transmission electron microscopy are used to analyze the crystal phase, film composition and microstructure of iron carbide films. Using this ALD process, Carbon cloth could be uniformly and conformally coated by a thin layer of Fe_3C to afford a nanostructured Fe_3C/CC composite. The ALD-prepared Fe_3C/CC composite is demonstrated to show excellent performance for electrocatalytic hydrogen evolution.

2:30pm **AA2-WeA-5 Gadolinia-doped Ceria Thin Film Fabricated by Atomic Layer Deposition for Enhancing ORR Kinetics of LT-SOFC***, **Hwichul Yang**, S Kim, Y Lim, Y Kim,* Hanyang University, Republic of Korea

Ceria(CeO_2)-based material, including gadolinia-doped ceria(GDC), samaria-doped ceria(SDC) and yttria-doped ceria(YDC), has emerged as an electrolyte for low temperature solid-oxide fuel cells(LT-SOFCs) due to the high oxygen ion conductivity and oxygen-reduction reaction(ORR) kinetics compared to yttria-doped zirconia(YSZ) which is a standard electrolyte material for SOFC. Mainly, it has been used as a functional layer on YSZ for enhanced ORR kinetics because it is hard to use ceria-based material as a single electrolyte due to the reduction characteristic in hydrogen environment. Typically, small grain and nanocrystalline structure of this functional layer shows higher ORR kinetics, and thin film fabricated by atomic layer deposition(ALD) is well known for showing that characteristics. In this study, characteristics and effects of GDC functional layer fabricated by atomic layer deposition(ALD) was studied. Surface morphology and crystal structure of ALD/GDC was investigated by physical analysis methods. ALD/GDC functional layer has a small surface grain and nanocrystalline structure, which has lots of oxygen incorporation site and reduces polarization loss. By electrochemical impedance spectroscopy(EIS) method, reduced polarization loss was observed for ALD/GDC-applied cell. Current-voltage characteristic shows enhanced performance of ALD/GDC-applied cell. These results about ALD/GDC indicates that ALD-fabricated functional layer has superior characteristics for SOFC performance.

2:45pm **AA2-WeA-6 Atomic Layer Deposition of Palladium Nanoparticles on Nickel for Direct Methanol Solid Oxide Fuel Cell Catalysts***, **Junmo Koo**, D Jang, H Choi, J Kim,* Korea University, Republic of Korea*; H Jeong,* University of Illinois at Urbana-Champaign*; J Shim,* Korea University, Republic of Korea

Direct usage of methanol as a fuel of solid oxide fuel cells (SOFCs) has several advantages compared to hydrogen gas fuel. Liquide form of methanol enables easy and safe storage, and it can be utilized as fuel without any cumbersome reforming process. These advantages of methanol have drawn much attention in the field of fuel cell society. However, catalyst poisoning originated from residual carbon monoxide and slow reaction of DMSFOC electrode is the most urgent issue of DMSOFC. Among various catalyst for DMSOFC, platinum-ruthenium bimetallic catalyst has shown the best performance for methanol oxidation. High cost of Pt, however, hinders the widespread commercialization of DMSOFC. Recently, nickel is regarded as promising substitute of Pt/Ru catalyst for its reforming performance of alcohol and hydrocarbon and inexpensive price. However, unwanted carbon formation is occurred during electrochemical oxidation of methanol using Ni catalyst. Therefore, nickel-based alloys have been widely studied for the effective oxidation of methanol and avoid unwanted carbon coking of nickel catalyst. Palladium (Pd) is one of the strong candidate material for bimetallic nickel-based catalyst. Previous studies reported the enhanced catalytic activity and unwanted carbon deposition on anode surface originated from the existence of Pd.

Optimum structure of Ni/Pd bimetallic catalyst would be composed of well-dispersed Pd nanoparticles on Ni substrate due to relatively high price of Pd compared to that of Ni. Atomic layer deposition (ALD) was used in order to fabricate Pd nanoparticles because of its unique availability to deposit uniform film even on complex structures. In this study, Ni/Pd bimetallic catalyst for DMSOFC were evaluated by fuel cell performance, electrochemical impedance spectroscopy, and long term-stability. ALD-made Ni/Pd catalyst revealed enhanced performance and stability compared to sputter-made Ni/Pd catalyst, which represents the effectiveness of ALD technique for fabricating surface-modified catalyst with increase surface area for desired reactions.

3:00pm **AA2-WeA-7 Diffusion-Limited Atomic Layer Deposition: Realizing the Encapsulation of Homogeneous Catalysts*, Bin Zhang*,** *S Zhang, H Liang, Y Qin,* Institute of Coal Chemistry, Chinese Academy of Sciences, China

The homogeneous metal complex catalysts play an important role in chemical engineering, biology and medicine industry. The heterogenization of homogeneous metal complex catalystshas performed both advantages of homogeneous (high activity and selectivity) and heterogeneous catalysts (reusability).Generally, the encapsulation of metal complexes via physical adsorption in the pore channels of porous materials is preferred, because it can maintain the properties and freedom of metal complexes. The big challenge is to precisely tailor the pore entrance size of the porous materials. Recently, we have realized the encapsulation of metal complexes into nanochannels of mesoporous materials by building a "hollow plug" at the pore entrance via diffusion-limited ALD[1]. The pore size of the hollow plug is precisely controlled on the sub-nanometer scale by changing the number of ALD cycles to encapsulate various metal complexes with different molecular sizes. Moreover, we have also investigated the effect of ALD parameters and cycles on the activity and reusability of heterogeneous catalysts by the encapsulation. This ALD-assisted encapsulation method has a wide application and can be applied to the encapsulation of most homogeneous catalysts into different mesoporous materials for various heterogeneous reactions.

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3:15pm **AA2-WeA-8 Ultrathin ALD Yttria-Stabilized Zirconia Overcoating on Metal Electrodes for Low Temperature Solid Oxide Fuel Cell*, Byung Chan Yang*,** *D Go, S Oh, J Shin, J An,* Seoul National University of Science and Technology, Republic of Korea

Solid oxide fuel cells (SOFC) have attracted much attention as highly efficient, fuel-flexible, and eco-friendly energy conversion device. However, conventional SOFC have practical issues in applications to various fields due to high operating temperature (up to 1000℃). Recently, studies on low temperature SOFC (LT-SOFC) (≤ 500℃) which can be operated at a relatively low temperature have been actively conducted. However, since it is operated at a low temperature, electrochemical reaction at the electrode is lowered; therefore, the use of noble metal electrode is essential. However, thermal stability, in this case, is also reduced by using noble metal electrode at elevated temperature.

In this study, we show how to improve the thermal stability of metal electrode by depositing yttria-stabilized zirconia (YSZ) overlayer. We have improved the SOFC performance and thermal stability by applying the ultrathin (2-3nm) YSZ overlayer with varying composition. YSZ overlayers were deposited by atomic layer deposition (ALD) on Pt electrodes with 0, 8, 15, 30, and 100 mol% of Y_2O_3-doping in ZrO_2, respectively. Doping level was controlled by the relative cycle ratio between Y_2O_3 and ZrO_2 in of ALD process. Fuel cell performance were analyzed through I-V-P and EIS measurements, and the thermal stability was measured using chronoamperometry. The performance of the reference cell decreased by more than 50% after 10 hours of operation, while that of the cell with YSZ overlayer was maintained at > 90% even after 10 hours of operation. Also, the performance of 8mol%-doped YSZ overlayer was 450℃ to 1.46mW / cm^2, which was not different from 1.4mW / cm^2 of the reference cell. However, the performance of the cell with 15mol%-doped YSZ overlayer was ~10% higher than that of reference cell. These results show that ALD can effectively tune the composition of the 2-3nm-thick YSZ overlayer, which can hugely affect the SOFC performance as well as the thermal stability.

ALD Applications
Room 116-118 - Session AA3-WeA

Functional Film Application
Moderator: Han-Bo-Ram Lee, Incheon National University

4:00pm **AA3-WeA-11 Catalyst Synthesis and Modification via Atomic Layer Deposition: From Supported Metal Catalysts to Complex Systems*, Mar Piernavieja Hermida*,** *R Naumann d'Alnoncourt, K Knemeyer,* Technische Universität Berlin, Germany*; V Strempel,* BASF SE, Process Research and Chemical Engineering*; A Trunschke, R Schlögl,* Fritz Haber Institute of the Max Planck Society, Germany*; M Driess,* Technische Universität Berlin, Germany*; F Rosowski,* BASF SE, Germany

Even though microelectronics has been one of the major adopters of atomic layer deposition (ALD) during the past 20 years, many other applications such as synthesis of battery materials, fuel cells or catalysis have been of increasing interest. A recent review from Junling Lu, Jeffrey W. Elam and Peter C. Stair summarizes the literature reports in the field of catalysis [1]. The vast majority of the cited contributions involve supported metal nanoparticle catalysts. Although in a lesser magnitude, metal oxides have been used as well due to their unique properties.

Our main focus lies on catalysts used for selective oxidation reactions, typically consisting of mixed metal oxides or phosphates. We aim to modify properties of bulk catalysts by changing the catalysts surface via ALD or using ALD for bottom up synthesis of complex systems as mixed metal phosphates or oxides on suitable supports. Thus, our main application of ALD is deposition in a submonolayer regime or deposition of very thin films (< 1 nm) rather than deposition of metal nanoparticles. A small number of ALD cycles can lead to homogeneous coverage of a catalyst surface with adatoms, leading to a higher catalytic performance.

For example, a combination of a thermal magnetic suspension balance and a fixed bed reactor [2] was used to deposit phosphorous on the surface of vanadia, changing its catalytic performance from total oxidation towards maleic anhydride formation [3]. The set-up was also used to deposit different compounds (promotors or poisons) on the surface of vanadyl pyrophosphate to influence its catalytic activity and selectivity. Our next step will be the deposition of vanadium containing layers, e.g. $(VO)_2P_2O_7$ or $VOPO_4$, on a suitable support.

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4:15pm **AA3-WeA-12 Atomically Controllable Ru@Pt Core Shell Nanoparticles Towards PROX's Reactions Modulated by Pt Shell Thickness*, Yun Lang*,** *K Cao, J Zhang, B Shan, R Chen,* Huazhong University of Science and Technology, China

Preferential oxidation of CO under excess H_2 (PROX) is an effective way to remove CO from steam reforming of hydrocarbons for application in proton exchange membrane fuel cell.[1] For PROX, the bimetallic core shell nanoparticles can tremendously improve total activity and selectivity of PROX reactions[2]. However due to the lack of precise control over the core shell structures, the studies of relationship between PROX reactions with nanoparticles' structural parameters remain very limited. Herein, we demonstrate synthesis of Ru@Pt core shell nanoparticles using area-selective ALD techniques based on precursors' partial pressure and deposition temperature adjustment. A near linearly growth rate of Pt on Ru surface monitored with in-situ quartz crystal microbalance indicates well-controlled shell thickness by varying ALD cycles. The catalytic activity and selectivity of Ru@Pt core shell structure are enhanced compared with single component Ru, Pt or alloyed structure, which results from electron transfer from Ru to Pt. The catalytic performance is sensitive with shell thickness that influences the extent of electron modification and lattice mismatch. A monolayer of Pt shell shows optimal catalytic performance and minimal Pt loading. Density functional theory simulations have also been carried out to verify the results.

[1] H . Xu, Q. Fu, X. Guo, X. Bao, ChemCatChem. 2012, 4, 1645

[2] A. U. Nilekar, S. Alayoglu, B. Eichhorn, et al, J. Am. Chem. Soc. 2010, 132, 7418

ALD Fundamentals
Room 113-115 - Session AF1-WeA
In-situ Monitoring and Analysis

Moderators: Christophe Detavernier, Ghent University, Belgium, Christian Dussarrat, Air Liquide

1:30pm **AF1-WeA-1 In Situ IR Spectroscopic Investigation of Thermal and Plasma-Enhanced ALD of Pt: Temperature Dependency of the Growth Rate***, **Michiel Van Daele**, C Detavernier, J Dendooven,* Ghent University, Belgium

The O_2-based processes of Pt using the $MeCpPtMe_3$ precursor have become a model system for oxidative noble metal ALD processes. The thermal process is characterized by a narrow temperature window (250-300°C; below this temperature range the growth rate quickly diminishes), while PE-ALD process has a much larger temperature window. An intriguing question is why the growth diminishes below 250°C for the thermal process. It has been suggested in literature that the precursor ligands dehydrogenate on the catalytic Pt surface and form a carbonaceous layer causing surface poisoning. However, direct identification of the surface species to support this hypothesis is missing. This is mainly because IR light is absorbed by metals, which complicates in-situ IR spectroscopy studies in transmission. In this work, in situ reflection IR spectroscopy is used during O_2 and O_2 plasma based ALD processes at different deposition temperatures to shed light on the reactions that take place on the surface during the processes.

The ALD setup used for this work is shown in Fig. 1. It concerns a pump type ALD chamber that is connected to a Bruker Vertex 70v IR spectrometer. To ensure steady state growth conditions, a sputtered Pt film is used as the substrate. Substrate temperatures of 100, 200, and 300°C are used. FTIR spectra are taken after every precursor and reactant pulse. Consecutive spectra are subtracted, giving difference spectra for each half cycle. Positive (negative) features in Fig. 2 are due to added (removed) surface groups.

We have found evidence that CH_3 and C=C containing species are present on the surface after precursor exposure at low substrate temperatures (<150°C), poisoning the surface during thermal ALD. These species are removed by O_2 plasma which enables PE-ALD below 150°C through combustion reactions. Above 150°C, no CH_3 groups were detected and the C=C vibrations diminished for both the thermal and PE-ALD process which indicates dehydrogenation reactions and ligand restructuring. Both processes show the presence of CO combustion products after precursor exposure. In addition, the PE-ALD FTIR spectra indicate the presence of ether and ester combustion products after precursor exposure, likely due to a higher amount of surface oxygen for the PE-ALD process compared to the thermal process. We conclude that the restructuring and dehydrogenation of the precursor ligands is necessary to allow the dissociation of molecular O_2 on the Pt surface, explaining the need for high substrate temperatures for the thermal Pt process.

1:45pm **AF1-WeA-2 Growth Mechanisms and Diffusion Behavior of Molecular Layer Deposition Films Deposited by Cyclic Azasilanes, Maleic Anhydride, and Water***, **Ling Ju**, N Strandwitz,* Lehigh University

Molecular layer deposition (MLD) using N-(2-aminoethyl)-2,2,4-trimethyl-1-aza-2-silacyclopentane (AZ), maleic anhydride (MA), and H_2O is used to grow hybrid organic-inorganic films.[1] The growth rate (~ 90 Å/cycle in the steady state at 100 °C) is much larger than for MLD/ALD chemistries that involve exclusively surface reactions, indicating that precursor diffusion into the MLD film plays a key role in the large growth rate.[1]

In-situ quartz crystal microbalance (QCM) measurement monitors the mass gains during individual reactions, and provides detailed information of precursor diffusion behavior by varying the precursor sequence, substrate temperature, and purging time. The mass profiles during the AZ and MA reactions are consistent with these two precursors diffusion into and out of the MLD films. The growth also displays a strong dependence on the substrate temperature and purge times of AZ and MA, that is consistent with the effects of the sub surface reactions. Diffusion coefficient and diffusion depth of different precursors were quantified. These studies provide better understanding of the structures and growth behavior of the MLD films, and avenues for basic studies of the effects of specific chemical functionalities on growth.

1 L. Ju, B. Bao, S. W. King and N. C. Strandwitz, J. Vac. Sci. Technol. A **35,** (2017).

2:00pm **AF1-WeA-3 *In-situ* RAIRS Investigation of the Oxidation and Reduction of Cu using UV/O_3 and Ethanol***, **Luis Fabián Peña,*** The University of Texas at Dallas*; M Todd,* Versum Material, Inc*; Y Chabal,* The University of Texas at Dallas

Copper is the most widely used material in semiconductor interconnect technology because of its superior conductivity and resistance to electromigration. Although several methods to deposit copper oxide on nanostructured surfaces with high aspect ratio have been developed using ALD,[1,2] a reduction step is required to convert the deposited copper oxide film into metallic copper. Promising results have been demonstrated using ethanol as the reduction agent but little experimental data is available on the reduction pathways; the reaction mechanisms and surface chemistry are poorly understood.

In this work we use *in-situ* reflection absorption infrared spectroscopy (RAIRS) to investigate each step of the oxidation (UV/O_3) and reduction (ethanol (EtOH)) process to achieve an ideal Cu metal surface in an ALD environment.

To understand the reduction of copper oxide thin films with ethanol, we investigate the role of ethanol partial pressure on the oxide reduction rate by monitoring the surface species after each dose. To illustrate, the IR spectra in **Fig. 1** shows that the initial reaction begins by reducing the concentration of surficial C≡O species (2209 cm^{-1}) and this frequency is red shifted to (2175 cm^{-1}) as the extent of dipole coupling is reduced after subsequent ethanol exposures. At the same time, the reduction of CO_2 (2337 cm^{-1}) takes place after the 2nd EtOH exposure at which point the reduction of Cu_2O also begins to take place (636 cm^{-1}). Eventually, 4 consecutive EtOH exposures are enough to reduce the oxide on Cu (632 cm^{-1}). Having established an understanding on the reactions taking place on the surface, the process is optimized to reduce by-product re-deposition using an ALD-like binary process with EtOH and nitrogen.

References

[1] Alnes, M. E., Chem. Vap. Deposition, 18: 173–178

[2] Waechtler, T*.,* J. Electrochem. Soc. *2009 156(6):H453-H459*

2:15pm **AF1-WeA-4 Real Time GISAXS Study of the Effects of Plasma Gas Chemistry on Growth of InN Films by Atomic Layer Epitaxy***, **Neeraj Nepal,*** U.S. Naval Research Laboratory*; V Anderson,* The American Society for Engineering Education*; S Johnson,* U.S. Naval Research Laboratory*; S Rosenberg, J Woodward, A Kozen,* The American Society for Engineering Education*; C Wagenbach,* Boston University*; D Meyer, B Downey, J Hite, V Wheeler,* U.S. Naval Research Laboratory*; Z Robinson,* SUNY College at Brockport*; D Boris, S Walton,* U.S. Naval Research Laboratory*; K Ludwig,* Boston University*; C Eddy, Jr.,* U.S. Naval Research Laboratory

III-N semiconductors have found application in a variety of technologies, however, the requisite heteroepitaxy on foreign substrates, miscibility gaps, substrate versatility and low strain heterojunctions challenge material developments. Among III-Ns, InN has the lowest growth temperature, which represents a significant challenge to epitaxial growth of single phase In containing layers. To address this, the growth temperature has to be reduced. Plasma assisted atomic layer epitaxy (ALEp) offers a new low temperature growth approach to achieve epitaxial thin films [1]. At reduced growth temperatures, plasma driven non-thermal equilibrium kinetics on nucleation and growth process is critical for improved material quality. As conventional, ultra-high vacuum growth monitoring methods generally difficult to employ, we have shown that using high intensity x-rays to monitor the evolution of grazing incidence small angle x-ray scattering (GISAXS) features directly correlate with the surface roughness, impurities, and electrical properties of the thin film [2].

In this paper, we present real time GISAXS Study of plasma gas chemistry and its effect properties on growth in the synthesis of high quality InN films by ALEp on a-plane sapphire substrate at 250°C. The total gas flow through the plasma source (N_2 +Ar = 275 sccm) was kept constant while the N_2 flow was varied from 15 to 95 sccm. During the initial cycles of InN growth on a-plane sapphire, the specular peak broadens and the correlated peak (CP) start to evolve along the native wing with different correlated length scales (CLSs). At N_2= 95 sccm surface scattering is higher and it appears to increase with N_2 flow fraction. During growth CLS remains constant at 11.56 nm for 94 sccm N_2 while it increases from 9.72 to 12.56 nm for 15 sccm of N_2. Separation between the diffuse scattering rod and CP is smaller for lower N_2 flow at the end of the growth. Lower N_2 flow through plasma increases reactive nitrogen species on the growth surface, which initiate coarsening by converging nucleation islands. Consistent with *in situ* GISAXS, post-growth atomic force microscopy shows that surface roughness decreases from 0.35 nm to 0.12nm by decreasing N_2 flow fraction from

34% to 5%. Post-growth x-ray photoelectron spectroscopy indicates shows no carbon for all films. In this paper we present plasma characterization results to understand the influence of relative gas flow on species production and their effect on growth besides structural, morphological, and electrical properties of ALEp grown InN films.

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2:30pm **AF1-WeA-5 Low-Temperature Plasma-Enhanced Atomic Layer Deposition of Cobalt Thin Films using Cyclopentadienylcobalt-dicarbonyl and N$_2$-H$_2$ Plasma**, ***Pouyan Motamedi***, *K Bosnick,* National Research Council Canada, Canada*; K Cadien, J Hogan,* University of Alberta, Canada

The field of thin and ultrathin metallic thin films has attracted a great amount of attention, owing to their various applications, including microelectronics, enhanced solar absorbers, and catalysts for growth of carbon nanotubes. In most cases, achieving the capacity to deposit a conformal thin film on a three-dimensional structure is an important factor. Plasma-enhanced atomic layer deposition (ALD) offers potential for growth of conformal thin films with a precise control over the thickness, and its capability for deposition at relatively low temperatures. A survey of the literature reveals that the field of growing metallic thin films via ALD is relatively under-studied. Specifically, cobalt has several applications as a magnetic material, and is being increasingly considered to be used as an interconnect in nanofabrication. Unfortunately, the amount of research available on ALD of cobalt thin films is extremely limited. Here, we demonstrate that, using an organometallic precursor and nitrogen plasma, cobalt thin films can be deposited at temperatures as low as 240°C. The deposited films show no sign of carbon and oxygen impurities. A comprehensive characterization analysis was performed on the films, in order to study their composition, physical properties, surface properties, and crystal structure. In addition, in-situ spectroscopic ellipsometry was utilized to observe and analyze the growth rate and optical properties of the films, as a function of growth cycles. All these analyses were performed for the growth temperature range of 120-500°C. The general conclusion was that the specific combination of the precursors and the recipe was very successful in deposition of smooth, crystalline, and chemically pure cobalt thin films with resistivity and optical properties close to those of the bulk material. A wealth of useful information was gathered about the growth mechanism of metals using ALD, which can be potentially applied to other metallic thin films.

2:45pm **AF1-WeA-6 A Surface Science Toolbox for Understanding Atomic Layer Epitaxy**, ***Charles R. Eddy, Jr.***, *S Rosenberg, J Woodward,* U.S. Naval Research Laboratory*; D Pennachio, C Palmstrøm,* University of California, Santa Barbara*; N Nepal,* U.S. Naval Research Laboratory*; V Anderson,* Kennesaw State University*; S Johnson,* U.S. Naval Research Laboratory*; C Wagenbach, K Ludwig,* Boston University*; A Kozen, S Walton, D Boris, V Wheeler,* U.S. Naval Research Laboratory

Atomic Layer Epitaxy (ALEp) is a promising subset of atomic layer processes (ALPs) which has the potential to open a new realm of non-equilibrium semiconductor growth. In ALEp, the objective is to grow crystalline, epitaxial layers on a crystalline substrate for active regions of electronic and optoelectronic devices. This requires expansion of the ALD processing space to higher temperatures and adds constraints of crystallinity and purity (electronic grade requires impurity concentrations less than ppm). While ALEp has been shown to maintain the self-limiting nature of ALD at temperatures up to 500°C, the additional materials quality criterion requires a more complete understanding of the ALEp process if it is to be fully successful. In this regard, it is essential to develop a set of surface science tools that can be employed either *in situ* or *in vacuo* to ensure that atmospheric exposure does not influence or interfere with observed process mechanisms.

In this work, we highlight the development and early application of a suite of *in situ* or *in vacuo* characterization techniques aimed at providing surface and near-surface structure assessments [reflection high energy electron diffraction/low energy electron diffraction (RHEED/LEED) and grazing incidence small angle x-ray scattering (GISAXS)] as well as surface chemistry assessments [(x-ray photoelectron spectroscopy (XPS), resonant ion trap mass spectrometry (RIT-MS) and reflection-absorption infrared spectroscopy (RAIRS)]. We present select results from these characterizations during efforts to develop ALPs for GaN surface preparation for epitaxy and for early ALEp growth of heteroepitaxial AlN and InN films on GaN and Al$_2$O$_3$ substrates as a function of plasma pulse conditions. As an example, GISAXS measurements have revealed a distinction in the growth mode of InN on sapphire vs. GaN substrates for an otherwise identical ALEp process, with the former proceeding by correlated island growth with short range order and the latter by long range order evolution on properly prepared surfaces. Further, the duration of the plasma pulse is shown to influence the growth mode between a bimodal distribution of islands for short pulses to a single mode distribution for intermediate pulses to etching for the longest pulses. Changes in plasma chemistry are also found to affect growth mode and film quality. These changes are correlated to independent measurements of plasma properties in an effort to establish plasma process – film property relationships. A combination of RAIRS and RIT-MS will be presented to further illustrate the role of plasma chemistry.

3:00pm **AF1-WeA-7 Investigation of the Temperature Dependence of Plasma-assisted Atomic Layer Epitaxy Growth of InN on GaN using *in situ* Grazing Incidence Small-angle X-ray Scattering**, ***Jeffrey M. Woodward***, *S Rosenberg,* The American Society for Engineering Education*; N Nepal, S Johnson,* U.S. Naval Research Laboratory*; C Wagenbach,* Boston University*; A Kozen,* The American Society for Engineering Education*; Z Robinson,* SUNY College at Brockport*; K Ludwig,* Boston University*; C Eddy, Jr.,* U.S. Naval Research Laboratory

Plasma-assisted atomic layer epitaxy (ALEp), a variant of atomic layer deposition in which relatively higher temperatures are utilized to promote surface diffusion for epitaxial growth, offers several potential advantages over conventional methods such as metalorganic chemical vapor epitaxy and molecular beam epitaxy for the growth of III-N materials and device structures. These advantages include significantly lower growth temperatures and highly controlled layer thicknesses, the latter of which is the result of the sequential pairs of self-terminating and self-limiting reactions that constitute the growth process. However, plasma-assisted ALEp is a relatively new method for III-N growth, and significant efforts will be required to better understand the nucleation and growth kinetics. To this end, grazing incidence small-angle X-ray scattering (GISAXS) has been previously utilized for the study of surface morphology during the plasma-assisted ALEp growth of InN[1] and AlN[2] on a-plane Al$_2$O$_3$ substrates. GISAXS is a non-destructive technique that can probe electron density fluctuations of length scales ranging from approximately 1 nm to 250 nm in an integral manner, making it well-suited to the study of epitaxial growth. The resulting intensity distribution from a collection of scattering objects is related to the form factor and structure factor, which are the Fourier transforms of functions describing the object shape and spatial arrangement, respectively.

In this work, we present *in situ* GISAXS studies performed at the Cornell High Energy Synchrotron Source during the plasma-assisted ALEp growth of InN on bulk GaN substrates, using 180°C, 250°C, and 320°C growth temperatures. We analyze the intensity distributions in order to extract information about the evolving morphologies. The data indicates that the InN islands are cylindrical, with mean inter-island spacings that scale with temperature. While deposition on GaN at 180°C was found to yield comparable inter-island spacings to those previously reported for deposition on a-plane Al$_2$O$_3$ at low temperatures[1], deposition on GaN at 250°C produced islands with increased spacing compared to a-plane Al$_2$O$_3$ at the same temperature. The inter-island spacing at 180°C was approximately constant throughout the growth process, which may indicate that such temperatures are insufficient for island coalescence. In contrast, the inter-island spacings at 250°C and 320°C were found to increase with growth time.

[1] N. Nepal et al., J. Vac. Sci. Technol. A **35**,031504 (20107)

[2] V. R. Anderson et al., J. Vac. Sci. Technol. A **35**, 031508 (2017)

3:15pm **AF1-WeA-8 In situ Investigations on the Crystal Structure Dependent ALD Film Growth of TiO$_2$**, ***Martin Knaut***, *M Albert, J Bartha,* Technische Universität Dresden, Germany

The ALD of TiO$_2$ from titanium tetraisopropoxide (TTIP) and water or ozone is a widely known and well-reviewed ALD process.[1-3] Nevertheless, there are papers reporting inhomogeneous film growth or non-ideal surface reactions which might cause CVD effects.[3-6] Additional, Kim et al. published an impact of the crystal structure of TiO$_2$ films on the density of surface hydroxyl groups and thus on the amount of chemisorbing TTIP molecules correlating with the film growth per cycle.[7] In this paper we present detailed in situ based investigations on the TiO$_2$ film growth and its interaction with process parameters and film properties. Quartz crystal microbalances were used to monitor the TiO$_2$ deposition at temperatures between 200 and 300°C showing a spontaneous thickness and substrate temperature dependent change in GPC (marked by black dots in figure 1). This change in GPC corresponds to the crystallization of amorphous TiO$_2$

films into an anatase phase which was confirmed by atomic force microscopy and Raman spectroscopy measurements. A detailed analysis of the mass changes during single ALD cycles revealed an impact of the crystal structure on the amount of chemisorbing precursor molecules and so on the growth per cycle. While Kim et al. addressed this effect to a higher density of surface hydroxyl groups this work shows that the change in film growth is also related to an enhanced thermal decomposition of TTIP molecules on an anatase film resulting in a non-saturating CVD-like film growth once the film crystallizes. To enable linear and reproducible processes Al_2O_3 buffer layers have been applied to suppress film crystallization even at elevated temperatures and thicknesses. This approach allows to deposit thick amorphous TiO_2 films with a constant growth per cycle (see figure 2).

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ALD Fundamentals
Room 113-115 - Session AF2-WeA

Process Development

Moderators: Woojin Jeon, Dankook University, Harm Knoops, Eindhoven University of Technology

4:00pm **AF2-WeA-11 Water Assisted ALD Process for Y_2O_3 Thin Films and Evaluation of the Y_2O_3 Containing Metal-insulator-capacitor Structures**, ***Nils Boysen***, *L Mai, E Subasi, C Bock, A Devi,* Ruhr-University Bochum, Germany

The development of new ALD processes involving promising metal-organic precursors and mild process conditions is important to gain advances in creating ultra-thin films with superior functional properties for various micro- and optoelectronic applications. ALD is the method of choice for these functional applications, as the deposition of conformal, dense and pure films at low temperatures and mild oxidizing conditions is possible, which renders ALD as an indispensable method for modern microelectronic devices. In this context, the development of a new ALD process for the material Yttrium(III) oxide is highlighted, as Y_2O_3 exhibits a large band-gap of 5.5 – 5.8 eV with a dielectric constant of k = 14-18, while also possessing a high thermal stability and a high mechanical strength, which makes this material a suitable choice for application as high-k gate dielectric in metal-oxide-semiconductor field-effect transistor (MOSFET) based devices. Among the reported precursors for the ALD of Y_2O_3 there are certain drawbacks, which include a narrow ALD-window, high deposition temperatures and low growth rates. To tackle some of these issues, we developed a new water assisted ALD process for the fabrication of ultra-thin Y_2O_3 films under mild process conditions involving the highly reactive precursor Tris(*N*,*N'*-diisopropyl-2-dimethylamido-guanidinato) Yttrium(III) [Y(DPDMG)$_3$]. Furthermore, detailed film characterization with a special focus on the functional properties of the Y_2O_3 thin films were performed and the results are highlighted. The Y_2O_3 thin films were deposited in a self-limiting ALD growth mode ranging from 175°C to 250°C (Figure 1) resulting in smooth, polycrystalline and oxygen-rich thin-films with low level of contamination (Figure 2). To prove the functionality of the yttria thin films in terms of dielectric applications, 20 nm Y_2O_3 thin films were used as the insulating material in Au/Ti/Y_2O_3/*n*$^+$-Si(100) capacitors which revealed a very high breakdown field between 4.0 and 7.5 MV/cm accompanied by a low leakage current density of about 10^{-7} A/cm^2 at 2 MV/cm (Figure 3)[1]. The dielectric permittivity in this capacitor stack was estimated to be k =11. The oxygen-rich features on the surface of the thin-films render this material promising as a passivation layer for metal oxide thin film transistors (MOTFT), to enhance their stability and electrical performance. The promising performance of our yttria films renders the new ALD process as a potential alternative to other established ALD processes for the deposition of yttria by successfully lowering the deposition temperature, while retaining growth rate and thin-film purity.

4:15pm **AF2-WeA-12 New Plasma-enhanced Atomic Layer Deposition Process for SnO_2: Process Development and Evaluation of SnO_2 for TFT Applications**, ***David Zanders***, *L Mai, E Subasi, C Bock, A Devi,* Ruhr-University Bochum, Germany

Tin (IV) oxide (SnO_2) is a promising n-type semiconducting material with excellent electrical and optical properties.[1,2] Hence, thin films of SnO_2 are employed in a broad range of devices such as photovoltaic cells[3] and thin film transistors (TFTs)[4]. With respect to TFTs, SnO_2 as a channel layer material is exceptionally attractive due to its high mobility and transparency. As the properties of metal oxide semiconductor thin films for optoelectronic applications are highly dependent on the deposition process, a wise choice must be made to this effect. Atomic layer deposition (ALD) and plasma enhanced ALD (PEALD) are favourable for such applications owing to the low processing temperatures, precise control of thickness as well as dense and conformal coverage over complex device geometries.

Herein we report a new and promising PEALD process using a new tin alkyl precursor for the deposition of SnO_2 thin films. The liquid precursor is volatile and thermally robust as evidenced by thermal analysis (Fig. 1) and temperature dependent NMR studies. The application of this precursor in a PEALD process using oxygen plasma resulted in high quality SnO_2 layers. The self-limiting ALD growth characteristics and the saturation behavior were confirmed at different substrate temperatures ranging from 60 – 150°C (Fig 2). The films were characterized by XRR, AFM, RBS, NRA and XPS to evaluate the structure, morphology and composition. The as-deposited SnO_2 films were amorphous and stoichiometric. The functional properties in terms of optical bandgap was determined to be 3.6 eV from UV-Vis measurements. Finally bottom-gate bottom-contact TFTs were fabricated using the SnO_2 as a channel layer. Mobilities up to 10 cm^{2}V^{-1}s^{-1} were achieved at low deposition temperatures (T = 60°C) thus making this PEALD process very attractive for flexible electronics. The devices also show a high I_{on}/I_{off} ratio of 10^7, which is more than sufficient for digital circuits.[5]

[1] S. Das, V. Jayaraman,*Progress in Materials Science,***2014**, *66*, 112.

[2] M. Y. Maximov *et al*., *Journal ofElec Materi,***2017**, *46*, 6571.

[3] C. Beneking *et al*., *Thin Solid Films,***1999**, *351*, 241.

[4] P. D.M., R. Mannam .,*Applied Surface Science,***2017**, *418*, 414.

[5] D. Geng *et al. IEEE Electron Device Lett,***2012**, 33, 1012.

4:30pm **AF2-WeA-13 Hollow Cathode Plasma-Enhanced Atomic Layer Deposition of Silicon Nitride using Pentachlorodisilane (PCDS) and Hexachlorodisilane (HCDS)**, ***Xin Meng***, *H Kim, A Lucero, S Hwang, J Lee, Y Byun, J Kim,* The University of Texas at Dallas*; B Hwang, X Zhou, J Young, M Telgenhoff,* Dow Chemicals

Plasma-enhanced ALD (PEALD) is an attractive method of depositing silicon nitride (SiN_x) due to its ability to grow high-quality films at low temperatures (≤400°C) for various applications [1]. Unlike other silicon precursors, chlorosilane precursors can be applicable to either thermal ALD process in combination with ammonia (NH_3), hydrazine (N_2H_4) or plasma-enhanced ALD process using NH_3 plasma. The use of chlorosilane precursors is also considered a practical approach for high-volume manufacturing (HVM). Among the reported chlorosilane precursors, hexachlorodisilane (HCDS, Si_2Cl_6) is a promising candidate due to its higher surface reactivity as well as the demonstration of a distinct self-limiting growth behavior in ALD SiN_x process [2]. Nevertheless, it is desirable to find an alternative chlorosilane precursor with a higher reactivity and a higher growth per cycle than HCDS.

In this work, a novel chlorodisilane precursor, pentachlorodisilane (PCDS, HSi_2Cl_5), was investigated for the growth of SiN_x via hollow cathode PEALD. Well-defined self-limiting growth behavior was successfully demonstrated over the growth temperature range of 270−360°C. At identical process conditions, PCDS not only demonstrated approximately >20% higher GPC than that of HCDS, but also delivered a better or at least comparable film quality determined by characterizing the refractive index, wet etch rate, and density of the films. Fourier transform infrared spectroscopy (FTIR) spectra suggested that N−H bonds were the dominant hydrogen-containing bonds in the SiN_x films without a significant amount of Si−H bonds originating from the precursor molecules. We contribute the significant improvement in GPC to the enhanced reactivity of the proposed precursor molecular structure simply by a hydrogen atom substitution. The minor change in the molecular structure can render a lower steric hindrance, a higher polarity of the precursor molecule, and an additional precursor adsorption reaction pathway via Si−H bonds cleavage.

[1] Meng, X.; Byun, Y.-C.; Kim, H. S.; Lee, J. S.; Lucero, A. T.; Cheng, L.; Kim, J. Atomic Layer Deposition of Silicon Nitride Thin Films: A Review of Recent Progress, Challenges, and Outlooks. *Materials* **2016,** *9* (12), 1007.

[2] Ovanesyan, R. A.; Hausmann, D. M.; Agarwal, S. Low-Temperature Conformal Atomic Layer Deposition of SiN_x Films Using Si_2Cl_6 and NH_3 Plasma. *ACS Appl Mater Interfaces* **2015,** *7* (20), 10806−10813.

Emerging Materials
Room 107-109 - Session EM-WeA

MLD & Emerging Materials

Moderators: Jiyoung Kim, University of Texas at Dallas, Charles Dezelah, EMD Performance Materials

1:30pm **EM-WeA-1 Physical, Chemical, and Electrical Properties of Molecular Layer Deposited Alucone Thin Films using Trimethyl-aluminum and Hydroquinone***, **Seung-Hwan Lee**, G Beak, J Lee, J Park,* Hanyang University, Republic of Korea

Molecular layer deposition has been rapidly emerged to fabricate an organic film, showing a self-limited reaction and half-reaction cycle by using metal precursor and/or organic monomer. The deposited films exhibit excellent conformality, uniformity and exact thickness control like atomic layer deposition. Many researcher groups reported alucone films using various organic monomers (ethylene glycol (EG), diethylene glycol (DEG), hydroquinone (HQ) etc.) but they have researched basic process conditions and film properties. [1-2] However, mostly the organic layers are very sensitive to air ambient. The water and oxygen may react with organic frames in MLD layers and destruct/decompose the structure of organic films. So, it is one of big challenges to utilize the functional films in emerging application areas.

In this work, we investigated the physical, chemical, and electrical properties of Alucone films, deposited by trimethyl aluminum (TMA) and HQ. The pristine alucone film didn't show any D and G peak in Raman spectra, indicating a carbon domain evidence. But the annealed alucone film did carbon domains like amorphous graphite carbon layers. The pristine films, including carbon-oxygen and carbon-hydrogen bond, dramatically turned to the dehydrated alucon filme during the annealing process. This change may stabilize the organic structure and improve the air-stability. Spectroscopic ellipsometer (SE), Auger electron spectroscopy (AES), Raman spectra and X-ray photoelectron spectroscopy (XPS) were used to understand film properties. Also, hall measurement and seebeck coefficient measurement were used to measure electrical properties of the annealed alucone film, which showed p-type carrier and conductivity. Thus, the process and material will be a promising layer because the stable organic layer may provide not only new functional surface but also functional coted films in emerging electronic applications.

[1] Steven M. George et al, Growth and properties of hybrid organic-inorganic metalcone films using molecular layer deposition techniques, Advanced Functional Materials, (2013), 23, 532

[2] Xueliang Sun et al, Safe and durable high-temperature lithium-sulfur batteries via molecular layer deposited coating, Nano letters, (2016), 16, 3545

1:45pm **EM-WeA-2 Molecular Layer Deposition of Boron Carbide Thin Films***, **Suhaib Malik**, R Thapa, L Dorsett, S Wagner, A Caruso,* University of Missouri-Kansas City*; D Merrill, J Bielefeld, S King,* Intel Corp.*; M Paquette,* University of Missouri-Kansas City

The drive towards smaller and more powerful integrated circuits (IC) has put increasing strain on both traditional circuit materials and electronics manufacturing. New materials must perform as better electrical components than their predecessors and, as is increasingly becoming the case, meet higher standards of thermal and mechanical properties for performance and miniaturization. The state of the art approach to building IC components is top-down; a pre-built material of a given thickness is etched into. The advent of atomic layer deposition (ALD) extends a top-down approach by allowing for smarter-designed materials with more exact layering and patterning, while also enabling a bottom-up approach by opening the door to capabilities like selective deposition. Boron carbide (BC) films provide a unique solution to the first half of the above problem: they display promising electrical and physical properties for applications ranging from corrosion protection to low-k dielectrics to electrical surface modification to neutron detection. We propose that if BC can be deposited using an ALD growth scheme, it could address many present challenges in engineering micro- and nano-scale electronics and introduce a unique set of materials to the ALD family for other applications. In this presentation we will describe the use of carboranes as molecular layer deposition precursors in growing thin BC films and the effect of growth parameters on deposition behavior.

2:00pm **EM-WeA-3 Achieving Room Temperature and Below Phase Transitions in ALD Doped VO_2 Films***, **Virginia Wheeler**,* U.S. Naval Research Laboratory*; A Kozen,* The American Society for Engineering Education*; M Currie, B Downey, D Meyer, C Eddy, Jr.,* U.S. Naval Research Laboratory

VO_2 undergoes a first order crystalline phase transition at a critical temperature (T_c = 68°C), resulting in significant changes in intrinsic electrical and optical properties, especially in the infrared. Optical changes with this phase transition are of particular interest as passive and active components of optoelectronic devices, specifically for thermal regulation. Realizing this type of device often requires the integration of thin, conformal VO_2 films with complex, non-planar structures (like metamaterials). Thus, atomic layer deposition (ALD) is the ideal deposition method in these cases. While the T_c of VO_2 may be appropriate for some applications, others require this transition to occur at lower temperatures. Traditionally, lowering the T_c has been accomplished through inducing strain or doping VO_2 films with small amounts (1-5 at%) of transition metals. Yet, similar doping induced changes have not been shown in ALD VO_2 films. Here, we achieve a T_c less than room temperature through ALD Nb doped VO_2 films.

Previous studies have shown that T_c near room temperature can be obtained through W doping. Unfortunately, the growth window for $W(CO)_6$ and ozone was above 200°C, which is higher than the vanadium precursor (TEMAV) decomposition temperature, rendering it incompatible with the VO_2 process. A variety of other compatible dopants were explored and Nb had the most potential, allowing the T_c to be reduced with minimal degradation in morphology, structure, and optical transition properties.

ALD Nb-doped VO_2 films were formed using supercycles of Nb_2O_5 (TBTDEA-Nb(V), O_3) and VO_2 (TEMAV, O_3) at 150°C on c-sapphire substrates. By varying the ratio of Nb_2O_5 to VO_2 cycles, doped films with 1-7 at% Nb were achieved. Initial studies suggest that the Nb_2O_5 layer may inhibit the subsequent nucleation of VO_2 layers, resulting in non-linear incorporation of Nb. A reduction in T_c of -11.2°C/Nb at% was attained, which is larger than reports of Nb-doped VO_2 films by other growth methods. Additionally, up to ~1.6 at% Nb, the magnitude of the optical transition is maintained while shifting the T_c to 36°C. To attain a room temperature T_c requires 3.3 at% Nb, which is accompanied by a reduction in optical transmission modulation to ~10%. Similarly, a 5°C T_c was obtained with 5.1 at% but with only a 5% optical modulation. TEM images show that films with a reduced optical modulation still have inclusion of amorphous grains, even after ex-situ annealing, which increases with increasing Nb doping. The extent of being able to fully crystallize VO_2 films with high Nb contents will be discussed to determine the realization of usable films with T_c near 0°C.

2:15pm **EM-WeA-4 Ozone Based High Temperature Atomic Layer Deposition of SiO_2 Thin Films***, **Su Min Hwang**, X Meng, A Lucero, H Kim, S Kim,* The University of Texas at Dallas*; B Hwang,* Dow Chemicals*; J Kim,* The University of Texas at Dallas

Recently, deposition of SiO_2 films with high quality and good conformality has drawn great attention as device structures have become more complicated. Conventionally used LPCVD and PECVD for SiO_2 deposition have limitations in terms of conformal deposition and thickness scalability. Since ALD is expected to overcome the challenging issues, several research groups have reported SiO_2 ALD using $SiCl_4$, SiH_2Cl_2, and Si_2Cl_6 at low temperature (250 – 500°C)). Unfortunately, the ALD films show less dense film qualities compared to thermal oxide [1-3]. For high quality SiO_2 films with good conformality, an ALD process at high temperature is desirable. However, research on high temperature ALD processes is scarce due to the difficulty of the process caused by decomposition of precursor resulting in CVD-like growth instead of self-limiting ALD growth.

In this work, oxidation of silicon wafers using various oxidants (H_2O, O_2 and O_3) was performed using a rapid thermal ALD system to identify if O_3 has higher reactivity for high temperature ALD of SiO_2. Although O_3 has a short lifetime above 300°C due to thermal decomposition, thermal oxide grown with O_3 at 300 to 800°C shows higher thickness compared to oxide films grown using H_2O and O_2. The activation energy of O_3 based process was calculated to 0.07 eV, which is a lower value than those of H_2O based process (0.14 eV) and O_2 process (0.16 eV). Among the possible oxidants, we confirmed that O_3 has a higher reactivity for ALD of SiO_2 due to reactive O radicals. Based on these results, ALD of SiO_2 thin films using Si_2Cl_6 and O_3 was performed at from 500 to 700℃. At 650°C we observe a saturated growth rate of 0.24 Å/cycle at a Si_2Cl_6 exposure of 2.0 10^6 L with fixed O_3 exposure. Growth rate is linear with the number of cycles indicating there is only a small or no incubation period observed. Our findings highlighted that reactivity of O_3 can be maintained at high temperature and it can be applicable to ALD of SiO_2 process.

We acknowledge TMEIC for ozone generator.

2:30pm **EM-WeA-5 Atomic Layer Deposition of High-T_c Magnesium Diboride (MgB_2) Film for Superconducting Radio-Frequency Particle Beam Accelerators***, **Alireza Nassiri**, D Mandia, A Yanguas-Gil, A Mane, J Elam,* Argonne National Laboratory

Atomic Layer Deposition (ALD) as a self-limiting coating process is an ideal technique relatively thick, high quality coating of high-T_c superconductor Magnesium Diboride (MgB_2) on radio frequency copper resonant structures (cavities) for particle beams accelerators. MgB_2 is considered one of the viable materials to substitute bulk niobium for superconducting radio frequency cavities. Utilizing a MgB_2 coating on the inner wall of a copper cavity will allow operation at higher temperatures (20–25 K) than Nb cavities due to the high transition temperature of MgB_2 (39 K) and the high thermal conductivity of Cu. Achieving higher accelerating fields and eliminating expensive capital and operating costs of large liquid helium refrigeration system by using highly efficient and cost effective cryo-coolers are amongst the major benefits of using magnesium diboride. Here, we will present initial results on this ongoing effort.

2:45pm **EM-WeA-6 Commerical Production of ALD-Coated Powders and Polymers***, **Daniel Higgs**,* ALD NanoSolutions, Inc.

Atomic and molecular layer deposition (ALD) can be economically scaled to coat tons of powder, kilometers of polymers and many thousands of specialty objects a day. ALD reached commercial scale for coating various chemistries onto silicon wafers in the semiconductor industry in the 1990s, which today is a multi-billion dollar market. ALD is now becoming the method of choice for coating ultrathin, precisely controlled films onto particles and other new material substrates.

This talk will discuss the cost-effective commercial production of ALD-enabled materials at >1000T/yr of powders and >50M m2 /yr of polymers. We will cover batch and continuous ALD systems that enable this high volume production as well as discuss various markets for the materials processed in these systems. Two current commercial products will be touched on and other pre-commercial products will be discussed.

ALD Nano helps customers solve particle material challenges by perfecting the necessary ALD coating chemistries, process conditions and manufacturing equipment systems. Our global leadership position is ALD on powders, also known as particles or particle ALD. Many Fortune 500 companies are among our customers and supply channel partners. ALD on particles has many benefits including:

- Superior precision and cost-effectiveness compared with chemical vapor deposition (CVD) and other techniques enable new or better applications for known substrates with improved end-device performance, lifetime, cost and safety.
- Novel atomic-scale material designs can be created with significant value to materials supply chain customers and end-device partners.
- Substrate functionality improvements occur by changing physical characteristics of particles including enhanced (or reduced) chemical stability, flowability, corrosion, oxidation, conductivity, hydrophobicity, optical properties, material compatibility, dispersion, sintering control, barrier performance, and other improvements that result in better end device performance.
- Particle agglomeration does not happen with proper ALD process conditions, regardless of particle size, shape and morphology.

3:00pm **EM-WeA-7 Ruthenium: Advanced Nodes and Supply Chain Implications***, **Oliver Briel**, D Zeng, A Wilk,* Umicore AG & Co. KG, Germany

Advanced new materials and chemistries may play an important role to extend Moore's law to continue miniaturization of chip design while at the same time increasing their performance. One of these promising materials is ruthenium partly due to its unique properties of interest to the industry.

In the early 2000's, there was a Ru hype at the R&D scale, however little or none of the new materials made to HVM, because the industry solved the problems by extending existing technologies, or by introducing alternative materials. Today we are in a similar situation as then except it seems to be more difficult to extend lifetime of the existing technologies or find other alternatives, hence we sense the optimism in ruthenium adoption for advanced chip nodes as foreseen in technology roadmaps provided by leading research organizations supporting the industry. While the outcome of Ru adoption remains to be seen, one thing we have learned is that many industry participants shared reservation in ruthenium based application development, because of the notion this material system being very "expensive" with "unpredictable price movements" and "unstable supply".

Umicore is a traditional platinum group metals company, active in the field for many decades, if not centuries. Through this presentation and discussion, we hope to shed light on and demystify the black box of PGM market dynamics. We will discuss a number of topics, such as where do PGMs come from, how much are available, which technologies/applications are the drivers of their demands, how are the PGMs priced, what procurement strategies can be used to mitigate cost impact due to price fluctuations, how does metal reclaim work, and who are among the key players in the value chain, all with a special focus on ruthenium.

In addition, we will introduce our most recent advanced Ru metal precursors as potential candidates for ALD and MOCVD applications.

3:15pm **EM-WeA-8 An Alternative Precursor for Safe Deposition of Aluminum Oxide Thin Films***, **Liao Cao**,* Ghent University, Belgium*; F Minaye Hashemi,* Delft University of Technology, Netherlands*; F Mattelaer,* Ghent University, Belgium*; J van Ommen,* Delft University of Technology, Netherlands*; C Detavernier,* Ghent University, Belgium

Aluminum oxide is widely used as a barrier layer, dielectric film and encapsulation material due to its excellent chemical and thermal stability, high field strength and high resistivity. Controlled deposition of aluminum oxide thin films via atomic layer deposition (ALD) is a well-developed process with applications ranging from semiconductor electronics to large-scale coatings.The most commonly used precursor for deposition of Al_2O_3 via a thermal ALD process is trimethylaluminum (TMA). TMA has a high vapor pressure and is very reactive towards most surfaces, acting as an ideal precursor for deposition of Al_2O_3 at various temperatures. However, TMA is pyrophoric, toxic, corrosive and expensive when aiming to coat surfaces at large scale, such as coating powders or roll-to-roll processes. Thus, alternative low-cost and safe precursors for deposition of alumina would facilitate economical and environmentally sustainable manufacturing of new surfaces and materials.

In this work we investigate an alkoxide precursor as a safe and stable alternative to TMA. Aluminum tri-isopropoxide (TIPA) is studied as the Al source for ALD of Al_2O_3 when different oxidizing agents including water, plasma and ozone are employed in the deposition process. We have explored the deposition of Al_2O_3 using TIPA in ALD systems operating in vacuum and atmospheric pressure conditions. Deposition process has been studied on both planar substrates and on different nanoparticles to explore the feasibility of using TIPA for various purposes including large-scale applications.

During thermal and plasma processes in vacuum ALD, we show a growth window of Al_2O_3 from 140°C up to 300°C . Growth rates achieved in the plasma process are comparable to the thermal ALD of TMA and water (1.1Å/cycle). X-ray reflectivity analysis confirm an increasing density of Al_2O_3 film when deposition temperature is increased. Scanning electron microscopy and atomic force microscopy show deposition of smooth films when TIPA is used as a precursor. X-ray photoelectron spectroscopy studies confirm stoichiometric deposition of Al_2O_3 with no presence of carbon contamination. The thermal water process at atmospheric pressure ALD (AP-ALD) resulted in a growth rate up to 1.1 Å/cycle with no residual carbon. No growth was observed when ozone was used as the oxidizing agent under atmospheric pressure conditions. AP-ALD on nanoparticles shows different growth modes on TiO_2 versus SiO_2 nanoparticle surfaces confirmed by transmission electron microscopy analysis. Using TIPA as an ALD precursor would open up the possibility for a safer and cost-effective process for deposition of Al_2O_3 in various applications.

4:00pm **EM-WeA-11 Application of PEALD Technique to the Fabrication of Vertical TFT for the Ultra High-Resolution Display***, **Kwang-Heum Lee**, S Lee, H Yeom, J Ko,* Korea Advanced Institute of Science and Technology, Republic of Korea*; C Hwang,* Electronics and Telecommunications Research Institute*; S Park,* Korea Advanced Institute of Science and Technology, Republic of Korea

1. Introduction

In nowadays, VR (Virtual Reality) and AR (Augmented Reality) are thought to be the key applications of future display. However, there still remain several obstacles, and one of them is the low resolution of display. To solve this problem, higher pixel density of several thousand PPIs is strongly required. Oxide semiconductor vertical thin-film transistor (VTFT) can be an appropriate candidate for the backplane component of the ultra high-resolution display. Its vertical channel structure makes it possible to reduce footprint size, which helps to make the pixels to be smaller and brighter at the same time. And also, it is possible to fabricate sub-micron scale channel length TFT by using the conventional photolithography techniques for the display industry more easier. This can give us high on-current characteristics. With these reasons, we conducted research for the oxide semiconductor based VTFT and tried to improve its electrical properties.

2. Experiments

Oxide semiconductor based VTFTs were fabricated on thermally oxidized Si wafer substrates. We used ITO for the source/drain electrodes, SiO_2 for the spacer, InO_x via plasma-enhanced atomic layer deposition (PEALD) method for the active layer, and Al_2O_3 for the protective layer (PL) + gate insulator. PL layer was adopted to reduce gate leakage current. All patterning steps except for the active and PL layer were conducted by dry-etching. Although, VTFTs have vertical spacer with taper angle of ≈80°, it does not make any problems with step coverage due to adopting PEALD technique for deposition of active & gate insulator layers.

3. Results

From our experiments, we could fabricate the VTFT with high on-current driven at low voltage. In addition, through pre-annealing process of InO_x active layer under oxygen atmosphere, we could verify broader process window for the post-annealing, which is needed for the LCD display. These results indicates the possibilities of VTFT for the Ultra High-Resolution display.

4. Conclusions

In this paper, we investigated the possibility of fabricating oxide semiconductor VTFT using PEALD. Through this result, we will continue to conduct our experiments for the process optimization and adopting to the ultra high-resolution display panel.

4:15pm **EM-WeA-12 Effect of Substrate on MoS_2 Deposited by Plasma-enhanced Atomic Layer Deposition***, **Asad Mughal**, T Walter, K Cooley,* The Pennsylvania State University*; A Bertuch,* Veeco-CNT*; S Mohney,* The Pennsylvania State University

Due to their promising physical properties, semiconducting two-dimensional transition metal dichalcogenides (2D TMDs) are a materials class receiving intense research attention. Molybdenum disulfide is one of the most widely studied materials in this class and has the potential for applications ranging from electronics to catalysis. However, achieving large-area uniform growth of MoS_2 is challenging and is typically accomplished at elevated temperatures using chemical vapor transport, chemical vapor deposition, or related techniques. Plasma-enhanced atomic layer deposition (PEALD) is a promising method for achieving control of film thickness at the atomic scale and with growth temperatures low enough to accommodate integration into traditional semiconductor device fabrication processes. In this work, we use PEALD to grow thin layers of MoS_2. Using the co-reactants $(N^tBu)_2(Nme_2)_2Mo$ and H_2S:Ar plasma, depositions were carried out in a hot-walled PEALD system from 250–450 °C. Higher purity layers were achieved using a sapphire rather than silica plasma tube. Films were characterized by spectroscopic ellipsometry, XPS, TEM, AFM, and resonance Raman spectroscopy (RRS) to determine growth rate, morphology, purity, and crystalline quality. RSS revealed the number of layers of MoS_2 ($A_{1g}(\Gamma)$- $E_{2g}(\Gamma)$) as well as crystalline quality ($A_{1g}(\Gamma)/LA(M)$). Interesting variations were observed among films deposited on different substrates, with better crystalline quality on (0001) sapphire than on SiO_2/Si or (0001) GaN/sapphire. Molybdenum disulfide was controllably grown down to single-layer thicknesses by adjusting the number of growth cycles. When deposited on silicon nitride membranes, MoS_2 layers were found to be polycrystalline with the (0001) plane parallel to the substrate. However, substrate-dependent out-of-plane growth was observed for thicker films, especially on silicon nitride, SiO_2/Si, and sapphire. Higher growth temperatures, as well as post-deposition annealing under sulfur vapor, was shown to increase the crystallinity of the films. We anticipate that this PEALD growth technique will be suitable for a wide array 2D TMDs thin films and devices.

4:30pm **EM-WeA-13 Single-crystal Ternary Perovskite $YAlO_3$ Epitaxial Growth on GaAs and GaN via Y_2O_3 Template Overcoming a Large Film/Substrate Lattice Mismatch***, **L. Bo-Yu Young**, C Cheng, K Lin, Y Lin, H Wan,* National Taiwan University, Republic of China*; R Cai, S Lo,* Industrial Technology Research Institute, Republic of China*; M Li,* National Applied Research Laboratories, Republic of China*; C Hsu,* National Synchrotron Radiation Research Center, Republic of China*; J Kwo,* National Tsing Hua University, Republic of China*; M Hong,* National Taiwan University, Republic of China

It is a challenge to perfect a hetero-epitaxial growth. Earlier successful examples are rare-earth metals/Nb/sapphire,[1] which led to the discovery of anti-ferromagnetic coupling through non-magnetic media, based on which the giant magnetoresistance (GMR) for the high-density recording was established, and GaN/sapphire, which led to the blue light emitting diode and lasers. Integrating atomic layer deposited (ALD) single-crystal perovskite onto semiconductor combines rich properties of the perovskites with advanced electronic and opto-electronic devices. Previously we presented hexagonal perovskite $YAlO_3$ (H-YAP) on GaAs and GaN. We have achieved excellent single crystal H-YAP on GaAs(111)A using ALD sub-nano-laminated Y_2O_3/Al_2O_3 multi-layers through post-deposition rapid thermal annealing with temperatures above 900^{o}C.[2,3]

From the high-resolution scanning transmission electron microscopy (STEM) images, we have observed a single atomic layer of Y-O at the YAP/GaAs(001) and /(111)A interfaces. In this work, we have further investigated the initial growth of the H-YAP on GaAs(111)A and GaN with and without a Y_2O_3(111) single crystal template. Fig. 1 shows the X-ray diffraction results of H-YAP grown on the Y_2O_3 template after 900^{o}C anneal. The pronounced fringes shown in Fig. 1(a) indicate excellent crystallinity of H-YAP and sharp interface between H-YAP and Y_2O_3. The narrow FWHM ~0.019^o of H-YAP(0004) θ-rocking scan confirmed the excellent crystallinity. From the STEM image shown in Fig. 2, H-YAP grew directly from Y_2O_3. The Y-sub-lattice in the atomic packing of Y_2O_3(111) has a hexagonal-like structure with a 2-D lattice constant a= 3.75 Å, similar to that of H-YAP(0001) with a = 3.68 Å as shown in Fig. 3. The top Y (Y-O) layer in the Y_2O_3(111) is the initial Y (Y-O) layer of the H-YAP. Notice their structural similarity. The excellent crystallinity of H-YAP may be attributed from the excellent starting Y_2O_3 layer with a FWHM ~0.017^o of Y_2O_3(444) θ-rocking scan. For the H-YAP/GaAs(111)A, the FWHM of H-YAP(0004) θ-rocking scan is ~0.026^o despite a large lattice mismatch ~8.5%. Fig. 4 shows the STEM image of the H-YAP grown on GaAs(111)A, where a Y-O layer was observed between H-YAP and GaAs dumbbell at the interface. This Y-O layer may also be the starting layer of the single crystal H-YAP. Our recent work on the initial growth of ALD- Y_2O_3 on GaAs using in-situ synchrotron radiation photoemission may shed the light on the understanding of the interfacial electronic characteristics, namely the chemical bonding.[4]

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

CHH, JK, and MH are the corresponding authors.

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