## ALD Applications
## Room Plaza Exhibit - Session AA-SuP

## ALD Applications Poster Session

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

[1] R. Matero, M. Ritala, M. Leskalä, T. Salo, J. Aromaa, O. Forsén, J. Phys. IV France 9 (1999) 493-499

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

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

Room temperature atomic layer deposition processes of $SiO_2$, $TiO_2$, $Al_2O_3$ and $ZrO_2$ were reported by using plasma excited humidified argon. In this work, we examine the RT-ALD deposited $Al_2O_3$ as an anticorrosion coating for stainless steels. Trimethylaluminum (TMA) as the aluminum precursor was introduced with mass flow controller (MFC). A remote plasma system generating excited humidified argon was installed to the ALD chamber. The source gas for the oxidizing gas is a mixture of water vapor and argon. The plasma was generated in a glass tube with an induction coil with 13.56 MHz and RF power of 100 W. For the $Al_2O_3$ deposition, we repeated the cycle of TMA saturation and oxidizing gas treatment at RT. The TMA exposure was set at $5.86\times10^{-3}$ Torr× 40 sec. The saturation of TMA on the hydroxylated surface was confirmed by the IR absorption spectroscopy. The plasma excited oxidizing gas was injected for 2 min. In the conference, we show the anticorrosion test of ALD coated stainless steel in an HCl solution. We used SUS430 plates with a size of $20\times50\times0.5$ $mm^3$ as the sample. In this test, we used a not-diluted HCl solution with a concentration of 35 %. All the samples were immersed in the HCl solution for a certain amount of minute at room temperature and we observed its surface coloring. In the conference, we discuss the applicability of the RT-ALD to the anticorrosion coating for metal components.

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

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

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

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

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

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

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

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

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

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

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

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

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

Reference

[1] J. M. Bustillo, R. T. Howe and R. S. Muller: Proc. IEEE **86** 1552-74 (1998).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

**AA-SuP-18 The Effect of SiOx/SiNx Multilayer Structure using Low Temperature Plasma Enhanced Atomic Layer Deposition for Gas Diffusion Barrier***, **Ju-Hwan Han,*** Hanyang University, Republic of Korea*; C Kim, K Lim, S Lee, H Choi,* LG Display, Republic of Korea*; J Park,* Hanyang University, Republic of Korea

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

**AA-SuP-19 Reduced Thermal Conductivity of ALD Synthesized PbTe/PbSe Nanolaminates Grown on Nanopatterned Substrates***, **Xin Chen,*** Old Dominion University*; M DeCoster,* University of Virginia*; P Lin, K Zhang,* Old Dominion University*; P Hopkins,* University of Virginia*; H Baumgart,* Old Dominion University

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

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

**AA-SuP-20 The Effect of Titanium Tetrachloride-based Plasma Enhanced ALD TiN on the Threshold Voltage of Gate Last-Like Processed FD-SOI MOSFET with ALD $HfO_2$ Gate Dielectric***, Y Kim, M Chae,* ***Changhwan Choi,*** Hanyang University, Korea

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

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

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**AA-SuP-21 Atomic Layer Deposition of Transition Metal Dichalcogenide $MoS_2$ Thin Films***, M Zeng,* George Mason University*;* ***Kai Zhang****, X Chen, P Lin,* Old Dominion University*; Q Li,* George Mason University*; C McCleese, C Kolodziej, C Burda,* Case Western Reserve University*; H Baumgart,* Old Dominion University

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Thin films of transparent conducting semiconductors (TCSs) are extensively used as electrodes in numerous technological applications such as solar cells, light emitting diodes, flat panel displays etc. Commercially available TCSs are mostly *n*-type conducting. However, to realize transparent electronics using bi-polar junction devices, growth of *p*-type TCSs are essential. There are only few metal oxides which are reported to be *p*-type TCSs such as binary oxides (NiO, doped ZnO:N/As/P) and ternary delafossites (CuMO$_2$; M = Cr, Al, Ga, In). However, high hole conductivity, decent optical transparency along with stable and reproducible electrical properties cannot be realized in these *p*-type TCSs.

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

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

### AA-SuP-32 All ALD Hybrid Photoelectrochemical Systems Based on Self-Organized TiO$_2$ Nanotubes Coated with Chalcogenides*, **Jan Macák**,* University of Pardubice, Czech Republic

Even though, the overall efficiencies of advanced photovoltaic devices (amorphous Si-H, CIGS, CdTe, perovskite cells) have grown up significantly, there is so far no solar cell that would have reliable stability and performance over many years of the cell service, that would be cheap, environmentally reasonable and potentially flexible . One of most competing technologies to silicon solar cells, when considering the efficiency, low-cost production and stability is based on thin films of semiconducting chalcogenides, such as Cu(In,Ga)Se$_2$ (CIGS) and Cu$_2$ZnSn(Se,S)$_4$ (CZTS). Both became recently materials of the choice as they represent in thin film solar cells chromophores of adjustable band gaps, good radiation stability and high optical absorption coefficient.

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

A promising pathway to improve the carrier mobility of semiconducting chalcogenides to the highest possible level is to use hybrid photocells employing a highly ordered TiO$_2$ nanotube film /chromophore interface . However, the major issue to extend the functional range of nanotubes is to coat homogenously tube interiors by semiconducting chalcogenides in order to achieve the best possible contact of both components on their interface. This is especially crucial when high aspect ratio semiconducting TiO$_2$ nanotube arrays are utilized and thus the Atomic Layer Deposition technique becomes beneficial.

The presentation will show initial photo-electrochemical results for anodic TiO$_2$ nanotubes employed as highly ordered electron-conductive supports for host materials coated using ALD with secondary materials to enhance light absorbing capabilities of such hybrid systems. We will focus on all ALD photo-electrochemical devices based on inorganic chalcogenides .

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

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

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

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

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

In this talk, a rotation fluidization coupled atomic layer deposition reactor will be introduced. In the deposition procedure, the coating process could be expedited due to the enlarged and homogenized void fraction in the particle bed, large gas distribution area and higher particle concentration in the rotating fluidized bed. The rotation not only enhances the gas-solid interactions to stabilize fluidization, but also provides large centrifugal force to break up soft agglomerates together with the fluid drag force and the inter-particle collision. Under high precursor feed rate, the precursor utilization was improved to nearly 100% with thicker rotating bed. As an example, magnetic Fe$_3$O$_4$ nanoparticles have been uniformly coated with ultrathin Al$_2$O$_3$ passivation layers. With 5 nm coating layer, the nanoparticle could be stable under oxidation resistance with minimum magnetization loss (less than 10%). This is quite attractive in practical magnetic based biomedical applications. Well controllable amorphous Al$_2$O$_3$ layers were also deposited on crystalline AlH$_3$ particles. The Al$_2$O$_3$ layers acted as physical barriers to prevent the particles from erosion by water and oxygen in ambient conditions, encapsulating hydrogen capacity nearly 4 times higher than the uncoated ones after hydrothermal aging. The oxide layers also served as thermal insulators to retard friction heat transferring to α-AlH$_3$ cores, as thin as 7 Å oxide layer on Al nanoparticles could effectively prevent them from reacting with hot water. All these examples show that ALD has a great potential as an effective nanoparticle surface passivation method.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$^{\dagger}$YHL and HWW have made equal contributions to this work.

* MH and JK are the corresponding authors.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

[1] Ocola, L *et al*. Infiltrated Zinc Oxide in Poly(methyl methacrylate): An Atomic Cycle Growth Study. *The Journal of Physical Chemistry,121* (3), **1893-1903** (2017)

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

A thin amorphous coating of $Al_2O_3$ obtained via atomic layer deposition (ALD) has demonstrated the ability to improve cycle-life for several cathode materials in rechargeable Li-ion batteries [1]. However, due to the insulating nature of $Al_2O_3$, the coatings on cathode particles impede the transport of Li-ion and electrons during the battery cycling. Therefore, a large overpotential on the cathode surface can develop leading to significant capacity loss at higher C-rates and for thicker coatings. In this work, we describe a method to estimate the overpotential of amorphous ALD $Al_2O_3$ coatings on $Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O_2$ (NMC) cathode and can be extended to any other coating materials. At 1C-rate (2.062mA), the estimated $Al_2O_3$ overpotential is about 0.82 mV/nm yielding an estimation of effective resistivity 6.3 MΩm and Li-ion diffusivity of $1.7\times10^{-14}$ $cm^2/s$.

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

[1] Y. S. Jung, A. S. Cavanagh, A. C. Dillon, M. D. Groner, S. M. George, S. H. Lee, J. Electrochem. Soc. 157, A75-A81 (2010)

[2] S. Xu, R. M. Jacobs, H. M. Nguyen, S. Hao, M. Mahanthappa, C. Wolverton, and D. Morgan, J. Mat. Chem. A 3, 17248-17272 (2015)

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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## ALD Applications
## Room Plaza ABC - Session AA-MoM

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

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

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

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

Specifically, I will address the following case studies:

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

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

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

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

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

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

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

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

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

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

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

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

### 9:15am **AA-MoM-6 Role of Fixed Charge in the Modification of Schottky Barrier Height of Metal Insulator Semiconductor Tunnel Structures***, **Roderick Marstell**, N Strandwitz,* Lehigh University

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

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

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

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

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### 9:30am **AA-MoM-7 Determination of Energy Barrier Heights between Amorphous Metals and ALD Dielectrics using Internal Photoemission Spectroscopy***, **Melanie Jenkins**, T Klarr, D Austin, J McGlone,* Oregon State University*; L Wei, N Nguyen,* National Institute of Standards and Technology*; J Wager, J Conley,* Oregon State University

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

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

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

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### 9:45am **AA-MoM-8 ALD Window and Buffer Layers in Thin Film Solar Cells***, A Palmstrom, K Bush, M McGehee, A Hultqvist, T Sone, **Stacey F. Bent**,* Stanford University

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

**References**

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## ALD Applications

## Room Plaza ABC - Session AA-MoA

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

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

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

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

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

**Reference**

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

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

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

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

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

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

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

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

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

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

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

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

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

MIMCAPs were fabricated using TaN bottom electrodes. 10 nm $Al_2O_3$ and 11 nm $HfO_2$ was deposited via ALD at 250 °C using $H_2O$ and either TMA or

TEMA-Hf in a Picosun R-200 or R-150, respectively. Ag, Au, Ni, Pd, and Pt were evaporated through a shadow mask to form the top gate.

Plots of normalized capacitance ($C/C_0$) vs. electric field ($E^2$) show a similar dependence of $\alpha E_{CC}$ (quadratic electric field coefficient of capacitance) on Ni, Au, and Ag (Fig. 1) for both $Al_2O_3$ and $HfO_2$. Most studies have concluded that interfacial oxides dominate the influence of metal electrodes on $\alpha V_{CC}$. However this cannot fully explain variation between near zero enthalpy of formation metals as they are unlikely to form substantial oxides. The $\alpha V_{CC}$ variation between these metals is likely due to an interaction between the bulk dielectric mechanism and an interfacial effect. One possible bulk mechanism for positive $\alpha V_{CC}$ materials is a decrease in film thickness due to voltage induced compression (Fig. 2). The compressive stress within the dielectric is modulated by the induced tensile stress at the metal interfaces. We see that metals with larger lattice mismatch show increased $\alpha V_{CC}$. The effect of lattice mismatch and additional results showing effect of dielectric and metal thickness will be presented at the meeting.

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2:30pm **AA-MoA-5 High-Voltage Nanolaminate Metal-Insulator-Insulator-Metal (MIIM) Tunnel Diodes using ALD $Al_2O_3$ and $Ta_2O_5$**, *D Austin, M Jenkins,* ***Konner Holden****, J Conley,* Oregon State University

ALD nanolaminate tunnel barriers have enabled enhancements of low voltage asymmetry ($\eta_{asym} = I^-/I^+$) and non-linearity ($f_{NL}$) in MIIM tunnel diodes for applications such as rectenna based energy harvesting.[1,2] In this work, we investigate ALD bi-layers of $Al_2O_3$ and $Ta_2O_5$ for use in high-voltage applications such as electrostatic discharge (ESD) protection and high-voltage logic.

Nanolaminate $Al_2O_3/Ta_2O_5$ stacks were deposited on TaN bottom electrodes via ALD. ALD was performed at 200°C in a Picosun R-150 without breaking vacuum using alternating pulses of $H_2O$ and either TMA or tris(ethylmethylamido)(tert-butylimido)tantalum. $Al_2O_3$:$Ta_2O_5$ thickness ratios of 1:1, 1:2, 1:3, 1:5, and 1:9 were fabricated, where the $Al_2O_3$ thickness is fixed at 30 nm. Bias was applied to Al top electrodes (formed by evaporation through a shadow mask).

I-V behavior (Fig. 1) was found to be a strong function of the $Al_2O_3$:$Ta_2O_5$ thickness ratio. Under positive bias, the reverse diode current for all devices remains low until the reverse "breakdown" voltage at which current increases rapidly. The reverse "breakdown" voltage increases with the thickness of the $Ta_2O_5$ layer, from 15 V for 1:1 to 53 V for the 1:9 devices. For small magnitude negative bias, in the range of 0 to -15V, the diode forward current *is higher* for thicker $Ta_2O_5$ layers, a somewhat counter-intuitive result. Beyond -15 V, the forward current is lower for thicker $Ta_2O_5$ layers, in line with expectations. Plots of $\log|\eta_{asym}|$ vs. V are shown in Fig. 2. That maximum asymmetry and voltage at which it occurs increases from ~900 at ~19 V for 1:1 to ~$10^5$ at ~52V for the 1:9 devices.

Multiple changes in slope of the I-V curves at both positive and negative bias reveal a number of competing conduction mechanisms. Overall, conduction and asymmetry are dominated by Fowler-Nordheim tunneling through the $Al_2O_3$ barrier and defect based conduction through the $Ta_2O_5$. The trends in conduction and $\eta_{asym}$ are well explained by the asymmetric barrier (inset Fig. 1) created by the pairing of $Al_2O_3$ ($E_G$ = 8.7 eV, $\chi$ = 1.4 eV, $\kappa$ = 8.7) and $Ta_2O_5$ ($E_G$ = 4.5 eV, $\chi$ = 3.2 eV, $\kappa$ ~26). The detailed explanation will be discussed at the meeting.

This work demonstrates that ALD bilayers may be used to effectively engineer the reverse breakdown voltage, maximum asymmetry, and operating range of high voltage MIM diodes. These diodes may be of interest for implementation in back end of the line as well as for large area electronics due to low temperature fabrication.

2:45pm **AA-MoA-6 Capacitance Maximization of Ultra-thin Si-capacitors by Atomic Layer Deposition of Anti-ferroelectric $HfO_2$ in High Aspect Ratio Structures***,* ***Stefan Riedel****, W Weinreich, C Mart, J Müller,* Fraunhofer IPMS, Germany

The increasing number of independent, electrical devices operating in networks intensifies the need for distributed and autonomous power supplies. Therefore, short term storage and buffering of electrical energy for both complete systems as well as individual integrated circuits is required for a multitude of applications. Anti-ferroelectric (AFE) capacitors are an emerging solution for this field of application due to their high energy density, low loss and fast charge and discharge rates.

Perovskite based materials like lead-lanthanum-zirconium-titanate (PLZT) are well known for showing promising energy storage properties [1]. However their scaling potential in thin films especially for three dimensional structures is limited due to the lack of conformal deposition methods. Additionally these materials contain heavy metals raising environmental concerns.

On the other hand $HfO_2$ based systems have been demonstrated to show both ferroelectric and anti-ferroelectric phases [2] and can be deposited by atomic layer deposition using well established chemistry. Additional $HfO_2$ is compatible with semiconductor processing enabling both an integration of AFE capacitors directly into semiconductor circuits or as stand-alone silicon based capacitors.

To demonstrate this applicability of AFE $HfO_2$ we fabricated metal insulator metal capacitors on 3D structured Si substrates. $TiCl_4/NH_3$ based ALD and CVD processes where applied to create metallic TiN electrodes. Silicon doped $HfO_2$ (Si:$HfO_2$) was used as anti-ferroelectric. These films were deposited using TEMAHf and 3DMAS as metalorganic precursors and ozone as co-reactant.

The Si:$HfO_2$ thin films have been characterized by means of XPS, XRR and XRD and electrical properties of these capacitors have been investigated in dependence of the silicon content, deposition temperature and post deposition thermal treatments. A maximum stored energy of >100 µJ/cm$^2$ could be achieved, which is sufficient to integrate these capacitors as buffer for low power integrated circuits.

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[2] T. S. Böscke, J. Müller, D. Bräuhaus, et al., Appl. Phys. Lett. 99, 102903 (2011)

3:00pm **AA-MoA-7 Ferroelectricity in Ternary $HfO_2$-$ZrO_2$-$La_2O_3$ Mixed Oxide Grown by ALD***,* ***Anna Chernikova****, M Kozodaev, A Markeev,* Moscow Institute of Physics and Technology, Russian Federation

Recently discovered ferroelectric (FE) properties of $HfO_2$ based thin films attracted much attention. The novel FE material is considered as promising candidate to replace perovskites in new generation of high density non-volatile memory concepts: FeFET, FeRAM [1-3] and even more challenging FTJ [4]. Notable feature of FE $HfO_2$ is complete compatibility with semiconductor fabrication process. Particularly, ALD is successfully applied to its growth. According to the previous works, FE in such films is caused by the presence of orthorhombic ($Pca2_1$) polar phase. Although numerous factors (thickness, annealing temperature, electrodes materials, etc.) were previously shown to affect stabilization of $Pca2_1$ phase, there is still strong focus to essentially promote FE (i.e. remnant polarization value $P_r$) of $HfO_2$ by doping with other elements [5,6]. Particularly, La doping of $HfO_2$ was already applied to achieve high $P_r$ and promising endurance behavior, while ALD (including plasma enhanced PEALD) could be successfully utilized to ensure the required low level of doping [7]. At the same time since La doping usually increases the crystallization temperature of $HfO_2$ its integration to the BEOL process of FeRAM could be challenging and some ways to avoid this rise of crystallization temperature have to be found.

In this work, the first attempt to obtain FE in ternary $HfO_2$-$ZrO_2$-$La_2O_3$ oxide was made**.** The strategy was to combine the advantages of La doping with lower crystallization temperature of $(HfO_2)_x(ZrO_2)_y$ system. For this purpose metal-insulator-metal (MIM) structures based on 10 nm thick $(La_2O_3)_x(HfO_2)_y$ as well as $(La_2O_3)_x(HfO_2)_y(ZrO_2)z$ were entirely grown by PEALD. TiN as a desired material in semiconductor industry and simultaneously well-known feasible electrode for $HfO_2$ based FE was utilized for MIM structures formation. As grown as well as annealed in wide temperature range stacks were investigated in terms of crystalline structure, FE response and endurance characteristics. Stabilization of $Pca2_1$ in $(La_2O_3)_x(HfO_2)_y(ZrO_2)z$ and robust FE response of fully PEALD grown TiN/$(La_2O_3)_x(HfO_2)_y(ZrO_2)z$/TiN stacks were confirmed after annealing at relatively low temperature and dependence of FE response on annealing temperature was elucidated in details.

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3:15pm **AA-MoA-8 A Study on the Oxygen Source and Annealing Temperature Effects of Atomic Layer Deposited Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ Thin Films***, **Si Joon Kim**, D Narayan, J Lee, J Mohan,* University of Texas at Dallas*; S Summerfelt,* Texas Instruments*; J Kim,* University of Texas at Dallas

Ferroelectric random access memory (FRAM) has several advantages such as fast read/write cycle time, non-volatile data retention, low voltage/power operation, and simplified process flow. Texas Instruments reported the use of 70-nm-thick $Pb(Zr,Ti)O_3$ (PZT) film to make FRAM devices using 1.5 V 130 nm CMOS technology [1]. This conventional PZT ferroelectric (FE) material has the primary problem which is the difficulty in scaling down. Recently, FE properties in very thin doped $HfO_2$ have been identified [2]. However, although most studies use an atomic layer deposition (ALD) process for doped $HfO_2$ film deposition, there is no report of the effect of oxygen sources on the FE properties.

In this study, FE properties of 10-nm-thick $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films deposited on the TiN bottom electrode by ALD (Cambridge Nanotech Savannah S100) using TDMA-Hf (Hf-precursor), TDMA-Zr (Zr-precursor), and ozone or water (oxygen sources) have been investigated. The wafer temperature was set to 250°C during the HZO deposition and annealing processes were performed for 60 s at 300-500°C in an $N_2$ atmosphere using rapid thermal annealing after TiN top electrode deposition. Then, a conventional photolithography/etching process was performed to form a precise area of capacitors (diameter of 50-100 µm). The polarization-electric field hysteresis curves of the ozone- and water-based HZO samples were measured at 20 kHz after wake-up field cycling. A pulse write/read test was also performed to extract the real FE switching polarization. The ozone-based HZO sample annealed at 400°C showed large remanent polarization ($2P_r$, 46 µC/cm$^2$), large switching polarization ($P_{sw}$, 45 µC/cm$^2$), and low FE saturation voltage (1.5 V) compared to those ($2P_r$ of 42 µC/cm$^2$, $P_{sw}$ of 38 µC/cm$^2$, and FE saturation voltage of 2.0 V) of the water-based HZO sample annealed at 400°C. Furthermore, the effect of the annealing temperature on the FE polarization of the ozone- and water-based HZO samples was examined. Both HZO samples annealed at 500°C exhibited a relatively high FE saturation voltage and also have high leakage current properties compared to the 400°C annealed HZO samples. Our investigations showed that the annealing temperature and oxygen source have a significant influence on the FE properties of HZO films.

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4:00pm **AA-MoA-11 Thickness Dependence of Polarization Response in $(Hf,Zr)O_2$***, **Sean Smith**, M Rodriguez, D Henry, M Brumbach, J Ihlefeld,* Sandia National Laboratories

$(Hf,Zr)O_2$ is an exciting recently discovered ferroelectric that can be deposited as a thin film by atomic layer deposition and has sparked interest in $(Hf,Zr)O_2$ FRAM and other thin film ferroelectric devices. $(Hf,Zr)O_2$ is unusual because its ferroelectric response is due to a metastable phase most commonly seen as a thin film and its polarization response has been shown to increase with decreased thickness -- at size scales that are unusual for conventional ferroelectrics. Still, like more traditional ferroelectrics, properties are expected to degrade at some point, as the thickness approaches that of a single unit cell. The surface limited growth of atomic layer deposition is a natural fit for producing the very thin films needed to investigate this thickness regime. We observe an increase in remanent polarization with decreasing thickness, from 16 µC/cm$^2$ for 20 nm films up to 20 µC/cm$^2$ for 15 nm films before the ferroelectric response drastically falls off for thinner films, dropping to 7 µC/cm$^2$ for 10 nm films,. We will discuss these results in the context of developing highly scaled (<20 nm) $(Hf,Zr)O_2$ ferroelectric thin film memory devices. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:15pm **AA-MoA-12 ALD as a Primary Contributor Towards Enabling Key Materials in the Memory Roadmap***, **John Smythe**,* Micron Technology **INVITED**

Atomic layer deposition methods for dielectrics and metals have been widely reviewed in the literature for over a decade. Though there are exceptions, cost and complexity have largely limited adoption in more than a few high volume applications. The transition from proof of concept to robust implementation can illuminate the need for alternative precursors, reactants and hardware in various combinations. Think of the following scene: Engineers stand at the white board and draw a sketch depicting the next amazing memory cell. After some reflection, a common phrase shortly thereafter is some version of, “How are we going to make the structure with the required materials characteristics?” This talk will explore a selection of cases to explore the nature of past, present and future transitions related to the memory space.

4:45pm **AA-MoA-14 Plasma-Enhanced Atomic Layer Deposition of Oxygen Deficient TaOx Thin Films for Resistive Switching Memory Applications***, **Konstantin Egorov**, D Kuzmichev, Y Lebedinskii,* Moscow Institute of Physics and Technology, Russian Federation*; C Hwang,* Seoul National University, Korea*; A Markeev,* Moscow Institute of Physics and Technology, Russian Federation

The plasma-enhanced atomic layer deposition (PEALD) process using $Ta(OC_2H_5)_5$ as a Ta precursor and plasma-activated hydrogen as a reactant for the deposition of TaOx films with a controllable concentration of oxygen vacancies (VO) is reported herein. The VO concentration control was achieved by varying the hydrogen concentration of the hydrogen-argon mixture inthe plasma, allowing the control of the leakage current density in the tantalum oxide films within the range of five orders of magnitude compared with the $TaO_5$ film grown via thermal ALD using the identical Ta precursor and $H_2O$.

The detailed chemical analysis and AFM topography were given for different growth temperatures and amount of ALD cycles. The saturation of growth rate for Ta-precursor pulse and reactant gas ( $H_2O$ and $H_2$/Ar plasma with different $H_2$ concentration) pulse time was studied too. Temperature-dependent current-voltage measurements combined with Poole-Frenkel emission modelling demonstrated that the bulk trap depthdecreases with the increasing hydrogen concentration, which could be attributed to the increase of the VO concentration. The change of VO quantity in the PEALD TaOx films grown under different hydrogen concentrations was confirmed by the *in-situ* X-ray photoelectron spectroscopy (XPS) measurements of the Ta4*f* core and valence band spectra. The comparison of the XPS-measured non-stoichiometry and the secondary ion mass spectrometry analysis of the hydrogen content allowed this study to conclude that the non-stoichiometry is largely related tothe formation of Ta-VO sites rather than of Ta-H sites.

Such oxygen-deficient TaOx layers were studied for application as a VO reservoir layer in a resistance switching random access memory stack ($Ta_2O_5$/TaOx) where the actual switching occurred within the stoichiometric $Ta_2O_5$ layer.The bilayer memory stack showed reliable resistance switching up to ~$10^6$ switching cycles, whereas the single-layer $Ta_2O_5$ memory showed only several hundred switching cycles.

5:00pm **AA-MoA-15 Monitoring Resistive Switching Properties of ALD Grown $Al_2O_3/HfO_2$ Nanolaminate ReRAM Structures by *iin-situ* Reducing Plasma Treatments***, **Marceline Bonvalot**, B Eychenne, P Gonon,* LETI-LTM, France

Metal oxide resistive random access memories (RRAM) are considered as strong candidates in novel memory and logic device applications, thanks to low power consumption, fast switching speed and easy down scaling below 20 nm. It is widely accepted that this soft breakdown is induced by the formation or rupture of a conductive filament (CF) based on oxygen defect migration upon voltage application. However, other mechanisms such as electrochemical reactions or Joule heating may also play a role in the switching. From the technological point of view, $HfO_2$ is undoubtly one of the most mature dielectric oxides under investigation for this purpose. One major issue that needs to be addressed before $HfO_2$ RRAM devices can be successfully implemented concerns the adequate control of their performance, in terms of variability and reliability of the switching parameters. To address this issue, $Al_2O_3$ has been used as an intercalation layer material in the $HfO_2$ dielectric oxide. Indeed, $Al_2O_3$ has a large band gap and a strong oxygen affinity. It also favors higher thermal stability of amorphous $HfO_2$ and thus impedes $HfO_2$ recrystallization potentially induced upon cycling, providing improved endurance.

$Al_2O_3$-$HfO_2$ bilayer structures have been deposited by ALD on Si/Ti/TiN bottom electrodes and capped with patterned Pt top electrodes using a shadow mask and a PVD process. Thickness values of each layer have been adjusted so as to maintain a 10 nm overall dielectric thickness.

We have observed that as deposited $Al_2O_3$-$HfO_2$ structures do not exhibit any memory effect. This is attributed to the defect free ALD $Al_2O_3$ layer which can sustain high electric fields without any breakdown. Subsequent reducing plasma treatments have then been applied in situ during the ALD $Al_2O_3$ growth in order to tune up a significant amount of oxygen vacancies which have been quantified by XPS analyses for several durations to plasma exposure (between 60 and 200 seconds). These treatments have proven to be necessary to trigger reversible switching in $Al_2O_3$-$HfO_2$ RRAM structures. Our results suggest that the formation energy of oxygen defects to a threshold concentration is too large to allow the CF formation. However, when preexisting in the insulating material, these oxygen vacancies can easily migrate along the applied electric field without significantly damaging the insulating matrix. Our results also indicate that both SET voltage ($V_{SET}$) and RESET voltage dispersion ($\Delta V_{RESET}$) can be significantly reduced by appropriate plasma exposure durations. All these results will be presented and discussed in the light of current knowledge on conductive filament propagation in the dielectric material.

5:15pm **AA-MoA-16 Properties of ALD Ferroelectric Si-doped $HfO_2$ Characterized with Noncontact Corona-Kelvin Metrology***, **Dmitriy Marinskiy**,* Semilab SDI*; P Polakowski,* Fraunhofer IPMS, Germany*; A Findlay, P Edelman, M Wilson, J Lagowski,* Semilab SDI*; J Metzger, R Binder,* GLOBALFOUNDRIES, Germany*; J Müller,* Fraunhofer IPMS, Germany

The recent discovery of ferroelectricity in Si-doped $HfO_2$ thin films opens an attractive possibility for new ferroelectric FET's based on $HfO_2$ already integrated in IC technology [1].

We report a pioneering application of rapid feedback noncontact corona-Kelvin metrology for characterization of the ferroelectric (FE) behavior of Si-doped $HfO_2$. The 10nm films with Si mol% of 3.5, 4.6, and 11.3 were deposited using a halide based ALD process on 300mm Si wafers. Based on previous studies, which showed enhanced ferroelectric behavior for capped layers, the films were covered with 10nm PVD-TiN and spike annealed at 800°C . For corona-Kelvin measurements, the top TiN was removed by SC1 etching. On sister wafers MIM capacitors were prepared for standard measurement.

In the corona-Kelvin method, corona deposits charge-bias pulses ($\Delta Q_C$) on the dielectric. The induced change of surface voltage ($\Delta V$) is measured with a Kelvin probe and capacitance is obtained as $C=\Delta Q_C/\Delta V$. Present results demonstrate that large charge bias provides a means for poling of the ferroelectric films similar to voltage biasing of MIM capacitors. Sequential small charge pulses are used for acquiring the Q-V and C-V characteristics that monitor the ferroelectric property again in good agreement with standard MIM polarization characteristics and permittivity derived from C-V.

Distinctly different properties are revealed in films with small and large Si doping. Based on structural analysis, the sample with 11.3% Si stayed amorphous after the anneal, while the samples with lower amount of silicon showed a distinct amount of orthorhombic, ferroelectric phase of $HfO_2$. The 11.3% Si film was found to be non-ferroelectric as demonstrated by linear Q-V and lack of hysteresis. For the two low Si films, a large Q-V hysteresis loop was measured after large positive corona charge poling ($Q_C$ of $30\mu C/cm^2$). In the hysteresis loop the coercive positive and negative fields were identified at about ± 1.2MV/cm for the 3.5% film and 1.0MV/cm for the 4.6% Si film.

For large positive charging the Fowler-Nordheim electron tunneling from TiN to $HfO_2$ conduction band was measured, showing a large effect of Si-doping manifested by the linear tunneling field decrease with %Si. This offers a possibility of %Si monitoring in $HfO_2$ with an estimated sensitivity of about 0.1mol%.

The corona-Kelvin technique facilitates whole wafer mapping of ALD film properties. Differences in maps that correlate with processing were observed showing promise for the technique as a fast, inline ALD and post deposition process monitor.

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## ALD Applications
## Room Plaza F - Session AA+AF-TuM

### Displays and Flexible Applications (8:00-10:00 am)/ALD Fundamentals: In-Situ Monitoring and Analysis (10:45 am-12:00 pm)

**Moderators:** Hyungjun Kim, Yonsei University, Korea, Jin-Seong Park, Hanyang University, Han-Jin Lim, Samsung Electronics, Tom Knisley, Applied Materials

8:00am **AA+AF-TuM-1 Functional Materials using Atomic Layer Deposition for Emerging Display Applications***, **Jin-Seong Park,*** Hanyang University, Republic of Korea **INVITED**

Atomic Layer Deposition (ALD) has remarkably developed in semiconductor and nano-structure applications since early 1990. The unique properties, including controlling atomic-level-thickness, manipulating atomic-level-composition control, and depositing impurity-free films uniformly, may accelerate ALD related industries and applications in functional thin film markets. One of big commercial industries, display market, just starts to look at the potential to adopt various functional inorganic/organic/hybrid films based on ALD/molecular layer deposition (MLD) techniques in emerging applications, such as transparent, flexible, and wearable electronics.

In this talk, I will take the brief emerging display market trend and forecast to understand what they are looking for. In fact, the AMOLED (active matrix organic light emitting diode) Television markets are just starting at early 2013. There are a few possibilities and needs to be developing for AMOLED, flexible and transparent Display markets. Then, firstly, the functional oxide conductor/semiconductor films deposited by ALD will be discussed for applying transparent conductor and thin film transistor as an active layer even on flexible substrates, including InOx, SnOx, ZnSnO, and InZnOx. Secondly, functional oxide and organic thin films, deposited by ALD/MLD have been demonstrated in emerging applications (flexible, transparent, and wearable things). In particular gas diffusion barrier property such as water and oxygen water vapor is important for passivation and encapsulation applications.

8:30am **AA+AF-TuM-3 Flexible Platinum Nanoparticle-based Piezoresistive Transducers Elaborated by Atomic Layer Deposition***, **Etienne Puyoo**, C Malhaire, D Thomas, R Rafaël,* Institut des Nanotechnologies de Lyon, France*; M R'Mili, A Malchère, L Roiban, S Koneti, M Bugnet,* MATEIS, France*; A Sabac, M Le Berre,* Institut des Nanotechnologies de Lyon, France

For the last ten years, the research on piezoresistive transducers has mainly been focused on the use of nanomaterials to optimize sensitivity, power consumption and sensor miniaturization. For instance, strain gauges based on Si nanowires, carbon nanotubes, graphene, MoS$_2$, Ag nanowires and metallic nanoparticle (NP) assemblies[1-4], have been developed at the laboratory scale to achieve very large gauge factors (GF) that compete with those of the state-of-the-art bulk Si gauges. Although the use of nanomaterials has attracted a lot of attention in literature these past few years, many technological obstacles (manipulation of individual nanostructures, complexity of the process, sensor reproducibility etc.) have yet to be overcome to make nanomaterials the preferred material for strain sensors. Consequently, alternative reliable technologies for the fabrication of nanostructured strain gauges with high GF are still sought-after by the industry.

In this work, platinum NP-based strain sensors are elaborated by means of Atomic Layer Deposition (ALD) on flexible polyimide substrates (Fig. 1). Pt NPs are grown by Plasma Enhanced ALD from (MeCpPtMe$_3$) precursor and O$_2$ plasma on thermal ALD alumina in subsequent process steps at 200°C in an Ultratech FIDJI F200 reactor. As presented in Fig. 1, several Pt NPs layers and Al$_2$O$_3$ tunnel oxide layers are stacked on polyimide in order to fabricate the flexible strain sensors. Their electro-mechanical response is tested under mechanical bending in both buckling and conformational contact configurations. A maximum gauge factor of 70 is reached at a strain level of 0.5% (fig.2). Although the exponential dependence of the gauge resistance on strain can be attributed to tunneling effect, it is shown that the majority of the junctions between adjacent Pt nanoparticles are in short circuit state. Finally, we demonstrate the feasibility of an all-plastic pressure sensor integrating Pt nanoparticle-based strain gauges in a Wheatstone quarter-bridge configuration (fig. 3).

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[2] N. M. Sangeetha, N. Decorde, B. Viallet, G. Viau, and L. Ressier, J. Phys. Chem. C **117**, 1935 (2013)

[3] H. Schlicke, M. Rebber, S. Kunze, and T. Vossmeyer, Nanoscale **8**, 183 (2016).

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8:45am **AA+AF-TuM-4 Color Coating of Electronic Textiles via Control of Refractive Index by Atomic Layer Deposition***, **Hyun Gu Kim**, W Kwon, H Lee,* Incheon National University, Republic of Korea

Attempts to integrate various electronic systems and sensors into textiles have been made for future wearable electronics. Conducting textile which is a key component for these wearable electronics is called by electronic textiles (e-textiles). Since most of conventional textiles are electrically insulator, metallic materials should be added to textiles during or after synthesis processes of textile. In the aesthetic point of view, however, the addition of metal for fabrication of e-textiles has a big disadvantage that is grey and black color of textile from the reflection and scattering of metal components. In addition, the conventional dying technology could not be applied to the e-textile systems after addition of metals. In our recent paper, we reported that conventional cotton textiles were successfully changed to e-textiles by Pt coating by atomic layer deposition (ALD). In this work, we report a novel approach to change the color of e-textile by using TiO$_2$/Al$_2$O$_3$ multilayer structures prepared by ALD. The various color combinations of the TiO$_2$/Al$_2$O$_3$ multilayer were simulated on planar Pt surface by computer simulation software that is based on change of refractive index. In the computational work, the film structures of TiO$_2$/Al$_2$O$_3$ multilayers and thickness of each layers were controlled to obtain desire colors. The simulation results were applied to experiments on planar structure as well as textile structures. The mechanical durability and optical properties of the TiO$_2$/Al$_2$O$_3$-multilayer-coated e-textiles were characterized. This approach for color coating of e-textiles presented here could provide more opportunities for the application of ALD-based e-textiles to other wearable electronics.

9:00am **AA+AF-TuM-5 Comprehensive Studies of Atomic Layer Deposited InGaO Thin Films using InCA-1, TMGa and H$_2$O$_2$ for Oxide Semiconductor Thin Film Transistor Applications***, **Jiazhen Sheng,*** Hanyang University, Republic of Korea*; B Shong,* Chungnam National University, Republic of Korea*; J Park,* Hanyang University, Republic of Korea

Oxide semiconductor thin film transistors (TFTs) have been extensively researched as a backplane technology in display industry, and among the well-known TFT active layer materials, including IZO, IGZO and ITZO, indium gallium oxide (IGO) has been suggested as a promising one due to its attractive performance. IGO thin films were deposited by ALD with different sequences at 200$^{o}$C using [1,1,1-trimethyl-N-(trimethylsilyl)silanaminato]indium (InCA-1) as the indium precursor, Trimethylgallium (TMGa) as the gallium precursor, and hydrogen peroxide (H$_2$O$_2$ 30%) as the reactant, that reactant pulse was launched before and after sequential metal precursor pulse to get a clear understanding on ALD multicomponent growth for oxide semiconductor materials. The gallium oxide shows successful deposition at 200$^{o}$C when accompany with InCA-1-H$_2$O$_2$ sequence (Ga% ~ 20.6 to 28.3%), while no growth appeared without indium oxide deposition. The potential energy of InCA-1 and TMGa precursors on the hydroxylated Si(100) surface and hydroxylated trivalent indium on Si(100) surface were calculated by DFT, that revealed TMGa cannot adsorb on hydroxylated Si while was able to adsorb on hydroxylated InO$_x$ surface. The ALD IGO shows controllable atomic composition and electrical characteristics, such as carrier concentration and resistivity, by adjusting supercycle in certain sequence. Thus, IGO thin film by ALD was applied to the active layer of TFT and the performance was optimized by adjust the supercycle, with mobility 9.45cm$^2$/Vs, threshold voltage -1.57V and subthreshold slop 0.26 V/decade.

Table 1. The growth rate and atomic composition of ALD growth thin film with various sequences (Growth rate obtained by SE and atomic percentages with AES)

| Sequence | Growth rate (Å/cycle) | at. %C | at. %Ga | at. %In | at. %O |
|---|---|---|---|---|---|
| GaO | - | - | - | - | - |
| InO | 0.97 | 0.5 | 0 | 42.8 | 56.7 |
| In-Ga | 0.77 | 0.7 | 3.8 | 39.6 | 55.9 |
| Ga-In | 0.33 | 0.4 | 28.3 | 14.9 | 56.4 |

| | | | | | |
|---|---|---|---|---|---|
| InO-GaO | 0.42 | 0.6 | 20.6 | 22.7 | 56.2 |

9:30am **AA+AF-TuM-7 Highly Sensitive VOCs Sensor Based on Atomic Layer Deposition of $TiO_2$ on Carbon Nanotubes***, Michela Sainato,* University of Illinois at Chicago*; R Divan, L Stan, Y Liu,* Argonne National Laboratory*; I Paprotny,* University of Illinois at Chicago

Volatile organic compounds (VOCs) are largely used in industries as reaction intermediates for the synthesis of chemicals and in research laboratories as solvents. The probability of over-exposure to such toxic agents is very high; therefore, the development of gas sensors for early detection of toxic VOCs is necessary. So far, attempts have been focused on the development of thin-film n-type semiconducting metal oxide-based gas sensors, such as $SnO_2$, ZnO, $TiO_2$.[1]

Our approach targets the fabrication of low-cost low-power chemi-resistor sensors based on multiwalled CNTs (MWCNTs) functionalized by ALD with metal-oxide(MOX). Specifically, we report the design and synthesis of high-surface-area $TiO_2$ functionalized MWCNT based sensors. Prior to ALD $TiO_2$ deposition on MWCNTs surface, we performed site-specific $O_2$-plasma activation on the MWCNTs surface. The creation of physical active sites is an effective way to enhance and spatially control the growth of $TiO_2$NCs (not limited to ZnO, $SnO_2$). By varying the deposition temperature during the ALD process, the morphology and crystallinity of the $TiO_2$ varies. At 175°C, a continuous amorphous $TiO_2$ layer on the MWCNT is observed (Figure 1a).

The $TiO_2$ /MWCNT heterostructure chemi-resistive sensor arrays for the selective detection of low concentrations of different VOCs at room-temperature (RT) have been tested. The resulting $TiO_2$ (at 200°C)/MWCNT sensors operate at RT and show fast and reliable responses to benzene ($C_6H_6$) and to toluene ($C_6H_5$-$CH_3$) (Figure 1b) while $TiO_2$ (at 175°C)/MWCNT sensors show no response (Figure 1c).

In this talk we will discuss the role of the $TiO_2$ deposition temperature on the morphology and crystallinity of the $TiO_2$ and its influence on the VOCs sensing.

Our aim is to elucidate the mechanism by which the ALD coating increases sensitivity to the final composite materials, thus paving a way toward the integration of chemi-resistor sensors with improved selectivity, lifetime, and reliability toward specific VOCs, as well as improved environmental sustainability.

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10:45am **AA+AF-TuM-12 *In-situ* Real-time and *in-vacuo* Study of the Temperature Impact on the $Al_2O_3$ ALD Nucleation upon Pristine Monolayer Graphene***, Marcel Junige,* Technische Universität Dresden, Germany*; J Kitzmann, C Chavarin,* IHP GmbH, Leibniz-Institut für Innovative Mikroelektronik*; M Geidel, J Reif, M Albert,* Technische Universität Dresden, Germany*; G Lupina, C Wenger,* IHP GmbH, Leibniz-Institut für Innovative Mikroelektronik, Germany*; J Bartha,* Technische Universität Dresden, Germany

Graphene (G) has attracted attention for THz switching capabilities in novel electronic device concepts: in a G-Base Transistor, a voltage at a sandwiched G-Base has been devised to control vertical electron tunneling through an emitter-base dielectric below, and hot electron tunneling through a base-collector dielectric above a G monolayer, respectively. This study strives for achieving these ultra-thin, demanding dielectrics by TMA–$H_2O$/–$O_3$ ALD.

Dielectric ALD has been applied to various types of G: either as-grown over the SiC/metal-catalyst substrate or transferred to another support substrate. Very distinct nucleation has been observed, largely depending on the G|substrate interaction, which in turn determines the energetic landscape of the G surface, i.e. the probability for initial precursor adsorption. SiC or metal underneath monolayer G have significantly enhanced dielectric ALD nucleation upon such G surfaces. In contrast, conducting ALD upon G over a dielectric or graphitic underground, substrate-inhibited island growth has commonly been exhibited due to G's intrinsic lack of dangling bonds, i.e. missing nucleation sites. However, such dielectric underlay is the relevant case for electronic applications. Accordingly, G has been pre-treated, functionalized, or seeded, entailing some additional effort along with the risk of defect generation. A rather simple approach for directly growing continuous, pinhole-free, and smooth films upon monolayer G over $SiO_2$ has recently been achieved by TMA–$H_2O$ ALD at 100°C without any other G modification. This low-temperature method has based on self-terminating surface reactions with physisorbed $H_2O$ molecules. Building on this, we systematically investigate here $Al_2O_3$ ALD nucleation phenomena upon pristine monolayer G in dependence on the deposition temperature by *in-situ* real-time Spectroscopic Ellipsometry (cf.Fig.) and complementing *in-vacuo* techniques, namely photoelectron spectroscopy as well as scanning probe microscopy.

On the downside of reduced deposition temperatures, ALD films then have exhibited lower mass densities, higher hydrogen concentrations (at unaffected Al:O ratios, indicating Al hydroxide), and lower electrical breakdown fields. Hysteresis in our I-V measurements also indicated charges at the interface or within the coating, pointing out insufficient electrical film quality for desired application as tunnel barrier. Therefore, we split the ALD process into two steps, switching from initially 100°C for better nucleation to subsequently higher temperatures for improved electrical properties. Likewise, we tested switching from initial $H_2O$ to following $O_3$, as well as post-deposition anneals.

11:00am **AA+AF-TuM-13 Investigation of the Influence of Plasma Parameters During Aluminum Nitride Atomic Layer Epitaxy using Grazing Incidence Small Angle X-ray Scattering***, Virginia Anderson, N Nepal, S Johnson, D Boris, S Walton,* U.S. Naval Research Laboratory*; Z Robinson,* SUNY College at Brockport*; A Kozen,* U.S. Naval Research Laboratory*; A Nath,* George Mason University*; S Rosenberg,* U.S. Naval Research Laboratory*; C Wagenbach,* Boston University*; J Hite,* U.S. Naval Research Laboratory*; K Ludwig,* Boston University*; C Eddy, Jr.,* U.S. Naval Research Laboratory

III-nitride semiconductors are tunable band gap materials, already in use in LEDs, and have additional uses in electronic switches and photovoltaics. Molecular beam epitaxy and metalorganic chemical vapor deposition (MOCVD) are performed at high temperatures, with AlN MOCVD growth requiring well over 1000°C. Early research investigating low-temperature plasma assisted atomic layer epitaxy (ALEp) to see if it could be added to the techniques able to produce high quality nitride semiconductor films is underway. Compared to conventional growth methods, ALEp offers elimination of miscibility gaps in ternaries and reduced thermal coefficient of expansion mismatch in heterostructures. Already published work shows that ALEp of AlN with high crystalline quality can be achieved at lower temperatures than those required for MOCVD[1], but more study is necessary to lower percentages of impurities and improve mechanistic understanding. Grazing incidence small angle X-ray scattering (GISAXS) can be carried out at ALEp process pressures in real time, and is sensitive to changes in surface morphology during nucleation, thus providing insight into the growth mode.

At the Cornell High Energy Synchrotron Source (CHESS) GISAXS probing of AlN ALEp on sapphire was performed. The AlN precursors were trimethylaluminum and either nitrogen/argon or hydrogen/nitrogen/argon plasma. Examination of the surface features during AlN growths at various growth temperatures and plasma conditions took place. The kinetics of the plasma were altered by changing the ratio of nitrogen-to-argon in the plasma feed gas, leading to differences in the relative production of nitrogen species. The GISAXS offers information about the surface feature evolution over the course of the film growth, and avoids *ex situ* surface oxidation of AlN, while atomic force microscope (AFM) measurements offer a final look at the surface once the samples are removed from the reactor.

Growths below 450°C were shown with *ex situ*, post-growth X-ray photoelectron spectroscopy to have higher impurities than samples grown at 480°C, and GISAXS shows an increase in short correlation lengths at the lower temperatures. Changing the plasma nitrogen/argon ratios also changed the impurity levels in the final films.

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

11:15am **AA+AF-TuM-14 Studies of Surface Structure and Surface Chemistry During Plasma-Assisted Atomic Layer Epitaxial Growth of InN Semiconductor Thin Films on GaN Substrates*, Samantha Rosenberg,*** U.S. Naval Research Laboratory*; D Pennachio,* UCSB*; V Anderson, N Nepal,* U.S. Naval Research Laboratory*; C Wagenbach,* Boston University, USA*; A Kozen,* U.S. Naval Research Laboratory*; Z Robinson,* SUNY College at Brockport*; J Logan, S Choi,* UCSB*; J Hite,* U.S. Naval Research Laboratory*; K Ludwig,* Boston University*; C Palmstrøm,* UCSB*; C Eddy, Jr.,* U.S. Naval Research Laboratory

III-N semiconductors such as GaN, AlN, and InN are the basis for creating compound ternary and quaternary semiconductor materials well suited for applications in several important technological areas including high current, normally-off power switches.[1-3] However, the full range of ternary and quaternary III-N semiconductors cannot be achieved with conventional growth methods due to the high temperatures required. While atomic layer deposition (ALD) is a versatile low temperature growth technique and has gained wide use, it does not offer the required level of crystallinity and purity needed for high-performance III-N semiconductor devices. Therefore, we have developed a technique adapted from ALD, called plasma-assisted atomic layer epitaxy (ALEp).[2] Using surface science techniques we are working to develop a fundamental understanding of the ALEp growth process to further enable the method as a powerful new growth technique for semiconductor materials.

Here we employ *in-situ* and *in-vacuo* surface studies of GaN substrate preparation and InN ALEp heteroepitaxial growth to advance our fundamental understanding of the ALEp process. We conduct *in-situ* grazing incidence small angle x-ray scattering (GISAXS) experiments at the Cornell High Energy Synchrotron Source, utilizing morphological evolution monitoring to investigate the growth surface during sample preparation and film deposition. GISAXS results have shown that bulk GaN surfaces develop a correlated surface feature at finite $q_y$ during the ALEp-based emulated Ga flash-off cleaning, while ALEp-based $H_2$ cleaning introduces additional short range order features. Neither of these features are found on Epi GaN surfaces suggesting they are associated with polish damage in the substrates. For both surfaces, features from ALEp-based preparations dominate the GISAXS scattering during subsequent ALEp InN growth and are quite different from ALEp InN growth on sapphire. GISAXS information is complemented with *in-vacuo* x-ray photoelectron spectroscopy and reflection high-energy electron diffraction studies conducted at the Palmstrøm Lab at UCSB. Initial results have shown a partial surface reconstruction after exposure to TEG and atomic $H_2$ commensurate with a reduction in carbon and oxygen from the surface. Further studies will consider traditional molecular beam gallium flash-off and further atomic hydrogen etching as ways to produce the most suitable GaN surface for our ALEp-based approach.

1. N. Nepal, et al., Appl. Phys. Lett. 103, 082110 (2013)
2. C. R. Eddy, Jr, et al., J. Vac. Sci. Technol. A 31(5), 058501 (2013).
3. R. S. Pengelly, et al., IEEE Trans. Microwave Theory Tech. 60, 1764 (2012).

11:30am **AA+AF-TuM-15 Plasma Gas Chemistry Influence on Growth of InN Films by Atomic Layer Epitaxy*, Neeraj Nepal,*** *V Anderson, S Johnson, S Rosenberg, A Kozen,* U.S. Naval Research Laboratory, USA*; C Hoskin,* Boston University*; D Meyer, B Downey, J Hite, V Wheeler,* U.S. Naval Research Laboratory, USA*; R Zachary,* SUNY College at Brockport*; D Boris, S Walton,* U.S. Naval Research Laboratory, USA*; K Ludwig,* Boston University, USA*; C Eddy, Jr.,* U.S. Naval Research Laboratory, USA

III-N semiconductors have been used in a variety of technologies such as high power transistors, emitters, detectors, and solar-cells. The relatively high growth temperature of III-N semiconductor synthesis techniques has impeded further development and application of the materials due to challenges with miscibility gaps for ternaries and strain related to thermal expansion mismatch with non-native substrates. To address these challenges, plasma-assisted atomic layer epitaxy (ALEp) offers a new approach with growth temperature less than half of those needed for conventional growth methods. Since growth using this technique is far from thermodynamic equilibrium, understanding the effects of ALEp growth parameter space on growth kinetics is essential to further improving the method and the resulting electronic materials.

In this paper, we report on the effect of plasma gas chemistry on growth of crystalline InN semiconductor films by ALEp on a-plane sapphire substrates at temperatures below 250 °C. First, the optimal ALEp growth windows and growth parameter space is identified. These studies involve variations in substrate surface preparation for epitaxy, plasma gas chemistry, growth temperature, precursor pulse/purge time. The effect of these parameters is assessed using different *ex situ* characterization methods such as atomic force microscopy, x-ray photoelectron spectroscopy, x-ray diffraction and four-point free carrier transport measurements. To further understand/develop plasma gas chemistry these optimal conditions are then applied to film growth monitored by real-time grazing incidence small angle x-ray scattering (GISAXS) measurements revealing changes in the growth mode through morphological evolution of the surface. It will be shown that the nature of GISAXS evolution directly relates to the material quality. Both *ex situ* and *in situ* growth studies show that the starting surface, $N_2$/Ar flow ratio, plasma time/pressure and $H_2$ content of the plasma significantly affects the surface chemistry, nucleation and growth of InN. For example, decreasing Ar flow through plasma source from 200 sccm to 25 sccm for constant $N_2$ flow of 75 sccm and adding $H_2$ at the last fraction of the plasma pulse in the ALEp cycle reduces impurities and increases the saturated growth rate. Based on various *ex situ* characterization methods, the quality of the ALEp grown semiconducting InN films is found to be similar or better than the material grown by conventional growth methods, such as molecular beam epitaxy, at much higher temperatures.

11:45am **AA+AF-TuM-16 Spectroscopic Ellipsometry of $WO_3$ Thin Films from ALD: *In-situ* Layer-by-Layer Growth Monitoring and *ex-situ* Optical Characterization*, Ufuk Kilic,*** *D Sekora, A Mock, M Schubert,* University of Nebraska Lincoln

Within the last two decades, tungsten tri-oxide ($WO_3$) ultra-thin films have been the subject of research for photovoltaic, gas sensing, and electrochromic applications due to its large band gap (3.4 eV) and photocatalytic properties [1,2]. In this study, we fabricated $WO_3$ ultra-thin films on silicon substrates by means of atomic layer deposition (ALD). Precise and accurate control of deposition conditions throughout the growth process is a critical challenge surmountable by integration of spectroscopic ellipsometry (SE). By utilizing in-situ SE monitoring of $WO_3$ depositions, we obtain thickness, film roughness, and substrate temperature throughout the layer-by-layer growth.

By implementing pressurized precursor control, $WO_3$ was deposited by subsequent exposures of $(tBuN)_2(Me_2N)_2W$, nanopure $H_2O$, and oxygen plasma to the substrate surface while under continuous SE observation. Due to lack of detailed reports on broad range optical properties of $WO_3$ thin films, a multi-sample analysis is necessary for accurate thickness and optical constant determination from SE [3]. Thus, two films are deposited for 75 and 150 cycles under the same conditions and ex-situ SE data is collected in the spectral range from 0.7-8.5 eV. The as-grown $WO_3$ dielectric function is determined along with the respective film thicknesses. Roughness was considered and verified by atomic force microscopy. With this information, the in-situ SE data is retroactively analyzed to attain inherent layer-by-layer deposition parameters.

We report the dielectric function of as-grown $WO_3$, accurate film thicknesses and growth rate. Further implementation of this method allows for precise control and real-time optimization of deposition parameters ultimately providing us with the ability to develop ALD recipes in-situ.

[1] Ping, Y., Rocca, D., & Galli, G., Physical Review B, 87(16), 165203, (2013).

[2] Liu, Rui, et al., Angewandte Chemie, 123.2: 519-522, (2011).

[3] Jarrendahl, K., and H. Arwin, Thin Solid Films, 313: 114-118, (1998).

## ALD Applications
## Room Plaza ABC - Session AA-TuM

## Batteries I (8:00-10:00 am)/Emerging Apps II (10:45 am-12:00 pm)

**Moderators:** Christophe Detavernier, Ghent University, Belgium, Christophe Vallee, LETI-LTM, France, Gary Rubloff, University of Maryland, Tero Pilvi, Picosun Oy

8:00am **AA-TuM-1 Designing of Surface and Interface of Electrodes for Highly-stable Li Ion Batteries, Li-S Batteries and Metal-Air Batteries*, Xueliang Sun,*** University of Western Ontario, Canada **INVITED**

The poor cell lifetimes of Li/Na batteries are rooted mainly in side reactions occurring at the electrode-electrolyte interface. The use of surface coatings to control of the electrode-electrolyte interface is an important strategy to design new electrodes. This talk will include two parts:

In the first part, we will report our work on the applications of atomic layer deposition (ALD) in Li ion batteries [1] including synthesis of coating materials such as $Al_2O_3$, $ZrO_2$, $TiO_2$, $AlPO_4$ and LiTaO3 [2,3,4] as well as the ALD coating materials to modify the anode ($Li_4Ti_5O_{12}$, $SnO_2$) [5] and the cathode (commercial $LiCoO_2$, NMC) [6].

In the second part, we will discuss MLD coating on Li-S batteries operating at 55C [7].

In the third part, we will discuss our recent results on ALD $Al_2O_3$ coating on Na metal for Na ion batteries and Na-Air batteries [8].

**Reference:**

[1] X. Meng, X.-Q.Yang, X. Sun. ***Adv. Mater.***2012, 24, 3589-3615.

[2] J. Liu, X. Meng, Y. Hu, D. Geng, M.N. Banis, M. Cai, R. Li, X. Sun. ***Carbon*** 2013, 52, 74-82.

[3] J. Liu, Y. Tang, B. Xiao, T.K. Sham, R. Li, X. Sun. ***RSC Adv***. 2013, 3, 4492-4495.

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**Funct. Mater.** 22 (2012) 1647-1654.

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[8]Y. Zhao, L. Goncharova, A. Lushington, Q. Sun, H. Yadegari, B. Wang, W. Xiao, R. Li, X. Sun., **Adv. Mater.,** (2017) In press

8:30am **AA-TuM-3 ALD Vanadium Oxides for 3D Thin-film Lithium Ion Batteries***, **Felix Mattelaer,*** Ghent University, Belgium*; K Geryl,* Ghent University*; T Dobbelaere,* Ghent University, Belgium*; G Rampelberg,* Ghent University*; J Dendooven, C Detavernier,* Ghent University, Belgium

Several pathways are investigated to obtain high power and high energy density thin-film lithium ion batteries. The high power aspect can be obtained by scaling down the film thickness, which unfortunately decreases the films actual capacity. By coating thin-film electrodes onto 3D-structured substrates, the high power inherent of thin-film electrodes can be achieved while the energy density per footprint area can be increased.

In addition to 3D structuring, materials selection is of key importance for achieving high power and high energy density in thin-film lithium ion batteries. Traditional electrode materials such as $LiCoO_2$ are limited to a reversible range of lithium insertion, which leads to capacities of 550-700mAh/cm³ for commercialized electrode materials. Traditionally, battery research mainly focuses on crystalline electrodes. Indications exist that higher energy density and higher power density can be achieved using amorphous materials. ALD is uniquely suited to deposit amorphous materials at low temperatures in a conformal way onto 3D structured substrates, validating the investigation of this class of materials.

In this work, crystalline and amorphous ALD vanadium oxides are deposited and examined as electrode materials. We demonstrate the deposition of amorphous $V_2O_5$ and two 'flavors' of $VO_2$ (water-based ALD and ozone-based ALD). By careful tuning of the post-ALD annealing conditions, the influence of initial ALD process, atmosphere, temperature and substrate on the crystallization and oxidation of the $VO_2$ films is revealed. Using this knowledge, the whole range of vanadium oxides can be obtained ($VO_2$–$V_6O_{13}$–$V_4O_9$–$V_3O_7$–$V_2O_5$), which are all displaying storage capacity with very high energy densities (e.g. 1380mAh/cm³ for $V_4O_9$). The amorphous initial states (amorphous $VO_2$ and $V_2O_5$) on the other hand also display very high capacities, and much better kinetics than their crystalline counterparts. Moving from crystalline to amorphous vanadium oxides more than doubles the storage capacity for a given film thickness. Finally, the conformal deposition is demonstrated on silicon micropillar arrays, which demonstrates the transfer of the thin-film kinetics to a higher energy density per footprint area electrode.

In conclusion, a wide range of ALD vanadium oxides was demonstrated as potential thin-film cathode. In particular, amorphous vanadium oxides, and $VO_2$ (B) show promise thanks to their high energy density and good kinetics, enabling a much higher storage capacity than the stable range of $V_2O_5$.

8:45am **AA-TuM-4 PE-ALD of Transition Metal Phosphates as Lithium-Ion Battery Electrode Materials***, T Dobbelaere, F Mattelaer, J Dendooven,* Ghent University, Belgium*; P Vereecken,* Imec, Belgium*; **Christophe Detavernier,*** Ghent University, Belgium

In today's power-hungry society, lithium-ion batteries are the current state of the art of electrochemical energy storage. Their usage ranges from applications on large scales (e.g. off-grid storage) to medium (e.g. electric vehicles) and small ones (e.g. smartphones). For certain applications, e.g. chip-scale integration, the goal is to make them also on the microscopic scale. Although thin-film batteries have been demonstrated, mostly using planar, sputter-deposited films, their capacity is necessarily low because of the small amounts of active material. By using 3D microstructured substrates rather than planar ones, the capacity can be drastically increased. However, coating these substrates requires a conformal deposition method, leading to ALD as a promising technique.

Using a trimethyl phosphate (TMP) plasma as the phosphorus source, we are able to deposit three well-performing electrode materials: iron phosphate[1], titanium phosphate[2], and vanadium phosphate[3]. The process sequences are similar, with each one consisting of three steps: TMP plasma exposure, followed by $O_2$ plasma exposure, followed by a metal precursor exposure. The metal precursor is either tert-Butylferrocene (for iron phosphate), titanium isopropoxide (for titanium phosphate), or tetrakisethylmethylamido vanadium (for vanadium phosphate).

Each of the three processes shows ALD-type growth at a substrate temperature of 300 °C, with properties including linearity and (slow) saturation. They all have high growth rates, resp. 1.1, 0.7, and 0.8 nm/cycle, as shown in Fig. 1 (a,c,e). This is attractive for depositing thicker films in a time-efficient manner. They have low impurity levels, with ERD-measured stoichiometries of resp. $FeP_{1.5}O_{4.7}$, $TiP_{1.7}O_{5.6}$, and $V_{1.1}PO_{4.3}$.

Although each material can be crystallized by post-deposition annealing, this is not necessary (nor beneficial) because the as-deposited amorphous forms can be directly electrochemically lithiated and subsequently cycled. They yield capacities of resp. 0.7 µAh/cm² between 2.3-4.3V, 1.0 µAh/cm² between 2.3-3.2V, and 2.2 µAh/cm² between 1.4-3.6V, as shown in Fig. 1 (b,d,f). They can be used as practical electrodes, given that their coulombic efficiencies are close to 100% and that they show good capacity retention upon extended cycling.

[1] Dobbelaere et al., Chem. Mater. 2016, 28, 3435-3445

[2] Dobbelaere et al., J. Mater. Chem. A 2017, 5, 330-338

[3] Dobbelaere et al., In preparation

9:00am **AA-TuM-5 Comparing Temporal and Spatial Atomic Layer Deposition for Enhanced Performance of Li Ion Battery Electrodes***, **Alexander Yersak**, A Dameron,* University of Colorado - Boulder*; X Li, Y Yang,* Colorado School of Mines*; K Hurst, R Tenet,* National Renewable Energy Laboratory*; S George,* University of Colorado - Boulder

Ultrathin atomic layer deposition (ALD) coatings on Li Ion battery (LIB) electrodes can improve the capacity stability for both anodes and cathodes. The remaining challenge is to scale-up the ALD on LIB electrodes for commercialization. This work focused on comparing temporal and spatial ALD methods for coating the LIB electrodes. If the temporal and spatial ALD methods deliver comparable LIB performance, then the next step will be to extend the spatial ALD to roll-to-roll (R2R) spatial ALD.

The experiments utilized our spatial ALD rotating cylinder reactor [1]. Using this reactor, we have already demonstrated uniform ALD coatings in nanoporous anodic aluminum oxide (AAO) membranes with aspect ratios of 250 at an equivalent web speed of 10 m/min [2]. Porous battery electrodes have an estimated aspect ratio of ~50. Based on Monte Carlo simulations of ALD in the nanoporous AAO membranes, uniform ALD coatings should be possible in the porous battery electrodes at an equivalent web speed of 100 m/min.

We first examined the capacity stability for $LiCoO_2$ (LCO) cathode electrodes that were uncoated or coated with 4 $Al_2O_3$ ALD cycles using either temporal ALD or spatial ALD. The temporal ALD coatings were deposited using trimethylaluminum (TMA) and water at 120ºC. The spatial ALD coatings were deposited using TMA and ozone at 60ºC and a rotation speed equivalent to a web speed of 10 m/min. The cathode electrodes were taped to the inner drum of the rotating cylinder reactor for the ALD coating. For electrochemical testing, the LCO electrodes were cycled at 3.3-4.5V and charge/discharge rates of 1C and C/3.

The electrochemical testing results are shown in the supplemental figures. For the uncoated LCO electrodes, a significant capacity fade was observed after 10 and 94 charge/discharge cycles for rates of 1C and C/3, respectively. The ALD-coated electrodes show much better capacity stability especially for the 1C rates. The performance of temporal ALD and spatial ALD coated LCO electrodes is also comparable. We are now extending our rotating cylinder spatial ALD reactor to full R2R operation. We hope to have results from this R2R spatial ALD reactor by the ALD2017 conference.

[1] K. Sharma et al., *J. Vac. Sci. Technol. A* **33**, 01A132 (2015).

[2] K. Sharma et al., *J. Vac. Sci. Technol. A***34**, 01A146 (2016).

### 9:15am **AA-TuM-6 All-Solid-State Thin-Film Battery with a Novel Organic Cathode Material by Atomic/Molecular Layer Deposition***, **Mikko Nisula**, M Karppinen,* Aalto University, Finland

The miniaturization of electronic devices creates demand for energy storage systems of the same length scale. As the downsizing of conventional liquid electrolyte cells is difficult, the current focus is on all-solid-state thin-film batteries. In order to increase the energy density while preserving the power density of the cells, various 3D architectures have been proposed to enhance the effective surface area. Such an approach places an apparent need for a thin-film deposition method capable of manufacturing the electrode and electrolyte materials on high-aspect-ratio substrates. A strong candidate for the task is the atomic layer deposition (ALD) technique and the recent years have seen the emergence of a number of ALD processes for both electrode and electrolyte materials.

An interesting choice for the electrodes is the group of organic electrode materials such as quinones and conjugated carboxylates. While impractical for conventional batteries due to conductivity and dissolution issues, these downsides can be circumvented by applying the organic electrode material in all-solid-state thin film batteries. Recently, we demonstrated that these materials are attainable using the combined atomic/molecular layer deposition (ALD/MLD) by depositing the lithium terephthalate anode material.[1] Compared to the more conventional inorganic materials, the ALD/MLD approach yields a number of advantages such as simple binary deposition processes, low processing temperatures (<200 °C) and no need for a post-deposition anneal. Moreover, given their environmentally benign constituents, organic electrode materials would be well suited for the emerging *transient electronics* technology.[2]

In this contribution, we present an all-solid-state thin-film battery based on a novel lithium-bearing organic cathode material by ALD/MLD combined with ALD-made LiPON[3] as the solid electrolyte. As well as investigating the electrochemical performance of the solid-state battery by cyclic voltammetry and galvanostatic charging/discharging, we discuss the aspects of device fabrication such as the effect of electrode and electrolyte layer thicknesses on the device performance as well as the role of the interfaces and methods for controlling them.

1. M. Nisula, M. Karppinen, *Nano Lett.***16** 2016 1276 – 1281

2. K. K. Fu, Z. Wang, J. Dai, M. Carter, L. Hu, *Chem. Mater.***28** 2016 3527 – 3539

3. M. Nisula, Y. Shindo, H. Koga, M. Karppinen, *Chem. Mater.***27** 2015 6987 – 6993

### 9:30am **AA-TuM-7 Atomic Layer Deposition of Hierarchical CNTs@$FePO_4$ Architecture as a 3D Electrode for Lithium-Ion and Sodium-Ion Batteries***, **Jian Liu,*** The University of British Columbia, Canada*; B Wang, Q Sun, R Li, T Sham, X Sun,* University of Western Ontario, Canada

Three-dimensional (3D) microbatteries hold great promise as on-board energy supply systems for microelectronic devices [1]. The construction of 3D microbatteries relies on the development of film deposition techniques that can enable coatings of uniform electrode and electrolyte materials in high-aspect-ratio substrates [2]. Herein, a 3D $FePO_4$ on carbon nanotubes (CNTs@$FePO_4$) structure is fabricated by coating $FePO_4$ on CNTs/carbon paper substrate using atomic layer deposition (ALD) [3]. Compared to $FePO_4$ on a planar substrate, the 3D CNTs@$FePO_4$ electrode exhibits significantly increased areal capacity and excellent rate capability for lithium-ion and sodium-ion storage. The 3D CNTs@$FePO_4$ maintained areal capacities of 64 µAh $cm^{-2}$ and 33 µAh $cm^{-2}$ after 180 cycles for LIBs and SIBs, which are 16 and 33 times higher than those of planar $FePO_4$ electrode, respectively (Figure 1). Moreover, hybrid 3D CNTs@$FePO_4$@$Li_3PO_4$ structure is fabricated by coating $Li_3PO_4$ solid-state electrolyte on 3D CNTs@$FePO_4$. The CNTs@$FePO_4$@$Li_3PO_4$ electrode shows stable cycling performance in lithium-ion batteries. Hard X-ray Photoemission Spectroscopy analysis discloses that $Li_3PO_4$ coating prevents the formation of undesirable LiF in the solid-electrolyte interphase layer, which is believed to be responsible for the performance degradation in CNTs@$FePO_4$ (Figure 2). It is expected that this work will pave the way to building reliable 3D nanostructured electrode and electrolyte architecture for high areal capacity microbatteries.

**References**

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[2] J. Liu, X. Sun, Nanotechnology, 2015, 26, 024001.

[3] J. Liu, B. Wang, Q. Sun, R. Li, T.-K. Sham, X. Sun, Adv. Mater. Interfaces 2016, 1600468.

### 9:45am **AA-TuM-8 Unravelling The Role of ALD $Al_2O_3$ and $TiO_2$ Protective Coatings on Lithium-Ion Battery Electrodes.***, **Felix Mattelaer,*** Ghent University, Belgium*; M Kurttepeli,* University of Antwerp*; S Deng,* Ghent University, Belgium*; D Cott, P Vereeceken,* IMEC, Belgium*; J Dendooven,* Ghent University, Belgium*; S Bals,* University of Antwerp*; C Detavernier,* Ghent University, Belgium

Nanoscaling of lithium-ion battery electrodes enhances the kinetics and footprint capacity, but also sensitively increases the electrode-electrolyte interfacial area. While this is beneficial for fast lithium-ion diffusion, most capacity fading mechanisms are also related to interface phenomena, such as solvent decomposition and metal dissolution. Interface stabilization by ALD coatings has been heavily investigated since 2010. Partially thanks to the ease of deposition, the main part of research has been devoted to ALD of $Al_2O_3$ as protective coatings. However, it is a poor lithium-ion conductor, and other ALD films can both provide enhanced cycle life while maintaining the excellent thin-film battery kinetics.

In this work, we use two thin-film lithium-ion battery electrodes as model systems to benchmark ALD $Al_2O_3$ and ALD $TiO_2$ as interfacial modifiers for lithium-ion batteries. On a near-ideal electrode (lithiated thin-film $TiO_2$), the lithium-blocking nature of ALD $Al_2O_3$ is revealed. $Al_2O_3$ films beyond 3nm are completely blocking, while thinner coatings impose an impedance of $>10^{12}$ Ωcm. ALD $TiO_2$ does not pose a kinetic bottleneck and is never blocking. On a less-than ideal model system (overcharged thin-film $LiMn_2O_4$), it is shown that 5nm ALD $TiO_2$ can prevent solvent decomposition, which more than 10 better capacity retention at 100C.

Finally, ALD is used to decorate a CNT forest with both a $V_2O_5$ film as a lithium-ion battery cathode, and an amorphous $TiO_2$ coating as a protective coating to extend cycle life. The dual-layer conformality is confirmed using EDX-STEM tomography. The electrode is cycled with two lithium-ions per $V_2O_5$ unit cell. A high areal capacity and excellent kinetics are found for the $V_2O_5$-coated CNTs, but a fast capacity degradation is observed and associated to vanadium dissolution during cycling. Coating the $V_2O_5$/CNTs with 5 or 25 cycles of ALD $TiO_2$ retained the excellent kinetics, but almost completely alleviated the vanadium dissolution issue, improving the cycle life dramatically. Furthermore, the coating was found to aid in the cycling-driven amorphisation of the $V_2O_5$.

In conclusion, ALD $Al_2O_3$ was identified as a very resistive coating towards lithium, using thin-film electrodes as model systems. ALD thin-film $V_2O_5$ on CNTs was demonstrated a high-power lithium-ion cathode. The deterioration mechanism of deep charging of the $V_2O_5$/CNTs is shown to be related to vanadium dissolution. ALD $TiO_2$ coatings improved the cycling performance by alleviating this dissolution issue, while maintaining the excellent thin-film battery kinetics.

### 10:45am **AA-TuM-12 ALD Layer Opportunties for Reversible Bonding of Ultrathin Glass Substrates***, **Messaoud Bedjaoui**, S Poulet,* LETI, France

Over the past few years, we are witnessing to a rapid development of flexible electronics leading to a number of promising devices in the area of energy sources and advancing displays (e.g microbatteries, organic state lighting, liquid crystals displays…) especially with the emergence of ultrathin and flexible glass substrates (<100µm). However, handling of ultrathin substrates is a great challenge for front-end and back-end processes. On the other hand, wafer bonding techniques are being increasingly used to achieve innovative stacking structures. In order to bond ultrathin substrates containing temperature-sensitive devices, a bonding process that yields high bond strengths operating at a moderate temperature (<600°C) is needed.

The purpose of this work is to present a new cost reduction concept of handling for ultrathin glass substrates covering both bonding and debonding processes. In order to elaborate flexible thin film components using this kind of ultrathin substrates, their bonding based on intermediate atomic layer deposition (ALD) as well as debonding from thick carrier has to be studied. First of all, we investigate the bonding behavior of glass/$Al_2O_3$, glass/$TiO_2$ and glass/$Al_2O_3$-$TiO_2$ layer structures submitted to room temperature up to 600°C annealing. Surface and bonding energies are measured in an anhydrous atmosphere and bonding defectivity is analysed using scanning acoustic microscope (SAM). Layers deposited by ALD onto glass carrier are suited for direct bonding.

This work is also focused on the debonding process by demounting the interface layer fabricated using atomic layer deposition in humid atmosphere conditions (>80%RH and T°>90°C). Spontaneous debonding phenomena occurred solely for low temperature (80°C to 150°C) $Al_2O_3$ layers on thick glass carrier even after annealing treatment. This debonding, unobservable for $TiO_2$ and $Al_2O_3$-$TiO_2$ bilayer bonding structures, may be explained by chemical or structural modification such as internal stress, pinholes formation or stoichiometry instability. The intermediate bonding layers have been also characterized using infrared spectroscopy, scanning electron microscopy (SEM) and complementary analysis (spectroscopic ellipsometry, X-ray photoelectron spectroscopy) before and after exposition to humid atmosphere (Figure 1, Figure 2, Figure 3 in supplemental document). Based on these results, an $Al_2O_3$ debonding mechanism is proposed. These studies demonstrated that the approach of this work provides a method to fabricate temperature-sensitive devices on bonded ultrathin glass and to achieve a low cost solution of debonding from glass carrier which can be repeatedly reused after simple cleaning.

11:00am **AA-TuM-13 Atomic Layer Deposition and Precursor Development for Chemoresistive Gas Sensing Materials***, **Rachel Wilson**, C Blackman, C Carmalt,* University College London, UK

Chemoresistive gas sensors are simple to use, have low cost, small size and high sensitivity. The performance of such sensors is defined by the composition, morphology and structure of the sensing materials. This work demonstrates the use of Atomic Layer Deposition (ALD) to engineer *n*- and *p*-type metal oxide films for gas sensor applications.

A major drawback of using *n*-type materials for gas sensing is their sensitivity to moisture and humidity. *P*-type gas sensing materials however, are believed to be less moisture sensitive, making them attractive materials within the semiconductor industry. However, *p*-type metal oxides have received relatively little attention compared to their *n*-type congeners, which may be ascribed to their apparently low sensitivities, limiting their potential applications. ALD provides atomic level control of film growth, allowing fabrication of materials with defined thickness, making it an ideal tool for exploring the fundamental sensing properties of these materials.[1] The long term goal is to identify the most promising new materials and provide key information regarding the optimization of the materials synthesis to obtain gas sensing materials with maximum sensitivity and selectivity.

Metal oxide thin films have been deposited using a flow-type ALD reactor which was built in house. $TiO_2$ films have been deposited using titanium isopropoxide and water precursors. Nickel and copper complexes have been synthesized for use as potential ALD precursors for the deposition of nickel (II) oxide (NiO), and copper (I) oxide ($Cu_2O$) using water as the co-reactant. These include but are not limited to; alkoxides, guanidinates and amides. NiO has been deposited via ALD and CVD methods.

Metal oxide films have been deposited onto alumina sensors, which have been exposed to different concentrations of gases. By measurement of the films electrical resistance the gas sensitivity can be determined and hence we can define the thickness which gives the maximum sensor response (and see if this is comparable with the Debye length). Although the use of $TiO_2$ as a gas sensor material is widely known, we have manged to obtain responses at very high resistance values with excellent kinetics of response. We have shown that the pattern responses of the electrical resistance towards certain gases indicate typical *n*-type semiconducting behavior. The $TiO_2$ film thickness plays a dominant role within the conduction mechanism. Gas sensitivity testing of *p*-type NiO films is currently underway.

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11:15am **AA-TuM-14 Physics with and Physics of Atomic Layer Deposited Nanofilms***, **Neal Sullivan**,* Arradiance*; A Lehmann,* Universitat Erlangen-Numberg*; A Brandt,* University of Texas at Arlington

In high energy physics (HEP), the need for precise timing (pico-seconds), was established by the inability to extract all measurable information (i.e. 4-vectors) from multi-TeV particle collisions at the Fermilab Tevatron in 2003[1] Psec-resolution requires a detector that is small enough that variations in the fastest transit times of the photons or electrons correspond to a time jitter smaller than the resolution. Microchannel plates (MCP) possess this requisite timing dimension, but MCP-based photodetectors, were not considered for these applications due to the high-cost / area, and poor lifetime – typically less than one month under use conditions. While photomultiplier tubes (PMTs) are the workhorse devices for photo detection, microchannel plate-based PMTs (MCP-PMT) significantly advance the state-of-the-art achieving more than 100-fold improvements in spatial and temporal resolution. This work presents the development of ALD-functionalized MCPs that have improved MCP-PMT performance and extended lifetimes by more than 40x.

ALD process development for both secondary emissive and conductive layers as well as the integration of these ALD nanofilms with the MCP device at Arradiance will be discussed in detail. The tradeoffs required and the overall device performance is compared to the standard reduced silicate lead glass (RSLG) MCP. Application lifetime and MCP-PMT performance results, collected by Dr. Lehmann at the PANDA experiment over the last 5 years and at Professor Brandt's lab at University of Texas Arlington, will be presented and the implications for high energy physics will be examined. Analytical studies, assessing the role of each of the functional ALD films in lifetime improvement will be presented, with an eye towards understanding the underlying physics of the nanofilm in the MCP-PMT

High speed photodetectors with micron space resolution and temporal resolution less than 10 picoseconds (psec) represent a disruptive technology across the physics frontiers of energy, intensity, and cosmic with the capability to support experiments addressing the origin of mass, neutrino physics and proton decay, and the nature of dark matter and energy. Additional technology and commercial areas such as: homeland security, astronomy, space instrumentation, remote night time sensing, TOF mass spectrometry, and medical imaging (PET scanning) all stand to benefit from this technology.

[1] Henry J. Frisch, et. al., A Brief Technical History of the Large-Area Picosecond Photodetector (LAPPD) Collaboration, http://arxiv.org/abs/1603.01843 March 2016

11:30am **AA-TuM-15 Highly Resistive ALD Coatings for Microchannel Plates Operating at Cryogenic Temperatures***, **Till Cremer**, B Adams, M Aviles, J Bond, C Craven, M Foley, A Lyashenko, M Minot, M Popecki, M Stochaj, W Worstell,* Incom Inc.*; J Elam, A Mane,* Argonne National Laboratory*; O Siegmund, C Ertley,* University of California, Berkeley

We report on the structure-property relationships of highly resistive nanocomposite films synthesized by atomic layer deposition (ALD). These nanocomposites are composed of metal nanoparticles dispersed in a dielectric matrix, resulting in an amorphous material with semiconductor-like electrical properties characterized by a negative thermal coefficient of resistance (TCR) . The material's (thermo-) electrical properties depend on film thickness, composition, nanostructure, and the chemical nature of the dielectric and metal components. We show how the structure-property relationships developed in this work can be used to design coatings with improved thermo-electrical properties.

Atomic layer deposition (ALD) has enabled the development of a new technology for fabricating microchannel plates (MCPs) with improved performance performance that offer transformative benefits to a wide variety of applications. Incom uses a "hollow-core" process for fabricating glass capillary array (GCA) plates consisting of millions of micrometer-sized glass microchannels fused together in a regular pattern. The resistive and secondary electron emissive (SEE) functions necessary for electron amplification are applied to the GCA microchannels by ALD, which – in contrast to conventional MCP manufacturing– enables independent tuning of both resistance and SEE to maximize and customize MCP performance.

Incom is currently developing MCPs that operate at cryogenic temperatures and across wide temperature ranges. All MCPs exhibit a negative TCR: when the MCP is cooled, the resistance increases, and when heated, the resistance drops. Consequently, the resistance of each MCP must be tailored for the intended operating temperature. This sensitivity to small temperature changes presents a challenge for many terrestrial and space based applications including for detectors capable of operation either at room temperature or at cryogenic temperatures. Our results demonstrate how the structural and compositional changes (dielectric-to-metal ratio and elemental composition) affect the resistivity and, specifically, the TCR of the nanocomposite. Developing structure-property relationships for the resistive material enables us to develop highly resistive materials with a) improved TCR characteristics, and b) fabricate MCPs optimized to operate at cryogenic temperatures.

11:45am **AA-TuM-16 Reactions on ALD $TiO_2$, ZnO, and $Al_2O_3$ Metal Oxides during Nucleation of UiO-66-$NH_2$ MOF Thin Films as Hydrolysis Catalysts for Chemical Warfare Agent Simulants.**, ***Dennis Lee***, *J Zhao*, *C Oldham*, North Carolina State University; *G Peterson*, Edgewood Chemical Biological Center; *G Parsons*, North Carolina State University

Highly toxic compounds such as chemical warfare agents (CWAs) (e.g., sarin (GB), soman (GD), VX), ammonia or chlorine gas, or $NO_x$-based pollutants can pose a severe chemical threat. Recently, highly crystalline, stable, and microporous metal-organic frameworks (MOFs), in particular UiO-66-$NH_2$ MOF, have become active materials to effectively degrade deleterious chemicals. These MOFs are readily formed as powders, but for effective application, new means are needed to create controllable and conformal MOF thin films, especially on high aspect ratio textiles and fibrous substrates. We recently reported that ALD metal oxides act as suitable nucleation agents for UiO-66-$NH_2$ thin films, but nucleation mechanisms and how they are driven by ALD oxide composition were not well understood.

Here, we describe surface reaction mechanisms on ALD $Al_2O_3$, $TiO_2$, and ZnO during nucleation of UiO-66-$NH_2$ MOF. The MOFs are excellent quality, with high crystallinity and net surface area exceeding 1000 $m^2/g_{MOF}$. We find that ALD $Al_2O_3$ and $TiO_2$ layers are fairly stable under solvothermal MOF growth condition. On the other hand, crystalline ALD ZnO surface partially dissolves in the synthetic environment. The chemical instability of ZnO promotes MOF nucleation in the liquid phase, likely via reaction on $Zn^{2+}$ ions, creating a significant amount of MOF crystals, up to 145 $m^2/g_{fiber+MOF}$, but limiting MOF thin film growth. The stability of ALD $Al_2O_3$ and $TiO_2$ enables good MOF coatings, but the density of nucleation sites is markedly larger on $TiO_2$ vs $Al_2O_3$, resulting in 65 $m^2/g_{fiber+MOF}$ on $TiO_2$ vs 34 $m^2/g_{fiber+MOF}$ on $Al_2O_3$. Accordingly, we find the MOF-fabric formed with $TiO_2$ performs better than those with $Al_2O_3$ for hydrolysis of dimethyl 4-nitrophenyl phosphate (DMNP), a chemical warfare agent simulant, allowing the half-life for degradation to be in the range of 10 minutes versus several days measured for control metal oxide samples without the conformal MOF thin film.

We will discuss how ALD surfaces with different composition can impact on the MOF mass loading, which correlates with DMNP destruction performance, and how functionalized textiles can be also utilized for removing hazardous gases, such as ammonia, chlorine, and hydrogen sulfide.

## ALD Applications
## Room Plaza ABC - Session AA1-TuA

### Batteries II (1:30-3:30 pm)/Emerging Apps III (4:00-5:00 pm)

**Moderators:** Ganesh Sundaram, Ultratech, Andy Sun, University of Western Ontario, Canada, Erik Østreng, Picosun Oy, Nicholas Strandwitz, Lehigh University

1:30pm **AA1-TuA-1 Highly Improved Performance of High Voltage ALD Coated Cathodes Showing Minimal Capacity/Voltage Fade at 4.8V**, ***Lamuel David****, D Mohanty,* Oak Ridge National Laboratory*; K Dahlberg,* Xalt Energy LLC*; D King,* Forge Nano (a PneumatiCoat Company)*; D Wood III,* Oak Ridge National Laboratory

Energy density of current lithium-ion batteries (LiBs) based on layered $LiMO_2$ cathodes (M=Ni, Mn, Co) needs to be improved significantly for widespread electric vehicle use in the automotive industry. In this work, we show that atomic layer deposition (ALD) of LiPON on Ni-rich NMC and Li-Mn-rich (LMR) NMC active particles substantially improves LIB performance even when cycled at increased upper cutoff voltage (UCV). Our results show that LiPON coatings prevented capacity degradation and decreased voltage fade when cycling at 1C-1C rate at UCV of 4.8 V. These samples also exhibited exceptional rate performance with 5x improvement (160 mAh/g) in capacity for NMC and 3x improvement (210 mAh/g) in capacity for LMR NMC when the particles were coated with LiPON. Electrochemical impedance spectroscopy (EIS) confirmed that LiPON-coated materials exhibited a significantly lower increase in the charge transfer component of impedance during cycling. The ability to mitigate surface related degradation mechanisms of these materials as demonstrated in this report provides insight into enhancing performance of high-voltage and high-energy LIBs.

1:45pm **AA1-TuA-2 Physical and Electrochemical Effects of Post-deposition Annealing on Atomic Layer Deposited $Al_2O_3$ Coatings on $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$**, ***David Jackson****, T Kuech,* University of Wisconsin-Madison

A systematic study investigating the effects of annealing on atomic layer deposited (ALD) $Al_2O_3$ coated Li-ion battery cathodes was performed. $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC) cathode powders were ALD coated at 100 °C, annealed from 300 to 700 °C, and then used to fabricate coin cells to investigate the electrochemical effects of the treatment. Analyses have shown that cell properties vary as a function of annealing temperature, and that the resulting electrochemical behavior and the cathodic solid-electrolyte interphase formed during cycling are significantly correlated.

Cells were characterized using charge-discharge cycling at 5C and C/5 rates, electrochemical impedance spectroscopy, charge endpoint slippage analysis, pre-assembly and postmortem X-ray photoelectron spectroscopy, and an elevated temperature storage test. It was observed that Al diffusion into the NMC bulk activates around 500 °C anneal temperature, where the Al atoms overcome a kinetic barrier allowing to them leave the surface $Al_2O_3$ layer. While efficiency of the cells during 5C rate cycling is higher in the unannealed samples, the starting capacity is also reduced, with Li likely being sequestered in the coating layer. At the highest temperature, 700 °C, the surface is similar to an Al “surface doped” NMC due to diffusion. This Al-doped surface leads to the highest self-discharge of all samples, though charge capacity retention in C/5 cycling is among the highest of all samples.

In samples annealed at 500 °C, an anomalous high charge slippage occurred between the first two cycles, indicating the presence of parasitic reactions. Postmortem XPS analysis of these samples show relatively high amounts of LiF formed in the SEI during cycling. Some connection between LiF formation and high charge slippage indicate the presence of uniquely active surface species formed during the initial stages of Al diffusion into the bulk.

These results demonstrate a new parameter that may be utilized to further control properties of ALD coated battery materials beyond that currently established with the well-studied $Al_2O_3$ coatings.

2:00pm **AA1-TuA-3 Novel Mechanism of Atomic Layer Deposition $Al_2O_3$ on $LiMn_2O_4$ for High Capacity Lithium-ion Batteries**, ***Lin Chen****,* Illinois Institute of Technology; Argonne National Laboratory*; R Warburton,* Purdue University*; K Chen,* Northwestern University*; J Libera,* Argonne National Laboratory*; M Hersam,* Northwestern University*; J Greeley,* Purdue University*; J Elam,* Argonne National Laboratory, USA

Previous studies demonstrated that $Al_2O_3$ coatings prepared by atomic layer deposition (ALD) improved the capacity of $LiMn_2O_4$ (LMO) cathodes for lithium ion batteries. This improvement was attributed to a reduction in surface area and diminished Mn dissolution. However, here we propose a different mechanism for ALD $Al_2O_3$ on LMO based on in-situ and ex-situ investigations coupled with density functional theory calculations. We discovered that $Al_2O_3$ not only coats the LMO, but also dopes the LMO surface with Al leading to changes in the Mn oxidation state as revealed by in-situ mass spectrometry and infrared spectroscopy as well as ex-situ X-ray photoelectron spectroscopy. Different thicknesses of $Al_2O_3$ were deposited on nonstoichiometric $LiMn_2O_4$ for electrochemical measurements. The LMO coated using one cycle of ALD $Al_2O_3$ (1 × $Al_2O_3$ LMO) yielded a high initial capacity, 16.4% larger than its uncoated LMO counterpart in full cells. The stability of 1 × $Al_2O_3$ LMO is also much better as a result of greatly stabilized structure with Al-doping. Furthermore, 4 × $Al_2O_3$ LMO demonstrates remarkable capacity retention, nearly reaching 100% at 0.5 C for 200 cycles while uncoated LMO only retains 78.2%. Stoichiometric $LiMn_2O_4$ was also evaluatedwith similar improved performance achieved. All superior results, accomplished by great stability and reduced Mn dissolution, is thanks to the synergetic effects of Al-doping and ALD $Al_2O_3$ coating. This new understanding offers a viable avenue to tune the performance of other Mn-containing, high capacity cathodes by employing $LiMn_2O_4$ as amodel system.

2:15pm **AA1-TuA-4 Atomic Layer Deposition of Superionic Solid-State Electrolytes for Lithium Batteries**, ***Xiangbo Meng****,* University of Arkansas*; J Connell, P Lopes, J Libera,* Argonne National Laboratory, USA*; K Zavadil,* Sandia National Laboratory*; J Zhang,* Pacific Northwestern National Laboratory*; J Elam,* Argonne National Laboratory, USA

Rechargeable lithium batteries are very promising energy storage devices for portable electronics, transportation, and smart grids. As an important component of lithium batteries, liquid electrolytes currently are widely utilized, serving as a lithium-ion conductor but an electrical insulator. The direct contact between the electrodes and the liquid electrolyte, however, causes undesirable electrochemical reactions the ubiquitous formation of solid electrolyte interphases (SEIs). SEIs differ in quality with the coupling selection of anodes, cathodes, and liquid electrolytes, but always adversely consume lithium and liquid electrolytes. On the other hand, the flammable nature of liquid electrolytes poses serious safety concerns in lithium batteries. Among various potential solutions, solid-state electrolytes are highly regarded.

Aimed at developing new superionic solid-state electrolytes, we recently explored two individual processes for binary Li-S and Al-S compounds, respectively, using atomic layer deposition (ALD). By combining the two ALD processes and tuning their cycle ratio, we then synthesized a series of ternary compounds of lithium aluminum sulfides, i.e., $Li_xAl_yS$. The subsequent impedance measurements verified that the resultants $Li_xAl_yS$ films are promising solid-state electrolytes with tunable ionic conductivities up to over $10^{-4}$ S/cm, 1000 times higher than the LiPON counterparts reported previously. We further characterized the growth and properties of the ALD $Li_xAl_yS$ films using *quartz crystal microbalance*, *inductively coupled plasmamass spectrometry*, and *X-ray photoelectron spectroscopy*. In addition, we also investigated the surface chemistry for the $Li_xAl_yS$ ALD using in-situ *Fourier transform infrared spectroscopy*. Very interestingly, the resultant $Li_xAl_yS$ films demonstrated an exceptional performance in inhibiting the growth of lithium dendrite structures in lithium batteries.

2:30pm **AA1-TuA-5 Cubic Garnet $Li_7La_3Zr_2O_{12}$ Solid Lithium Electrolyte by ALD**, ***Eric Kazyak****, K Wood, K Chen, A Bielinski, A Davis, T Thompson, J Sakamoto, N Dasgupta,* University of Michigan

Lithium-conducting solid-state electrolytes (SSEs) are a promising platform for achieving the high energy density, long-lasting, and safe rechargeable batteries needed for a wide range of applications. By eliminating the need for flammable and unstable liquid electrolytes, SSEs dramatically reduce the risk of fire while enabling high voltage and energy density chemistries including Li metal. In particular, the ceramic oxide material cubic garnet $Li_7La_3Zr_2O_{12}$ (LLZO) is a promising option due to its stability and high ionic conductivity. Two major challenges to commercialization are manufacturing of thin layers and creating stable, low-impedance, interfaces with both anode and cathode materials. Atomic Layer Deposition (ALD) has recently been demonstrated as a powerful method for depositing both solid electrolytes and interfacial layers to improve stability and performance at electrode-electrolyte interfaces in battery systems. The self-limiting reactions afford the ability to conformally coat arbitrary geometries for 3D batteries, powders, and porous cathodes, an important advantage over the current state-of-the-art LiPON solid electrolyte and previous approaches for thin-film LLZO.

In this study, we present the first reported ALD of the pentenary oxide Al-doped LLZO. Constituent binary processes are successfully combined in a thermal ALD process at 225°C to deposit high purity, dense amorphous LLZO films. The cycle-by-cycle growth of the multi-component film is quantified by in situ quartz crystal microbalance (QCM) measurements. We demonstrate the ability to tune composition within the amorphous as-deposited film, anneal to achieve the desired cubic garnet phase, and characterize the annealed films via *in situ* synchrotron XRD during annealing. The ability to conformally coat high aspect ratio structures of arbitrary composition with ultrathin layers of dense, amorphous LLZO is shown, demonstrating the potential for integration into 3D battery architectures, including porous electrode structures. Approaches to overcome Li loss and phase segregation during annealing are demonstrated and discussed.

The film exhibits preferential orientation when annealed on single crystal substrates, and the cubic-tetragonal phase transition was observed at ~500°C, significantly lower temperature than reported for bulk synthesis methods. By tuning the composition and annealing conditions, the resulting film can be tuned from pure-phase $La_2Zr_2O_7$ pyrochlore, a high temperature thermal barrier material with several commercial applications, to high purity tetragonal LLZO or high phase-purity cubic LLZO, the superionic solid electrolyte material.

2:45pm **AA1-TuA-6 Improving Interfacial Stability of Sulfide-Based Lithium-Ion-Conducting Solid Electrolytes with ALD***, **Jasmine Wallas**, A Heist, S Lee, S George,* University of Colorado - Boulder

Rechargeable solid state Li-ion batteries may revolutionize energy storage. Solid state Li-ion batteries also have the potential for better safety, cycling performance, SEI stability and energy density than liquid electrolyte Li-ion batteries. However, solid electrolytes generally suffer from low ionic conductivity and/or poor interfacial stability. In this work, we demonstrate that the interfacial stability of solid electrolytes can be improved with ALD coatings.

$Li_{10}GeP_2S_{12}$ is a sulfur-based ceramic electrolyte with extremely high ionic conductivity of ~$10^{-2}$ S cm$^{-1}$. This ionic conductivity is comparable with liquid electrolytes at room temperature. However, $Li_{10}GeP_2S_{12}$ solid electrolyte suffers from interfacial instability with Li metal. Contact with Li metal leads to substantial electrolyte decomposition and the formation of a resistive interphase. However, $Al_2O_3$ ALD coatings can greatly increase the interfacial electrochemical stability.

In this work cells were composed of symmetric Li electrodes with $Li_{10}GeP_2S_{12}$ solid electrolyte (see supplemental Figure 1). The $Li_{10}GeP_2S_{12}$ solid electrolytes were coated with various numbers of $Al_2O_3$ ALD cycles. The Li metal was then pressed into the $Li_{10}GeP_2S_{12}$ solid electrolyte. The thickness of the $Al_2O_3$ ALD coating was varied to optimize interfacial stability. Internal cell resistance measurements were used to monitor the formation of the resistive interphase. The experiments were conducted at 60°C.

The uncoated $Li_{10}GeP_2S_{12}$ solid electrolyte developed extremely high internal resistance and reached the defined failure point (>1000 Ω) within the first 40 hours of the test (see supplemental Figure 2). The $Al_2O_3$ ALD coatings substantially increased interfacial stability and maintained lower internal resistance. The $Li_{10}GeP_2S_{12}$ solid electrolyte coated with 25 $Al_2O_3$ ALD cycles increased the chemical stability and extended the time to the failure point to 400 hours (see supplemental Figure 2). The lifetime of the $Al_2O_3$ ALD-coated $Li_{10}GeP_2S_{12}$ solid electrolyte is more than a factor of 10 longer than the uncoated $Li_{10}GeP_2S_{12}$ solid electrolyte.

3:00pm **AA1-TuA-7 Atomic Layer Deposition of Solid-State Electrolytes for All-Solid-State Lithium Ion Batteries***, **Biqiong Wang**, J Liu, Y Zhao, A Lushington, R Li, T Sham, X Sun,* University of Western Ontario, Canada

The development of batteries with higher energy density, longer cycle lives, and assured safety levels have been the pressing need to satisfy the stringent demands of portable electronic devices, electric vehicles and grid-energy storage systems. [1] Replacement of the conventional liquid electrolytes with solid-state electrolytes (SSEs) will not only eliminate the inherent safety issues but also provide more flexibility in battery design and management. [2] Atomic layer deposition (ALD) offers exclusive advantages of highly controllable thin film depositions especially on high-aspect ratio three-dimensional substrates. [3, 4] In our group, various SSEs have been developed by ALD including $Li_3PO_4$, lithium silicate, lithium silicophosphate, $LiTaO_3$, and $LiNbO_3$. [5-7] All of the as-deposited thin films presented acceptable ionic conductivity, among which $Li_3PO_4$ exhibited the best value of 3.3x $10^{-8}$ S/cm at room temperature (Figure S1). Nevertheless, the electrochemical properties of materials by ALD have shown deviations from those obtained by other methods. Synchrotron-based spectroscopy, including X-ray Photoemission Spectroscopy (XPS) and X-ray Absorption Spectroscopy (XAS), were performed to study their detailed electronic structures. Insightful information on both local chemical environment and structures can be extracted. Further analysis of the spectra can give semi-quantitative information. In Figure S2, Nb L-edge X-ray absorption near edge spectra (XANES) show that Nb in the $Li_xNb_yO$ systems by ALD exists as Nb5+ in an octahedron structure with oxygen. While introducing more Li content by controlling the ALD subcycle number of Li, the higher degree of the splitting of the double feature due to the crystal field splitting indicates a probable more distorted local structure in the thin films. To summarize, developing SSE by ALD is indispensable to building reliable high-energy-density batteries. Fundamental studies of the ALD materials are crucial to revealing the growth mechanisms and the correlations between electronic structures and electrochemical properties, shedding lights on future designs of SSEs by ALD.

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3:15pm **AA1-TuA-8 Highly Stable $WS_2$ Thin Film Anode Grown by Plasma-enhanced Atomic Layer Deposition (PEA LD ) for Na-ion Battery***, **Dip Nandi**,* Yeungnam University, Republic of Korea*; S Yeo,* Yonsei University, Republic of Korea*; M Ansari,* Yeungnam University, Republic of Korea*; H Kim,* Yonsei University, Republic of Korea*; T Song, S Kim,* Yeungnam University, Republic of Korea

Plasma-enhanced atomic layer deposited (PEALD) tungsten sulfide ($WS_2$) thin film was used as an anode in sodium-ion battery (NIB) without any carbon and binder. Thin films of $WS_2$ were directly grown using an alternate exposure of $W(CO)_6$ and $H_2S$ plasma at a relatively low temperature of 350 °C using shower-head type ALD reactor without any post sulfurization process. The stoichiometric presence of W and S in the as-deposited films was observed from Rutherford backscattering spectroscopy (RBS) analysis. The films were crystalline in nature with (002) orientation as revealed by the transmission electron microscopy (TEM) analysis. For NIB application, the $WS_2$thinfilms were directly grown on stainless steel (SS) current collector and used as an electrode without any further modification. Coin cells were then fabricated and tested in a half-cell configuration against Na. The electrochemical reactions during cathodic as well as anodic sweep were studied using cyclic voltammetry (CV) measurements. Reversible conversion and intercalation reactions were evident from the CV which was repeatable in nature after 1st cycle. Improved electrochemical reactivity of the ALD grown thin film against $Na^+$ ion could be observed from this CV measurement. Films with five different thickness using different ALD cycles were used for charge-discharge cyclic measurements. Cells with ALD-$WS_2$ as an anode showed high electrochemical stability up to 200 charge-discharge cycles with more than 95% Coulombic efficiency. Different current rates were also used for cyclic measurements to show the suitability of these ALD grown thin film anodes for a wide range of portable electronic appliances.

4:00pm **AA1-TuA-11 ALD-Tin Oxide as Impermeable Electron Extraction Layers for Temperature Stable Roll-to-Roll-Compatible Perovskite Solar Cells***, **Lukas Hoffmann**,* University of Wuppertal, Germany*; K Brinkmann,* University of Wuppertal*; J Zhao, T Hu,* Nanchang University, China*; D Schlamm, J Malerczyk, T Becker, D Theirich,* University of Wuppertal*; S Olthof, K Meerholz,* University of Cologne*; H Gargouri,* Sentech Instruments, Germany*; B Cheng, Y Chen,* Nanchang University, China*; T Riedl,* University of Wuppertal

Organo-lead halide perovskite-based solar cells (PSCs) reached power conversion efficiencies (PCE) beyond 20% within the past years [1]. Nevertheless, the decomposition of the active material in the presence of water or elevated temperatures and follow-up corrosion of e.g. metal electrodes are showing to be one of the big issues to overcome before commercialization [2].

Here we demonstrate the use of tin oxide ($SnO_x$) grown by ALD, which is electrically conductivity and shows outstanding permeation barrier properties [3], as electron extraction layer (EEL) and concomitant permeation barrier against moisture and decomposition products of methylammonium lead iodide perovskites, perovskite solar cells with outstanding long-term stability can be achieved [4]. Specifically, the tin oxide layers in this study were fabricated by Tetrakis(dimethylamino)tin and different oxidants (water, ozone, O-plasma) at low temperatures (80°-100°C) in low and atmospheric pressure ALD. Strikingly, the solar cells based on SnO$_x$ remain stable over 4500 hours at elevated temperatures as well as in ambient air, whereas devices based on other EELs, without sealing properties, degrade to roughly 50% of their initial efficiency within 100 h. Moreover, SnO$_x$ enables the design of ITO-free semitransparent electrodes based on ultra-thin metal layers (e.g. SnO$_x$/Ag/SnO$_x$)[5]. Based thereon, semi-transparent perovskite solar cells with about 70% average transmittance in the near-infrared region (λ > 800 nm) and an average transmittance of 17% in the visible region (λ = 500-750 nm) have been realized [5]. For SnO$_x$ as EEL, we unravel the critical importance of the of the oxidant used in the growth of the SnO$_x$, e.g. the use of ozone is essential for optimizing the fill factor of the solar cells by minimizing the potential barrier in the SnO$_x$-perovskite boundary layer. These results provide a general avenue to design PSCs incorporating indium-free transparent top- and bottom electrodes based on corrosion sensitive metals [6]. Finally, tin oxide growth by spatial ALD at atmospheric pressure is presented and its compatibility to replace its low-pressure analogs is shown. With this findings, an all-step roll-to-roll fabrication of highly stable, indium-free PSCs could be realized.

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4:15pm **AA1-TuA-12 Nano-Structured Ceramic ALD Coatings to Stabilize SiC Against Reaction in High Temperature Steam***, **Amanda Hoskins**, A Coffey, C Musgrave, A Weimer,* University of Colorado - Boulder

Silicon Carbide (SiC) is an ideal material for many high-temperature applications due to its resistance to thermal shock and high thermal conductivity. However, SiC degrades in water-rich environments limiting its applications in extreme oxidative environments such as combustion engines, heat exchangers, and high temperature reactor materials. Current deposition methods for environmental barrier coating (EBCs) such as plasma spraying and aerosol spraying generate micron-scale films with inherent grain boundaries and cracks. Atomic layer deposition (ALD) generates nano-scale films that are dense, crack-free, and chemically bonded to the surface without the use of excess precursor. We have found that the application of mullite nanostructured films grown with ALD significantly improves the oxidation resistance of SiC in extreme environments with a film much thinner than standard applications. In addition to mullite, we have targeted a variety of high temperature coating materials chosen based on thermal properties, structural characteristics, and stability in oxidative environments. We have grown ALD layers of our desired materials on high surface area SiC particles using a fluidized bed particle ALD reactor. Using thermogravimetric analysis, it has been shown that these coatings improve the oxidation resistance of SiC by up to 64% at 1000°C. We have applied density functional theory (DFT) to model the performance of these mullite coatings in an oxidative environment. Computational modeling of oxygen diffusion through mullite and other candidate materials allows identification of promising coatings to further extend the lifetime of SiC. We expect to use this understanding to develop more advanced stabilizing coatings for SiC and the myriad of other applications that require high-temperature oxidation resistant materials.

4:30pm **AA1-TuA-13 Mechanical, Physical, and Electrical Properties of Plasma-Enhanced Atomic Layer Deposition of TiVN***, **Mark Sowa**,* Ultratech*; N Strandwitz, L Ju,* Lehigh University*; A Kozen,* U.S. Naval Research Laboratory*; B Krick,* Lehigh University

Specific ternary transition metal nitrides are known for their excellent mechanical, electrical, and chemical properties. TiVN thin films for hard, wear-resistant coating applications have been deposited by sputtering[1,2] and arc ion plating[3]. Compared to pure TiN and VN, TiVN films of intermediate stoichiometry are reported to be harder (H = 32.1GPa for Ti$_{0.77}$V$_{0.23}$N vs H = 20.2GPa for TiN and H = 5.6GPa for VN) and stiffer (E = 410GPa for Ti$_{0.87}$V$_{0.13}$N vs E = 395GPa for TiN and 307GPa for VN).[4] Plasma-enhanced atomic layer deposition (PEALD) of TiN has been extensively studied[5,6,7] and PEALD VN has also been reported[8]. We will report on PEALD Ti$_x$V$_{1-x}$N$_y$ (x = 0 to 1) films deposited using tetrakis(dimethylamido)titanium and tetrakis(ethylmethylamido)vanadium with N$_2$ plasma. Stoichiometry has been varied through control of the TiN:VN deposition cycle ratio. Analyses include spectroscopic ellipsometry(thickness and optical properties), four point probe(resistivity), XPS(stoichiometry and impurities), XRD(crystallinity), XRR(density and thickness), and sliding wear testing(tribological properties).

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## ALD Applications
## Room Plaza E - Session AA2-TuA

### ULSI, High-k and III-V I (1:30-3:30 pm)/ULSI, High-k and III-V II (4:00-5:00 pm)

**Moderators:** Scott Clendenning, Intel Corporation, Elton Graungard, Boise State University, Sven Van Elshocht, IMEC

1:30pm **AA2-TuA-1 ALD as an Enabler of Self-aligned Multiple Patterning Schemes***, **Sven Van Elshocht**, Z Tao, J Everaert, S Demuynck, E Altamirano-Sanchez,* IMEC, Belgium **INVITED**

Dimensional scaling is since many decades one of the main drivers of technological advancement. It is captured in what is often referred to as Moore's law: a doubling of the number of transistors every ~2 years for the same cost. The last couple of years this trend has been slowing down, but is still very much alive.

One of the main issues is the difficulty to keep printing ever smaller features in a well-controlled and reliable matter. While smaller wavelength lithography tools are not yet into mass production, alternative techniques are being used to extend the current 193nm litho capability.

As an alternative to single exposure, multipatterning techniques are employed. One approach is multiple litho-etch (LE), where the litho print is divided into multiple partial prints that together form the targeted image. The pattern can as such be split in for example 2 or 3 prints, i.e. LELE or LELELE. The biggest concern with this method is overlay or the alignment of the different partial prints to each other.

To circumvent the problem of overlay, one has implemented self-aligned multiple patterning (SAMP). The first print forms a pattern on which a conformal spacer is deposited. After removal of the first material, referred to as the core or mandrel, one obtains a pattern with twice the density and where the width of the features is determined by the deposited spacer thickness. This procedure can be multiple times and result in double or quadruple patterning schemes.

In this presentation, we will demonstrate that Atomic Layer Deposition (ALD) is highly suited to fulfill the requirements as spacer deposition technique for SAMP. In addition, we will discuss the requirements of patterning materials in general toward. As a concrete example we will discuss fin patterning for a 7-nm logic technology node using Self Aligned Quadruple Patterning (SAQP).

2:00pm **AA2-TuA-3 Thin Film Dopant Sources Grown by PALD for Shallow Semiconductor Doping***, **Bodo Kalkofen**, M Silinskas,* Otto von Guericke University, Germany*; M Lisker,* IHP GmbH, Leibniz-Institut für Innovative Mikroelektronik*; Y Kim,* Lam Research Corporation

Plasma-assisted atomic layer deposition (PALD) was carried out for growing thin oxide films containing dopants for silicon, germanium, and SiGe. The applicability of these films as dopant sources for shallow doping of those semiconductor materials using various rapid thermal annealing methods, such as RTP, flash lamp and laser annealing, was investigated. Remote conductively coupled plasma and inductively coupled plasma sources were applied for generating oxygen radicals in the PALD processes. Tris(dimethylamido)borane was used as boron containing precursor for p type doping, source layers for n type doping were grown using triethylphosphite and triethylantimony for phosphorus and antimony containing oxides, respectively.

The as-deposited films of boron oxide were highly unstable in ambient air and could be protected by capping with in-situ PALD grown antimony oxide films. Phosphorus containing films were stabilized by incorporating them into a silicon dioxide matrix by carrying out ALD processes with supercycles of phosphorus and silicon precursor reactions with oxygen radicals. Also capping of the phosphorus containing films was applied. Antimony oxide films were stable at ambient air conditions.

Boron and phosphorus doping of Si could be obtained using the respective oxide films as dopant sources. This was confirmed by SIMS and sheet resistance measurements. A phosphorus dopant level >1E20 cm$^{-3}$ in silicon could be formed with ALD doping and short time annealing by laser or flash, while a level of >1E19 cm$^{-3}$ was obtained with RTP (950 °C) annealing. Diffusion of antimony into SiGe and Ge from antimony oxide could be shown. The influence of source layer thickness and different annealing conditions during rapid thermal annealing processes on the doping results was investigated.

2:15pm **AA2-TuA-4 Effective Work-Function of PEALD Metal Nitrides and its Tuning by Co-deposition***, **Ekaterina Zoubenko**, I Krylov, B Pokroy, M Eizenberg,* Technion - Israel Institute of Technology, Israel

The implementation of nitride based metallic compounds (e.g. TiN, WN) as metal gate materials is attractive for complimentary metal-oxide-semiconductor (CMOS) applications. Tuning the effective work-function (EWF) is challenging. The effective work-function of metal nitride has a wide range of values and depends on the dielectric material, the metal microstructure and its chemical composition. Recently, plasma enhanced atomic layer deposition (PEALD) at high vacuum (10$^{-6}$torr) using amid-based metalorganic precursors has enabled the deposition of low resistivity metal nitrides. The ALD technique, which is based on self-limiting surface reactions, enables the co-deposition of various metals and provides an additional degree of freedom to EWF engineering. However this issue was not investigated systematically in literature.

In the current work, EWF on $SiO_2$ of pure metal nitrides (TiN, WN, TaN and MoN) is presented. In addition, EWF tuning by metal nitride alloying at various compositions (e.g. TiN+WN) and its evolution with thermal annealing temperature will be discussed. The thickness, microstructure, chemical composition and electrical resistivity of the films were determined by X-ray reflectivity (XRR), X-ray diffraction (XRD) and transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and four-point probe (4PP), respectively. The EWF of metal nitrides on $SiO_2$, using MOS structure, was studied using capacitance-voltage (CV) measurements and plotting the flat-band voltage ($V_{FB}$) versus the effective oxide thickness (EOT).

As an example, as deposited TiN films of 30[nm] have poly-crystalline FCC structure, as determined by XRD and TEM. XPS depth profiling indicated carbon and oxygen concentrations of 3at%, which leads to a low value of resistivity of 110 [μΩ·cm]. The EWF of TiN on $SiO_2$ was determined to be 4.6±0.1 [eV], namely that the position of Fermi level is close to Si midgap. This combined with the low resistivity make TiN a good candidate for CMOS applications. Similar systematic study will be presented for other metal nitrides and their alloys.

2:30pm **AA2-TuA-5 Surface Morphology, Crystallinity and Electrical Properties of Some Rare-earth Oxide ALD Films***, **Satu Ek**, R Ritasalo,* Picosun Oy, Finland*; T Sarnet,* Picosun Oy*; J Kalliomaki,* Picosun Oy, Finland*; E Østreng,* Picosun Oy*; S Vangelista, A Lamperti, S Spiga,* CNR-IMM - MDM Laboratory*; R Piagge, G Ghidini,* STMicroelectronics

Rare-earth oxides (REOs) have interesting optical and electrical properties that make them useful for several applications. Many REOs have high dielectric constant (k), which can easily reach values k > 20. Therefore, they are relevant for the microelectronics industry. At present, there is a growing need for thinner gate dielectrics of current materials, such as $SiO_2$, which might lead high leakage currents, subsequently leading to increased power dissipation, reliability problems and unaccepted electrical breakdown [1,2]. The implementation of high-k gate dielectrics is one of several strategies developed to allow further miniaturization of microelectronic components. A possible gate dielectric material needs to fulfill certain requirements [1]: (i) k-value high enough to fulfill the roadmap of components scaling, (ii) thermodynamically stable with Si, (iii) kinetically stable, and compatible with processing to 1000°C for few seconds, (iv) act as an insulator, by having band offsets with Si of over 1eV to minimize carrier injection into its bands, (v) form a good electrical interface with Si, and (vi) have few bulk electrically active defects.

In this work, we have succeeded in the deposition of various REOs, such as $CeO_2$, $La_2O_3$,$Y_2O_3$, and $Y_2O_3$-doped $Al_2O_3$ ($Y:Al_2O_3$), in a uniform manner on 200mm Si wafers using a Picosun R-200 Advanced atomic layer deposition (ALD) reactor. REO films were deposited using $Ce(thd)_4$, $La(thd)_3$ and $Y(thd)_3$ as metal-containing precursors, and ozone as oxidizer.

The surface morphology, crystallinity and grain size of the deposited layers were studied. Conformality maps, AFM surface morphology and XRD analysis of $Y_2O_3$ and $Y:Al_2O_3$ films are presented in Fig. 1 as an example. The results show that uniform ALD layers were deposited, i.e. 1.4-2.5% (1σ non-uniformity), with a very smooth surface, with 0.5 nm roughness. Additionally, electrical measurements of the REO films were studied. Fig. 2 shows an example of the effect of $Y_2O_3$ content in $Al_2O_3$ on the breakdown field and leakage current. The $Y_2O_3$ films exhibit a high dielectric breakdown field (>6 MV/cm), a relatively high k value (~11), and a low-leakage current density (<10$^{-8}$ A/cm$^2$at 3 MV/cm) with 100nm layer deposited at 300 °C, well-comparable to the values obtained by de Rouffignac et al. [2]. By adjusting the amount of $Y_2O_3$ in $Al_2O_3$ a good compromise can be reached with relatively high growth rate, low leakage and high breakdown together with relatively high k-value.

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[2] de Rouffignac et al., Chem. Mater., 17 (19) (2005) 4808-4814.

Acknowledgements: This work received funding from TEKES and ECSEL-JU R2POWER300.

2:45pm **AA2-TuA-6 Atomic Layer Deposition of High-k Oxide Films from La($NO_{33}$·6$H_2O$ Solution Oxidant***, **In-Sung Park**, S Kim, T Lee, S Seong, Y Jung, J Ahn,* Hanyang University, Republic of Korea*; J An, J Yun,* Korea Research Institute of Standard and Science (KRISS), Korea

High-k films have been widely applied on the gate dielectric, capacitor dielectric, insulator in resistive memory, and even optical layer. ALD is a leading method in the formation of ultrathin layer of nm scale and the uniform/conformal coating on the complex substrate structure. In the fabrication of binary metal oxide films, the complete cycle of ALD typically consists of four steps: (1) pulsing with metal precursor; (2) purging with inert gas; (3) pulsing with oxidant; and (4) purging with inert gas.

In the ALD of metal oxide, the choice of both metal precursor and oxidant is very important for a successful ALD process. Various oxidants have been reported such as $H_2O$, $O_3$, and plasma-$O_2$ for the fabrication of metal oxide films. The oxidant can change the characteristics of the deposited oxide films such as crystalline structure, growth rate, and electrical properties. In this work, the high-k metal oxide films of $ZrO_2$ and $HfO_2$ were synthesized by using atomic layer deposition method with $La(NO_3)_3{\cdot}6H_2O$ solution as oxygen source. The high-k oxide films formed with $La(NO_3)_3{\cdot}6H_2O$ have been investigated by comparing the films formed with $H_2O$ oxidant on the material and electrical properties.

Several findings are highlighted by the alternative introduction of $La(NO_3)_3{\cdot}6H_2O$ solution to $H_2O$.

La elements in the deposited high-k films are not detected using the X-ray photoelectron spectroscopy, meaning La plays like a catalyst during ALD process.

The introduction of $La(NO_3)_3{\cdot}6H_2O$ solution effectively altered the crystalline structure, grain size, and surface roughness of the grown high-k films. For example [1], the crystalline structure of the $ZrO_2$ film changed from a mixture of tetragonal and monoclinic phases to monoclinic phase. The average grain size is doubled from 140 nm to 200-280 nm by using $La(NO_3)_3{\cdot}6H_2O$ solution, and the resulting film surface became rougher.

However, the concentration of $La(NO_3)_3{\cdot}6H_2O$ solution had little influence on the above crystalline properties.. The average grain sizes of the $ZrO_2$ films prepared from $La(NO_3)_3{\cdot}6H_2O$ solution at concentrations of 10, 20, 30, and 40% were 280, 256, 208, and 200 nm, respectively.

Considering the relation between optical bandgap energy and crystalline properties of high-k films, the controlled properties of crystalline films using $La(NO_3)_3{\cdot}6H_2O$ solution contribute to the optical and electrical devices.

[1] N. K. Oh et al., Applied Surface Science 394, 231 (2017).

3:00pm **AA2-TuA-7 Great Enhancement of Dielectric Constant via High Temperature Annealing ALD Bi-layered Oxides*, Keng-Yung Lin*,** *L Young, C Cheng, Y Lin, H Wan,* National Taiwan University, Republic of China*; R Cai, S Lo,* Industrial Technology Research Institute, Republic of China*; M Hong,* National Taiwan University, Republic of China*; J Kwo,* National Tsing Hua University, Republic of China

To push the high-speed, low-power device performances beyond Si-based MOSFETs, incorporating high-mobility GaAs as the channel material onto Si wafers is a promising way. Moreover, by utilizing high dielectric constant (k) oxides as the gate stacks, enhanced drain current is expected by capacitance effective thickness (CET) scaling, without the severe gate leakage caused by tunneling. Thus, enhancement of the dielectric constant in the high-k/GaAs system is vitally important. In this work, we have *in-situ* deposited atomic-layer-deposited (ALD) $Y_2O_3$(2.3nm)/$Al_2O_3$(5.0nm) and $HfO_2$(1nm)/HfAlO(9nm) bilayers respectively on freshly grown molecular beam epitaxy GaAs(001), followed by *ex-situ* post-deposition rapid thermal annealing and top/back gate electrodes formation. The dielectric constants of the gate stacks and the high-k/GaAs interfaces are characterized by conventional frequency-dependent capacitance-voltage (C-V) measurements. The k value of the $Y_2O_3/Al_2O_3$ bilayer increased from 11.1 to 15.6, a 40% enhancement, for the 900$^o$C-annealed sample, compared to that of the as-deposited one. Note that the thicknesses of the oxide films have been verified by scanning transmission electron microscopy (STEM). The interfacial electrical characteristics between $Y_2O_3/Al_2O_3$ and GaAs also significantly improved by having smaller frequency dispersion in accumulation/depletion region as shown in Fig.1. We have also discovered a dielectric constant enhancement for $HfO_2$/HfAlO on GaAs. We have used an initial $HfO_2$ layer to prevent direct inter-mixing between $Al_2O_3$ and GaAs, which was known to degrade the CV characteristics during high temperature annealing. After annealing over 850$^o$C in helium ambience, the dielectric constant increased from 17.6 to 22, a 25% enhancement, as shown in Fig.2. In addition, the frequency dispersion at accumulation region was reduced from 18.3% to 10.7%, indicating a lower interfacial trap densities ($D_{it}$) and high thermal stability at the $HfO_2$/GaAs(001) interface. In summary, we have greatly increased dielectric constant of ALD oxides in $Y_2O_3/Al_2O_3$ and $HfO_2$/HfAlO bilayers by mixing them via a thermal approach. Note that no new phases formed, as were studied using high-resolution synchrotron radiation X-ray diffraction and STEM (Fig.3). The high temperature annealed high-k/GaAs(001) interfaces are significantly improved, showing excellent thermal stability. The method for the formation of high quality mixed high-k materials could be generic for other ALD bi-layered oxides for future applications.

$^†$K. Y. Lin and L. B. Young have made equal contributions to this work.

* M. Hong and J. Kwo are the corresponding authors.

3:15pm **AA2-TuA-8 Atomic Layer Deposition of Novel Interface Layers on III-V Channel Devices***, F Tang,* ***Xiaoqiang Jiang****,* ASM*; Q Xie,* ASM, Belgium*; M Givens,* ASM*; J Maes,* ASM, Belgium*; S Sioncke, I Tsvetan, L Nyns, D Lin, N Collaert,* IMEC, Belgium

III-V compound semiconductors are considered promising transistor channel materials to enable further scaling beyond Si technology due to their high bulk electron mobility values. However, unlike Si, III-V materials have poor quality oxides, and high-k dielectric deposited directly on the III-V surface is problematic due to high density of interface states ($D_{it}$) and oxide traps. A surface treatment is typically required to passivate the semiconductor surface to minimize the interface states. In addition, a deposited interface layer (IL) is required for the integration with high-k dielectrics to reduce the impact of oxide traps while maintaining a low $D_{it}$. Although extensive study has been done on searching appropriate IL, commonly investigated high-k metal oxides appear limited in ability to meet the performance requirements for a robust III-V channel transistor.

In this work, a thermal ALD process of a novel material is demonstrated for application as IL in III-V channel devices. The IL material is deposited using a commercially available, hot walled cross flow reactor (ASM Pulsar 3000®). Saturated thickness is demonstrated over a wide range of pulse times in Fig. 1(a) and (b), indicative of operation in the ALD regime. The growth per cycle of is 0.23Å shown in Fig. 1(c). The $In_{0.53}Ga_{0.47}As$ MOSCAPs demonstrate superior $D_{it}$ values <1x10$^{12}$ cm$^{-2}$eV$^{-1}$, low accumulation dispersion (<1%), and hysteresis (<30 mV) values, extracted from CV characteristic as shown in Fig 1(d). The device performance matches previously published benchmark device metrics for InGaAs channel devices [1]. By employing this novel IL, high performance InGaAs nanowire MOSFETs built on 300 mm silicon wafers is also demonstrated with transconductance reaching 2200 [2].

To further improve the hysteresis or reliability of device, a secondary lanthanum silicate ($La_xSi_{1-x}O$) IL is introduced prior to the deposition of $HfO_2$ high-k. This lanthanum silicate is deposited by a $H_2O$-based ALD processes. An ALD master cycle includes a lanthanum oxide sub cycle and silicon oxide sub cycle, shown in Fig. 2(a). Fig. 2(b) shows the growth per master cycle and [Si] content extracted from RI values of bulk films. By using novel IL/lanthanum silicate IL/$HfO_2$ gate stack, the InGaAs MOSFET demonstrates an excellent electron mobility with a reduced oxide traps meeting the reliability target for 10 years operation [3].

In a summary, we developed novel ALD films for IL application, yielding excellent electrical properties on III-V devices.

[1] M. Radosavljevic et al., IEDM Tech. Dig., 765 (2011)

[2] N. Waldron et al. IEDM Tech. Dig., pp 31.1 (2015)

[3] S. Sioncke et al. submitted to VLSI (2017)

4:00pm **AA2-TuA-11 $ZrO_2$ as a High-k Gate Dielectric for Enhancement-mode AlGaN/GaN MOS HEMTs*, Charles R. Eddy, Jr.*,** *V Wheeler,* U.S. Naval Research Laboratory*; D Shahin,* University of Maryland*; T Anderson, M Tadjer, A Koehler, K Hobart,* U.S. Naval Research Laboratory*; A Christou,* University of Maryland*; F Kub,* U.S. Naval Research Laboratory

Advanced applications of AlGaN/GaN high-electron-mobility transistors (HEMTs) in high-power RF and power switching are driving the need for an insulated gate technology. We present here basic and early applied studies of the use of zirconium oxide ($ZrO_2$) as a high-k, high breakdown gate dielectric for reduced gate leakage and a fully-recessed barrier structure for enhancement-mode operation of AlGaN/GaN HEMTs. We include the study of GaN surface preparations for dielectric deposition, surface/interface characterization and device operation wherein a world record threshold voltage of +3.99V is achieved.

An optimum GaN surface preparation involving a piranha etch followed by a thermal oxidation of the surface has previously been shown [1] to result in smooth, clean GaN surfaces that exhibit the best electrical performance when ALD high-k dielectrics are deposited thereon. This same preparation is applied to ALD $ZrO_2$ dielectrics. $ZrO_2$ films were deposited by atomic layer deposition (ALD) using two different metal precursors [zirconium (IV) tert-butoxide (ZTB) and tetrakis(dimethylamido)zirconium(IV) (TDMAZ)] and water. For the former we also assessed both water and ozone as the oxygen precursor. $ZrO_2$ films grown by ALD with ZTB were found to be slightly oxygen rich whether ozone or water were used as the oxygen source. However, films grown with ZTB and ozone did have carbon contamination. Films grown with TDMAZ and water were found to be stoichiometric and free of carbon.

Films grown with ZTB and water on optimally prepared surfaces again shown the best electrical performance for the dielectric-semiconductor interface in terms of smoothness, low leakage in forward and reverse bias (< 10$^{-5}$ A cm$^{-2}$) and low hysteresis. Unlike in previous studies with ALD deposited $Al_2O_3$ and $HfO_2$, where total trapped charge was in the mid-10$^{11}$ to low 10$^{12}$ cm$^{-2}$ range, $ZrO_2$ films show considerably higher trapped charge densities in the high 10$^{12}$ to mid-10$^{13}$ cm$^{-2}$ range. The nature of this charge is uncertain at this time but believed to be due to excess oxygen in ZTB deposited films and is directly responsible for a 1.5 – 2 V positive shift in threshold voltage.

[1] C.R. English, et al., J. Vac. Sci. & Technol. B 32,03D106 (1-17) (2014).

4:15pm **AA2-TuA-12 Investigation of High-quality Silicon Nitride ($SiN_x$) Thin Film Grown by Low-temperature Hollow Cathode Plasma-Enhanced ALD as a Gate Dielectric for AlGaN/GaN MIS-HEMTs*, Xin Meng*,** *Y Byun, J Lee, H Kim, J Lee, A Lucero, L Cheng, J Kim,* University of Texas at Dallas

AlGaN/GaN metal-insulator-semiconductor high electron mobility transistors (AlGaN/GaN MIS-HEMTs) have been studied for power device applications. To mitigate current collapse and address the instability in threshold voltage ($V_{th}$), silicon nitride ($SiN_x$) has been widely investigated as a gate dielectric and passivation layer. This attributes to the low density of $SiN_x$/III-N interface states, achieved by passivating the defects related with nitrogen-vacancy and suppressing the formation of interface traps related with the Ga-O bonds. Recently, AlGaN/GaN MIS-HEMTs using a PEALD $SiN_x$ gate dielectric have shown improved device performance [1]. Nevertheless, the film properties of the low-temperature $SiN_x$ employed in these studies ($SiH_4/N_2$ plasma: low refractive index 1.7-1.85 and low density ~2.5 g/cm$^3$) cannot compete with those of the high-quality films grown by a high-temperature CVD process (e.g. MOCVD or LPCVD).

In this work, we report AlGaN/GaN MIS-HEMTs using high-quality PEALD $SiN_x$ as the gate dielectric. $SiN_x$ was deposited at a calibrated wafer temperature of 310 °C (16 nm,1500 cycles, set temp. 400 °C) in a home-made ALD system equipped with a Meaglow™ hollow cathode plasma source (Figure 1). Tris(dimethylamino)silane (TDMAS or 3DMAS) and $N_2$ plasma were used. High-quality $SiN_x$ films were obtained (e.g., high refractive index 2.0, high mass density 2.9 g/cm$^3$, very low wet etch rate 0.8 nm/min in 100:1 dilute HF, dielectric constant ~7, and high breakdown electric field 11 MV/cm). *Ex-situ* XPS analysis showed a low oxygen content (2 at. %) and a negligible carbon content (<1 at. %) in the bulk film. Growth per cycle (GPC) was approximately 0.11 Å/cycle. The AlGaN/GaN MIS-HEMTs ($L_{SG}$=4.5 µm, $L_G$=5 µm, $L_{GD}$=6.5 µm, $V_{DS}$=10 V) showed a maximum drain current ~550 mA/mm, a high on/off ratio $10^9$, a large gate bias swing, and a steep subthreshold swing of 72 mV/dec. Furthermore, negligible $V_{th}$ shift and a small hysteresis (~ 100 mV) were observed between forward and reverse sweep under a large gate bias ($V_{G,\,max}$= 10 V), as shown in Figure 2. The excellent stability of $V_{th}$ indicated fewer interface/border traps near the dielectric/III-N interface. The capacitance-voltage characteristics also showed a negligible hysteresis (Figure 3) and small frequency dispersion. A detailed comparison with Schottky barrier HEMTs and thermal ALD $Al_2O_3$ MIS-HEMTs will be presented. Our work has demonstrated that PEALD is a suitable technique to grow high-quality $SiN_x$ film for AlGaN/GaN MIS-HEMTs applications.

[1]. X. Meng et al., "Atomic Layer Deposition of Silicon Nitride Thin Films: A Review of Recent Progress, Challenges, and Outlooks," Materials, 9 (12), 1007 (2016)

4:30pm **AA2-TuA-13 Atomic Layer Annealing for Atomic Layer Epitaxy of AlN Ultrathin Films at a Low Growth Temperature***, M Chen,* ***Wei-Hao Lee,*** *H Shih, W Kao, Y Chuang,* National Taiwan University, Taiwan*; R Lin,* Chang Gung University, Taiwan*; H Lin,* National Taiwan University, Taiwan*; M Shiojiri,* Kyoto Institute of Technology, Japan

Atomic layer deposition (ALD) is an attractive technique for preparing high-quality nanoscale thin films, and has been widely exploited in a great variety of nanoscale applications including solar cells, memories, and transistors. However, the as-deposited thin films prepared by ALD are generally of amorphous-like structure due to the requirement of a low deposition temperature to keep the self-limiting chemical reactions in ALD. As compared with amorphous films, crystalline films or even single-crystalline epitaxial layers are more favored because of the significantly improved optical and electrical properties. Therefore, it is highly demanded to improve the crystallization of the ALD-deposited thin films. In this work, a novel concept and approach termed as “atomic layer annealing” (ALA) was proposed in the ALD process to realize the low-temperature atomic layer epitaxy, i.e., to achieve high-quality epitaxial growth of AlN at a low deposition temperature of 300ºC on sapphire substrate. Rather than a high growth temperature which is needed in conventional epitaxial growth techniques, a layer-by-layer, in-situ Ar plasma treatment was introduced into each ALD cycle to realize the ALA effect. The Ar plasma treatment during each ALD cycle provides sufficient crystallization energy to the surface of thin films from the incident radicals or ions, leading to the dramatic transformation of the AlN ultrathin film from the amorphous phase to a single-crystalline epitaxial layer. The X-ray diffraction and high-resolution transmission electron microscopy clearly indicates a high-quality single-crystal AlN epilayer with only a few tens of nanometer in thickness. In addition, the two-dimensional electron gas (2DEG) characteristic of the AlN/GaN heterojunction was also observed by the ALA treatment on the AlN layer. The result demonstrates great potential for further extension of the ALD tools from the conventional deposition of amorphous thin films to high-quality epitaxial growth at a low temperature, which can be utilized in a variety of fields and applications in the near future.

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