ALD Applications
Room Grand Ballroom A-C - Session AA1-MoA
ALD for Biological and Space Applications

Moderators: Elton Graugnard, Boise State University, Mato Knez, CIC nanoGUNE

1:30pm **AA1-MoA-1 Atomic Layer Deposition on Pharmaceutical Particles for Inhaled Drug Delivery***,* ***Damiano La Zara****,* Delft University of Technology, Netherlands*; D Zhang, M Quayle, G Petersson, S Folestad,* AstraZeneca, Sweden*; J van Ommen,* Delft University of Technology, Netherlands

Drug delivery by inhalation provides a targeted treatment for respiratory diseases such as asthma and chronic obstructive pulmonary disease. A growing amount of new inhaled active pharmaceutical ingredients (APIs) includes amorphous drugs, which are often very moisture-sensitive, as well as expensive and less potent drugs, which require improved flowability and aerosolization efficiency to meet the drug load requirements and to minimize their cost. Moreover, there is no commercially viable extended-release technique for inhaled drug particles. Therefore, there is an unmet need for novel solutions to provide surface modification of inhaled pharmaceutical powders that lead to improved processability and stabilization of solid state forms (e.g., amorphous, metastable, polymorphs, hydrates) and, most importantly, clinical benefits, e.g., controlled release of API from dosage forms.

In this work, we demonstrate the use of atomic layer deposition (ALD) as a route to modify the properties of inhaled pharmaceutical particles, namely (i) dispersibility, (ii) stability to moisture and (iii) dissolution rate. We deposit ultrathin oxide ceramic films, namely Al_2O_3, TiO_2 and SiO_2, on both API (e.g., budesonide and salbutamol) and excipient (i.e., lactose) particles, both crystalline and amorphous. The ALD process is carried out at ambient conditions in a fluidized bed reactor for a range of cycles from 10 to 50, using TMA/O_3, $TiCl_4$/H_2O and $SiCl_4$/H_2O as precursors for Al_2O_3, TiO_2 and SiO_2 ALD, respectively. The deposition strongly depends on the surface crystal structure of the particles. Time-of-flight secondary ion mass spectrometry and transmission electron microscopy reveal the deposition of uniform and conformal nanofilms on crystal surfaces, whereas uniform but non-conformal nanofilms are observed on amorphous surfaces. The dispersion properties are evaluated both in the liquid and dry state. The ALD-coated particles exhibit considerably higher dispersibility in both water and ethanol solutions, thus suggesting higher bioavailability, than the uncoated ones. In-vitro aerosolization testing by the next generation impactor shows improved fine powder delivery (<5 µm, i.e., particle size range relevant for inhalation) and greatly reduced powder retention in the inhaler for the ALD-coated particles. The dispersion and aerosolization properties are retained even upon different conditions of temperature (25-40 °C) and relative humidity (60-75 %) over 3 weeks. Finally, in-vitro dissolution tests and cell absorption studies reveal more sustained release with increasing film thickness.

1:45pm **AA1-MoA-2 The Use of Atomic Layer Deposition to Increase the Availability of Medical Radio-Isotopes***,* ***Ruud van Ommen****, J Moret, B Wolterbeek, E Pidko, A Denkova,* Delft University of Technology, Netherlands

Since the first use of the radionuclide phosphorus-32 for treatment of haematological patients in the 1930s, the use of radioisotopes in medicine has expanded into a mainstream clinical speciality . It encompasses both diagnostic imaging (exploiting the tissue penetration of gamma rays released in nuclear decay) and targeted therapy (exploiting the cellular toxicity of beta minus and alpha particles) [1]. Radioisotopes are typically applied in single photon emission computed tomography (SPECT, e.g., ^{67}Ga, ^{99m}Tc, ^{111}In, ^{177}Lu) and positron emission tomography (PET, e.g., ^{68}Ga, ^{64}Cu, ^{44}Sc, ^{86}Y, ^{89}Zr), as well as in therapeutic applications (e.g., ^{47}Sc, ^{177}Lu, ^{90}Y, $^{212/213}$Bi, ^{212}Pb, ^{225}Ac, $^{186/188}$Re) [2].

In targeted radionuclide therapy a major hurdle is the dependence on a very limited number of nuclear reactors worldwide to produce these radioisotopes. Especially when some of these reactors are down due to unforeseen maintenance, critical situations for patients relying on the radionuclides can appear.

Atomic layer deposition (ALD) can provide a way to either exploit production in smaller nuclear reactors while still producing radionuclides of high specific activity (i.e. activity per unit of mass) or in some cases to prepare radionuclide generators, that can be placed in hospitals, providing on-site and on-demand supply [3]. In this presentation, we will compare the periodic table for medical radio-isotopes [1] with the periodic table for ALD precursors [4,5]. It will be discussed in which ways ALD can aid in the production of medical radio-isotopes . We will illustrate this by some examples, such as the production of ^{177}Lu and ^{99}Mo.

1. Blower, P. J. (2015). A nuclear chocolate box: the periodic table of nuclear medicine. *Dalton Transactions*, *44*(11), 4819-4844.
2. Price, E. W., & Orvig, C. (2014). Matching chelators to radiometals for radiopharmaceuticals. *Chemical Society Reviews*, *43*(1), 260-290.
3. Moret, J.L.T.M., Wolterbeek, H.T., Denkova, A.G., & van Ommen, J.R., (2016). Thin layer deposition of Lutetium on nano-particles. Presented at 16th International Conference on Atomic Layer Deposition (ALD 2016), Dublin, Ireland, 24–27 July 2016.
4. Puurunen, R. L. (2005). Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/water process. *Journal of applied physics*, *97*(12), 9.
5. Miikkulainen, V., Leskelä, M., Ritala, M., & Puurunen, R. L. (2013). Crystallinity of inorganic films grown by atomic layer deposition: Overview and general trends. *Journal of Applied Physics*, *113*(2), 2.

2:00pm **AA1-MoA-3 Atomic Layer Deposition for Biosensing Applications***, O Graniel,* ***Matthieu Weber****, S Balme, P Miele, M Bechelany,* Institut Européen des Membranes, France

Atomic layer deposition (ALD) is a thin film deposition technique currently used in various nanofabrication processes for microelectronic applications. The ability to coat high-aspect-ratio structures with a wide range of materials, the excellent conformality, and the precise thickness control have made ALD an essential tool for the fabrication of many devices, including biosensors[1].

In this study, we combined ALD, nanosphere lithography (NSL), and electrodeposition to fabricate hollow ZnO urchin-like structures covered by a Au film for surface-enhanced Raman spectroscopy (SERS) applications. The morphology of the structures was investigated using scanning electron microscope (SEM) and transmission electron microscope (TEM). These three dimensional, high-aspect-ratio organized nanostructures enabled the detection of thiophenol with concentrations as low as $1x10^{-10}$ M. The impact of the gold layer thickness, and annealing conditions were investigated. Samples that were not annealed had a better overall reproducibility, whereas the ones annealed presented a stronger enhancement of the Raman signal due to the coalescence of Au into nanoparticles. Lastly, the biosensing capability of the urchin-like ZnO structures was demonstrated by successfully detecting adenine. These proof-of-concepts enabled for a better understanding of the properties of these peculiar nanostructures, and open prospects for the biosensing community.

1. Graniel, O., Weber, M., Balme, S., Miele, P. & Bechelany, M. Atomic layer deposition for biosensing applications. *Biosens. Bioelectron.* **122,** 147–159 (2018).

2:15pm **AA1-MoA-4 Multi-layer Stacked ALD Coating for Hermetic Encapsulation of Implantable Biomedical Microdevices***,* ***Joonsoo Jeong****,* Pusan National University, Republic of Korea*; S Sigurdsson, F Laiwalla,* Brown University*; R Ritasalo, M Pudas, T McKee, T Pilvi,* Picosun Oy, Finland*; A Nurmikko,* Brown University

Introduction and Main Findings:

Implantable biomedical electronics are a promising technology for medical diagnosis and treatment if they can be made safe for chronic use. There is thus a growing need for compact-volume hermetic packaging methods for miniaturized biomedical implants. Here we describe the use of multi-layer ALD films comprising HfO_2 and SiO_2 (Picosun Oy, Finland) to hermetically encapsulate microscale wireless active electronic implants for use in the brain. The robustness of the 3-D conformal ALD coatings is validated using an accelerated aging test by application of thermal stress (87°C saline) and quantified in terms of water/ionic ingress (leakage currents) as well as overall device performance (the latter via wireless interrogation). ALD coated devices have an extrapolated physiologic temperature lifetime of > 10 years under active electric field stress. Failed devices maintain the layer integrity, and only show gross anomalies on SEM at sample edges likely consistent with handling stresses. This performance is not impacted by opening apertures in the coating (for fabrication of sensing/actuating interface electrodes).

Experimental:

All films were grown in Picosun™ R-200 advanced reactors using thermal ALD processes, and comprised alternating layers of HfO_2 and SiO_2 for a total thickness of 100 nm. The ALD temperature was varied between 150°C and 300°C. Samples were batch processed in a wire-mesh bag (Fig S2 (d)) for full 3-D conformal multilayer encpasulation, and carefully poured on to Al foil and loosely packed for transportation. Sample handling was done using plastic-tip or vacuum tweezers. Three types of substrates were coated: 500 µm x 500 µm passive silicon die, active wireless microelectronic chiplets, and wired interdigitated electrodes. The substrates were subjected to an accelerated aging test by immersion in saline at 87 C. A subset of active microelectronic chiplets were constantly powered on using RF energy at 915 MHz. Failed samples were analyzed by scanning electron microscopy.

Results:

ALD-coated samples had an accelerated aging test survival time which can be extrapolated to > 10 years at physiologic temperatures (37°C) for passive as well as active samples (where the latter had continuous electric fields across the ALD films). Analysis of the failed samples shows areas of film breakdown at the edges, likely associated with post-encapsulation handling. There is no evidence of delamination of the ALD layer stack at the periphery of the failure, indicating that point-failure rather than a gradual degradation of the films.

Acknowledgements:

This work was supported by DARPA NESD Program Contract # N666001-17-C-4013)

2:30pm **AA1-MoA-5 Modification of Spaceflight Radiator Coating Pigments by Atomic Layer Deposition for Thermal Applications***, **Vivek Dwivedi,*** NASA Goddard Space Flight Center*; R Adomaitis, H Salami, A Uy,* University of Maryland*; M Hasegawa,* NASA Goddard Space Flight Center

The optical and physical properties of spacecraft radiator coatings are dictated by orbital environmental conditions. For example, coatings must adequately dissipate charge buildup when orbital conditions, such as polar, geostationary or gravity neutral, result in surface charging. Current dissipation techniques include depositing a layer of ITO (indium tin oxide) on the radiator surface in a high temperature process. The application of these enhanced coatings must be such that the properties in question are tailored to mission-specific requirements.

The deposition of thin films by atomic layer deposition is a natural technological fit for manufacturing spacecraft components where weight, conformality, processing temperature, and material selection are all at a premium. Indium oxide (IO) and indium tin oxide (ITO) are widely used in optoelectronics applications as a high quality transparent conducting oxide layer. In this work, we present the thickness-dependent electrical and optical properties of IO thin-films synthesized by ALD with the aim of finding the optimum condition for coating a variety of substrates from Si(100) wafers, glass slides, and especially radiator pigments. Radiators are given surface finishes with high IR emittance to maximize heat rejection and low solar absorptance to limit heat loads from the sun. The surface finish is typically a white paint composed of nano/micron particle sized pigments with a silicate binder. It is the encapsulation of these particles that dictate the charge bleed off properties of the finished coating. Trimethylindium and ozone were used as precursors for IO, while a tetrakis(dimethylamino)tin(IV) source was used for Sn doping to produce ITO. As-deposited IO films prepared at 140 ° C resulted in a growth per cycle of 0.46 Å /cycle and relatively low film resistivity.

For the case of ITO thin-films, an ALD process supercycle consisting of 1 Sn + 19 In cycles was shown to provide the optimum level of Sn doping corresponding to the 10 wt.% widely reported in the literature. By using the inherent advantage of ALD in coating high aspect ratio geometries conformally, modification of these pigments can be accomplished during coating application preprocessing. The preprocessing is rendered directly on the dry pigment/particle before binding and not on the finished coated radiator geometry thus saving reactor volume.

Samples of our coating were recently launched into space and are currently onboard the International Space Station (ISS) as part of the one-year MISSE-10 materials test mission where the IO coated pigments are exposed to the harsh environment of space.

2:45pm **AA1-MoA-6 Novel Atomic Layer Deposition Process/Hardware for Superconducting Films for NASA Applications***, **Frank Greer,** D Cunnane,* Jet Propulsion Laboratory

Future sub-millimeter telescopes and spectrometers have the potential to revolutionize our understanding of the formation of the modern universe. Sub-millimeter astronomy can probe the fine structure of the cosmic microwave background, giving glimpses into the early universe immediately following the Big Bang. Recent advances in design have enabled the production of large arrays of cryogenically cooled superconducting detectors with sufficient sensitivity for photon counting applications. Transition edge sensors (TES) and other types of detectors, fabricated from thin films of metal nitrides and such TiN, NbN, TaN, VN, and their mixtures or high temperature superconductors like MgB2, are cryogenically cooled to just below their superconducting transition temperature. Atomic layer deposition is a chemical technique that can deposit extremely conformal and uniform films with angstrom level precision that would seem ideal for deposition of films of this type. However, one significant limitation of the technique is that it is often confined to those films that can be achieved through equilibrium processes. This is a significant limitation when the material of choice, such as MgB2, which is an excellent superconducting material, is Mg deficient as deposited by conventional chemical vapor deposition and only stoichometric MgB2 is a superconductor. Superconducting MgB2 thin films have been grown using hybrid physical/chemical vapor deposition when there is an excess of magnesium in the gas phase created by evaporation of elemental magnesium in the deposition chamber. The method for doing this is to have a charge of magnesium metal that is heated above its sublimation temperature in the very near vicinity of the substrate susceptor. Unfortunately, this method is currently only appropriate for small samples (1-2" in diameter) and for thick films (100nm or thicker). To overcome these limitations, we have built a custom lid for an existing atomic layer deposition reactor was machined to include a cavity to enable magnesium evaporation during deposition. We have subsequently used this approach to deposit MgB2 thin films detectors. This presentation will focus on our thin film results from both of the nitrides and MgB2 (composition, superconducting transition temperature, morphology, etc.) as well as the possible applicability of this generalized in situ thermal evaporation technology concept to other ALD materials.

3:00pm **AA1-MoA-7 Fluoride-based ALD Materials System for Optical Space Applications***, **John Hennessy,*** Jet Propulsion Laboratory, California Institute of Technology

In this work we describe space technology applications that plan to utilize the recent development of atomic layer deposition (ALD) processes for metal fluoride materials like MgF_2, AlF_3, and LiF. These materials are valuable optical thin films in the deep ultraviolet, and are being used at NASA JPL to fabricate protected-aluminum mirror coatings, anti-reflection coatings, and detector-integrated filter coatings. Such systems are currently being implemented in a variety of sub-orbital missions including sounding rockets, cubesats, and high-altitude balloons that are relevant to astrophysics, heliophysics, and planetary science observations. We describe how ALD thin film properties may offer performance advantages over conventional methods with respect to film uniformity, microstructure, and integration with back-illuminated imaging sensors. We also describe the development of mitigating approaches to enhance the environmental stability of typically-hygroscopic fluoride materials through the use of ALD nanolaminates and mixed-composition fluorides. The same fluoride-based ALD approach has also been exploited to perform low-temperature atomic layer etching (ALE) to enhance the optical performance of some of these devices, and to pursue strategies for the development of protective coatings for lithium metal anodes relevant to future Li-ion battery applications.

3:15pm **AA1-MoA-8 Atomic Layer Deposition of Aluminum Fluoride for use in Astronomical Optical Devices***, **Alan Uy,** H Salami, A Vadapalli, C Grob, R Adomaitis,* University of Maryland*; V Dwivedi,* NASA Goddard Space Flight Center

Solid state metal halides typically have a high bandgap and low refractive index. Aluminum trifluoride (AlF_3) exhibits these properties, having a band gap greater than 10 eV and a refractive index of 1.35, making it an attractive material for thin film applications that include mirrors and optical devices [1]. Techniques to deposit thin films of AlF_3 include physical vapor deposition, sputtering, sol-gel, and atomic layer deposition (ALD) [2].

An important application of metal halides films in spacecraft missions has been for the protection of aluminum mirror from oxidation, which can severely affect overall reflectance in the far ultraviolet region. These coatings must maintain the underlying reflectivity of pure aluminum by having high transparency over the broad spectral range. To this end, AlF_3 stands out from other metal halide protective coatings, having higher transparency at the 100-200 nm wavelength region [1]. Due to long duration missions and the inability to service observatories in orbit, coatings of aluminum fluoride are also investigated for robustness and low interactions with potential foulers such as low earth orbit atomic oxygen.

These thin coatings must be pinhole free to prevent access and reaction with underlying layers.

The highly conformal dense films and thickness control by ALD are attractive for this application. In this work, the growth of AlF_3 by ALD using precursors trimethyl aluminum (TMA) and titanium tetrafluoride (TiF_4) is investigated. Deposition of AlF_3 is performed in a custom hot-wall bench-scale reactor. We have shown that our deposition system can generate growth rates of ~0.5 Å/ALD cycle at relatively low temperatures of 180 °C. Varying ALD process parameters such as the exposure and purge times of precursor were found to have interesting effects to the film growth rate, especially those concerning the precursor TiF_4. These developments also give insight into potential reaction mechanisms between TMA and TiF_4, leading towards an overall hypothesized reaction mechanism for ALD process. Furthermore, optical properties, composition, and uniformity of film are analyzed. Lastly, the generated AlF_3 film quality over months under ambient conditions for robustness also is discussed.

[1] J. Hennessy, K. Balasubramanian, C. S. Moore, A. D. Jewell, S. Nikzad, K. France, M. Quijada, J. Astron. Telesc, Instrum. Syst. 2.4 (2016) 041206

[2] M. Mäntymäki, M. J. Heikkilä, E. Puukilainen, K. Mizohata, B. Marchand, J. Räisänen, M. Ritala, M. Leskelä, Chem. Mater. 2015, 27, 2, 604-611

ALD Applications
Room Grand Ballroom A-C - Session AA2-MoA

ALD for Solar Cells, Fuel Cells, and H_2 Storage

Moderators: Christophe Detavernier, Ghent University, Belgium, Nicholas Strandwitz, Lehigh University

4:00pm **AA2-MoA-11 Nucleation Layer for Atomic Layer Deposition Enabling High Efficiency and Flexible Monolithic All-Perovskite Tandem Solar Cells*, Axel F. Palmstrom*,** *G Eperon, T Leijtens,* National Renewable Energy Laboratory*; R Prasanna,* Stanford University*; S Nanayakkara, S Christensen, K Zhu,* National Renewable Energy Laboratory*; M McGehee,* University of Colorado Boulder*; D Moore, J Berry,* National Renewable Energy Laboratory

The emergence of metal halide perovskites as high efficiency, low-cost photovoltaic materials with a tunable band-gap has led to significant interest for perovskite-based tandems. Of existing perovskite-based tandem technologies, pairing wide-gap and low-gap perovskites in a monolithic all-perovskite tandem arguably offers the greatest potential by enabling efficiencies beyond the single-junction Shockley-Queisser limit with low-cost solution processing on a flexible, lightweight substrate. As of yet, efficiency of all-perovskite monolithic tandems has lagged behind perovskites paired with silicon or CIGS despite significant improvement to low-gap perovskite materials. A barrier to effectively combining state-of-the-art wide and low band gap perovskites in a monolithic tandem is the lack of a high-quality recombination layer that sufficiently protects an underlying perovskite thin-film to enable subsequent perovskite solution processing and minimal device shunting.

In this work, we aim to understand metal oxide growth by low-temperature atomic layer deposition (ALD) on C_{60} to develop improved recombination layers for all-perovskite 2T tandems. The effect of C_{60} surface modification with ultra-thin nucleophilic-containing materials is studied on ALD nucleation, growth, and film properties. We show, for multiple ALD systems, nucleophilic surface modification improves the water and dimethylformamide barrier properties of the grown oxide film. This strategy enables the fabrication of improved ALD recombination layers that are thinner and less laterally conductive (reduced shunting) than currently reported strategies. We demonstrate ALD-grown aluminum-doped zinc oxide (AZO) as an effective recombination layer for two-terminal all-perovskite tandems with efficiencies over 23% for rigid devices and 21% for flexible devices.

4:15pm **AA2-MoA-12 Perovskite Solar Cells Fabricated using Atomic Layer Deposited Doped ZnO as a Transparent Electrode*, Louise Ryan,*** *M McCarthy, S Monaghan, M Modreanu, S O'Brien, M Pemble, I Povey,* Tyndall National Institute, Ireland

Power conversion efficiencies of perovskite (PK) solar cells have rapidly improved in recent years obtaining efficiencies in excess of 20% [1]. Good absorption properties in the visible and infrared spectrum, high efficiencies and low fabrication costs have brought PK solar cells to the forefront. With single junction PK solar cells soon reaching theoretical efficiency limits a requirement for tandem cells, where materials of differing absorption characteristics convert a wider spectral range, is in demand. However, such tandem solar cells introduce fabrication complexities due to the thermal budget restrictions imposed by the complex layer structure [2].

Fluorine-tin oxide (FTO) and indium-tin oxides (ITO) are widely used transparent contacts in solar cells. However, the high deposition temperatures and energetic processes required for its production are detrimental to the fabrication of delicate perovskite based tandem solar cells and thus the need to find an alternative TCO is vital.

Here we have considered Ti-doped ZnO, produced by a ALD laminate doping method, as an alternative transparent contact and have incorporated it into perovskite solar cells in conjunction with an ALD-grown SnO_2 electron transport material. Detailed analysis of the influence of the growth process on the performance of the Ti-doped ZnO electrode is presented. Finally, the efficiency of the optimised perovskite solar cells are evaluated relative to the current state of the art.

[1] NREL: Efficiency Chart (2018). Https://www.nrel.gov/pv/assets/pdfs/pv-efficiencies-07-17-2018.pdf

[2] F. Sahli, et al*.,* Nature Materials, 17(9) (2018) 820-826.

4:30pm **AA2-MoA-13 Metal Oxide Barrier and Buffer Layers by Atomic Layer Deposition and Pulsed-Chemical Vapor Deposition for Semi-Transparent Perovskite Solar Cells*, Helen Hejin Park*,** *T Eom, R Agbenyeke, S Yeo, G Kim, S Shin, T Yang, N Jeon, Y Lee, C Kim, T Chung, J Seo,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

For *n-i-p* structured semi-transparent perovskite solar cells, thermal evaporation has been a common technique to deposit the sputter buffer material, such as molybdenum oxide and tungsten oxide, to protect the organic hole transporting layer (HTL) from damage due to sputtering of the transparent conducting oxide. However, thermal evaporation does not guarantee stoichiometric and uniform pinhole–free coverage of films, leading to inefficient protection against sputtering and poor air stability. While there have been well-established buffer materials by atomic layer deposition (ALD), such as SnO_2, for *p-i-n* structured semi-transparent perovskite solar cells, this is not the case for *n-i-p* structured devices. In addition, thermal evaporation has also been commonly used to deposit a barrier layer at the perovskite/HTL interface to improve the fill factor and open-circuit voltage, however, ALD can provide more precise control and conformal coverage for this layer. In this presentation, we demonstrate metal oxide deposition techniques by pulsed-chemical vapor deposition and ALD in perovskite solar cells for the sputter buffer and barrier layers, which result in efficiencies over 16% for semi-transparent devices. Effects of the optical and electrical properties of barrier/buffer layers on the performance of working devices will be addressed, and the mechanisms involved in the enhanced performance and stability will also be discussed.

4:45pm **AA2-MoA-14 Particle Atomic Layer Deposition of Tungsten Nitride Environmental Barrier Coatings from Bis(t-butylimido)bis(dimethylamino)tungsten(VI) and Ammonia*, Sarah Bull,*** *A Weimer,* University of Colorado - Boulder

Ultra-thin tungsten nitride (WN) films were deposited by atomic layer deposition (ALD) on zirconia nanoparticles and yttria stabilized zirconia (YSZ) micropowders using a fluidized bed reactor. The film's intended use as a hydrogen barrier coating motivated the investigation of hydrogen diffusion in W using density functional theory (DFT) and differential thermal analysis (DTA). The lowest energy diffusion pathway was determined and the hydrogen charges at various sites along the pathway were calculated. DTA was used to investigate the efficacy of the W/WN films in preventing hydrogen attack. The temperature at which hydrogen reacted with the sample increased with film thickness, thereby indicating that the film inhibited this reaction. However, the existence of a hydrogen reaction peak in the thicker film indicated a material with greater than 2.0 eV energy barrier is necessary for a substantial decrease in hydrogen interaction with the substrate. This is the first study for ALD of WN on particles from bis(t-butylimido)bis(dimethylamino)tungsten(VI) and the use of ultrathin WN ALD films as environmental barrier coatings (EBCs) for high-temperature H_2 above 1000°C.

5:00pm **AA2-MoA-15 Atomic Layer Deposition on $Mg(BH_4)_2$: A Route to Improved Automotive H_2storage*, Noemi Leick,*** National Renewable Energy Laboratory*; K Gross,* H₂ Technology Consulting LLL*; T Gennett, S Christensen,* National Renewable Energy Laboratory

In order to meet the U.S. Department of Energy requirements for on-board solid-state hydrogen (H_2) storage in fuel-cell powered vehicles, metal borohydrides are of particular interest. However, while materials such as magnesium borohydride, $Mg(BH_4)_2$, have a hydrogen capacity up to

~14wt%, challenges associated with hydrogenation-dehydrogenation cyclability need to be overcome. Specifically, improve the operating temperatures for adsorption/desorption; increase the hydrogen absorption-desorption kinetics; and eliminate the formation of the toxic diborane (B_2H_6). Prior research has indicated that nano-encapsulation (*e.g.* through graphene nanosheets) and chemical additives (*e.g.* catalysts) are areas of significance to address these challenges.

This work is the first to approach these two strategies simultaneously using atomic layer deposition (ALD). ALD coatings have been shown to protect and enhance heterogeneous catalyzed rates, as well as to precisely control the amount of chemical additive incorporated. In this project, metal-oxides (*e.g.* Al_2O_3, TiO_2, CeO_2), metal-nitrides (*e.g.* TiN, BN), pure metals (*e.g.* Ru, Pd) and combinations thereof were deposited by ALD on γ-$Mg(BH_4)_2$. We investigated how the deposition temperature, the use of water for some of these ALD processes and the composition of the additive affected the H_2storage properties of γ-$Mg(BH_4)_2$.

Compared to uncoated γ-$Mg(BH_4)_2$, we found that the ALD depositions lowered the H_2desorption temperature by 60–120 ˚C, doubled the desorbed gravimetric H_2capacity at temperatures below 250˚C, increased the desorption kinetics by a factor of ~6, and suppressed the formation of B_2H_6 substantially during the dehydrogenation step. The ALD-modified γ-$Mg(BH_4)_2$was also explored with respect to the structure, the effects of the total hydrogen capacity, and catalytic effects. In this presentation we will discuss data supporting these results from temperature programmed desorption, pressure composition temperature manometric measurements, inductively coupled plasma mass spectrometry, nitrogen physisorption measurements, nuclear magnetic resonance, transmission electron microscopy and diffraction spectroscopy.

5:15pm **AA2-MoA-16 Plasmonic Mediated Hydrogen Desorption from Metal Hydrides***, **Katherine Hurst**, A Gaulding, M Martinez, N Leick, S Christensen, T Gennett,* National Renewable Energy Laboratory

Excitation of plasmonic coatings deposited by atomic layer deposition (ALD) can provide important routes for tuning the performance of gas adsorption and desorption of hydrogen storage materials. 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 hydrides are an important class of materials that can reach DOE system capacity targets for hydrogen storage. However, the gas uptake and release of hydrogen by metal hydrides requires high pressures and temperatures, and exhibits slow kinetics. It is well known that modification of a bulk hydride to the nanoscale phase, and the addition of catalyst additives can both greatly enhance the kinetics, lower operating temperatures, and increase cyclability. This work takes a unique route to alter the process of desorption through the incorporation of plasmonic materials into the hydride matrix. This allows for low-power-LED-illuminated systems to achieve the same rates of hydrogen desorption as radiative thermal heating

Specifically, recent work at the National Renewable Energy Laboratory has applied ALD to enable the use of plasmonic material coatings to alter the mechanism for hydrogen desorption. Through localized heating via surface plasmon excitation, the bulk thermal signature for hydrogen release can be significantly reduced. Furthermore, hydrogen desorption induced via plasmonic heating offers a completely new approach to using hydride materials. Temperature programmed desorption spectroscopy is used to monitor the kinetic changes associated with desorption by varying the conditions and type of plasmonic material introduced. The effects of partial coverages, ALD film thickness and crystallinity on the resonant plasmonic frequency are explored. This presentation will discuss advancements in enabling gas desorption via plasmonic excitation especially with respect to hydrogen carrier applications. These exciting results also point towards new applications for ALD in nano-scale photo-thermal processes.

5:30pm **AA2-MoA-17 Surface Modification of Solid Oxide Fuel Cell Cathodes by Atomic Layer Deposition***, **Dong Hwan Kim**, H Choi, J Koo,* Korea University, Republic of Korea*; J Park, J Son,* Korea Institute of Science and Technology (KIST), Republic of Korea*; J Shim,* Korea University, Republic of Korea

Development of high-performance cathode is key to the commercialization of solid oxide fuel cells (SOFCs). Doped perovskite-type oxides including lanthanum strontium cobaltite (LSC) and lanthanum strontium cobalt ferrite (LSCF) are the most typical materials in practical SOFCs. However, degradation of LSC and LSCF from dynamic on-off operation at high temperature (600-1000 ºC) has been considered as the most serious technical obstacle. Many kinds of literature have reported that segregation of cations near the cathode surface leads to this degradation. Specifically, the A-site element of the cathode perovskite is subjected to electrostatic attraction to the surface due to excess oxygen vacancies on the cathode surface, which brings out the A-site element to segregate on the surface [1]. To solve this problem, we have proposed surface modification by atomic layer deposition (ALD) [2]. In this study, 1-4 cycles of ALD Al2O3 has been attempted on porous LSC to suppress the cation segregation and improve the surface redox kinetics. Performance of SOFCs with the ALD Al2O3-treated LSC cathodes has been evaluated in I-V-P and impedance. Finally, long-term stability at 500-600 °C has been examined in the potentio -static mode. In this presentation, the progress of this research will be shared in details.

[1] Cai et al. Chemistry of materials 24.6 (2012): 1116-1127.

[2] Choi et al. Advanced Energy Materials 8.33 (2018): 1802506.

ALD Applications
Room Grand Ballroom E-G - Session AA1-TuM

ALD for Catalysts, Electrocatalysts, and Photocatalysts

Moderators: Jeffrey W. Elam, Argonne National Laboratory, Parag Banerjee, University of Central Florida

8:00am **AA1-TuM-1 ALD for Solar Fuels: Rendering Halide Perovskites Acid-Compatible + Precision Cluster Electrocatalysts***, **Alex Martinson**, I Kim, M Pellin,* Argonne National Laboratory **INVITED**

Although solution-processable halide perovskite semiconductors exhibit optoelectronic performance comparable to the best photoabsorbers for solar fuel production, halide perovskites rapidly decompose in the presence of water or even humid air. We show that a hybrid electron transport layer, a $PC_{61}BM + TiO_2$ film (18–40 nm thickness) grown over the sensitive absorber by atomic layer deposition, enables photo-assisted proton reduction without further encapsulation. These semitransparent photocathodes, when paired with a Pt catalyst, display continuous reduction of H^+ to H_2 for hours under illumination, even while in direct contact with a strongly acidic aqueous electrolyte (0.5 M H_2SO_4). More affordable and active catalysts for more challenging solar-to-fuels reactions (e.g. N_2 or CO_2 reduction) will require catalysts with exquisite precision. The bottom-up, selective ALD synthesis of controlled-atom-number clusters will also be discussed as a potentially powerful route to designer solar fuels catalysts.

8:30am **AA1-TuM-3 Plasma-Assisted ALD of Cobalt Phosphate: Process Development and Electro-Catalytic Activity Towards Oxygen Evolution Reaction***, V Di Palma,* Eindhoven University of Technology, Netherlands*; G Zafeiropoulos, R van de Sanden,* Dutch Institute for Fundamental Energy Research*; E Kessels,* Eindhoven University of Technology, Netherlands*; M Tsampas,* Dutch Institute for Fundamental Energy Research*; **Mariadriana Creatore**,* Eindhoven University of Technology, Netherlands

Water splitting is a viable approach to enable storage of renewable energy in the form of fuels. Major issues hampering the development and implementation of this technology, are: the high cost associated with the use of noble-metal-based electro-catalysts; the sluggish kinetics of the oxygen evolution reaction (OER). Cost-effective, transition metal- based electro-catalysts [1], e.g. cobalt phosphate (CoPi), show promising results in terms of performance towards OER. So far, CoPi has been synthesized by electro-deposition with severe limits in the control of layer thickness and chemical composition, the latter being highly influenced by the choice of precursors, electrolyte and pH. Instead, a higher level of control in terms of layer thickness and tunable stoichiometry is expected when adopting ALD.

In the present work we synthesize CoPi thin films by plasma-assisted ALD [2]. The process is based on an ABCD scheme, where A and C are the cobaltocene (CoCp) and trimethylphosphate (TMP) exposure steps. B and D correspond to O_2 plasma steps. CoPi layers, characterized by a stoichiometry of $Co_{3.2}(PO_{4.3})_2$, are deposited at 300˚C with a growth per cycle of 1.1 Å, as determined by *in-situ* spectroscopic ellipsometry. Cyclic voltammetry shows that the ALD CoPi layer exhibits a current density peak of 1.8 mA/cm^2 at 1.8 V vs. Reversible Hydrogen Electrode (RHE). This value is comparable to those reported in literature for electro-deposited CoPi. Since cobalt is recognized in literature as reactive center governing the electrocatalytic activity [3], we also investigate the effect of Co-to-P concentration ratio on the OER. The deposition process is then based on a $(AB)_x(CD)_y$ supercycle. For just 1 extra AB cycle, accompanied by 11 cycles of CoPi (x= 12; y= 11), a Co-rich stoichiometry ($Co_{3.8}(PO_{4.7})_2$) is achieved. The latter leads a higher current density peak (2.9 mA/cm^2 at 1.8 V vs RHE) than the earlier addressed CoPi sample. When comparing the performance of the ALD Co-rich CoPi layer with electro-deposited CoPi [4] in terms of current density, the former exhibits superior OER performance. These results highlight the role that stoichiometry of cobalt phosphate has on its OER activity, suggesting that tuning the Co-to-P ratio can be adopted as approach to design efficient Co-based electro-catalysts for OER.

[1]M.W. Kanan, D.G. Nocera, *Science* 321, 1072 (2008)

[2] V. di Palma *et al*., Electrochemistry Communications 98, 73 (2019)

[3] J. Surendranath *et al*., *J. Am. Chem. Soc*., 132, 13692 (2010)

[4] K. Klingan *et al*., ChemSusChem 7, 1301 (2014)

8:45am **AA1-TuM-4 Improved Electrochemical Activity of Pt Catalyst Fabricated by Vertical Forced-Flow Atomic Layer Deposition***, **Tzu-Kang Chin**, T Perng,* National Tsing Hua University, Republic of China

Currently, carbon black is the most commonly used support material for depositing platinum (Pt) nanoparticle catalyst by wet chemical reduction of Pt salts in aqueous solution. However,oxidation of carbon black occurs under highly humid atmosphere and corrosive operating condition of proton exchange membrane fuel cell (PEMFC), which results in agglomeration of Pt nanoparticles, leading to degradation of catalytic performance. In addition, Pt nanoparticles fabricated by wet chemical reduction require additional steps to purify, such as removing the residual capping agent, and post-treatment to increase the crystallinity of Pt. Consequently, it is urgent to develop a novel support material with high electrical conductivity and electrochemical stability and a more facile fabrication method for Pt catalyst. Titanium oxynitride (TiO_xN_{1-x}) is an intermediate phase which is regarded as a solid solution of titanium nitride (TiN) and the cubic titanium oxide (TiO). It has been reported that the Pt deposited on TiO_xN_{1-x} results in significant enhancements of specific activity, mass activity, and corrosion resistance compared to that deposited onto carbonous support material. Atomic layer deposition (ALD) is a dry process that is able to deposit materials without contamination from capping ligands and residual organic compounds. Pt catalyst prepared by ALD has advantages of high activity and precise particle size control. However, the uniformity and conformity of the coating by conventional ALD equipment on high aspect-ratio or porous substrate is still a great challenge to overcome. To solve this problem, a novel forced-flow configuration was designed recently by our group, i.e., vertical forced-flow ALD. In this study, conductive TiO_xN_{1-x} nanoparticles were fabricated and investigated for the potential application in PEMFC as a catalyst support material. Vertical forced-flow ALD was utilized to deposit Pt nanoparticles with very small particle size uniformly on TiO_xN_{1-x}. The electrochemical activities were examined by cyclic voltammetry and oxygen reduction reaction. The Pt nanoparticles deposited on TiO_xN_{1-x} with 30 cycles show 2-3 times higher electrochemical surface area and also larger half-wave potential of oxygen reduction reaction than those of Pt prepared by conventional wet chemical reduction and commercial E-tek electrocatalyst.

9:00am **AA1-TuM-5 Improved Catalyst Selectivity and Longevity using Atomic Layer Deposition***, C Marshall,* Argonne National Laboratory*; A Dameron, R Tracy,* Forge Nano*; C Nicholas, L Abrams, P Barger,* Honeywell UOP*; T Li, **Lu Zheng**,* Argonne National Laboratory

Introduction

Many important industrial scale chemical reactions rely on catalysts and require high temperatures to achieve commercially viable product yields. However, catalysts deactivate over time and lose surface area due to thermal degradation (sintering), fouling, and poisoning. Decreased catalytic activity results in lower selectivity and higher yields of unwanted byproducts. In many cases, the remedy for sintering of metals is to raise the reactor temperature and thus increase energy consumption, or to remove and replace the spent catalyst, which is expensive and leads to loss in productivity.

This project is overcoming catalyst degradation issues via an ALD overcoating technology that deposits protective layers around the active metal, preserving catalyst integrity under reaction conditions. The ALD overcoating technique applies one or more protective layers to the catalyst to inhibit metal sintering. Channels introduced into the ALD layers provide reactants with access to the catalyst's active metal and improve reaction selectivity. This project is applying the overcoating technology to extruded platinum-based catalysts used in the propane dehydrogenation (PDH) to propylene. Improvements in both the efficiency and selectivity reduce the energy required for the process.

Materials and Methods

Alumina extrudates were synthesized by peptizing Versal-251 and extruding it into 1/16" cylinders. The dried extrudates are calcined at temperatures ranging from 500ºC to 1185ºC to generate Al_2O_3 bases with varying surface area and porosity. Pt is impregnated via standard incipient wetness techniques.

ALD is performed in fixed bed reactors typically at 200 °C during all depositions. Precursors for Al_2O_3 were TMA and H_2O, while for TiO_2 they were $TiCl_4$ and H_2O. Depositions are monitored in situ by measuring the reaction composition downstream of the reactor with a quadrupole mass spectrometer.

Results and Discussion

The project team applied overcoatings with different shell thicknesses and compositions. Initial investigations were carried out with $TiCl_4$ to distinguish overcoated layers from the catalyst base. The growth rate of TiO_2 measured by ellipsometry is 0.4Å/cycle, which is similar to previously reported studies. The $TiCl_4$ dose and soak time were then increased simultaneously until the Ti loading reached saturation on 1/16" Al_2O_3 extrudates. We report that loading of Ti after one cycle is 4.5%. No crystalline TiO_2 phase is visible in XRD.

We investigated, and report on, the effect of these overcoated layers on the propane dehydrogenation reaction rate, selectivity and catalyst deactivation.

9:15am **AA1-TuM-6 Enhancing Co_2C Activity for C_{2+} Oxygenate Production from Syngas using ALD Promoters***, **Sindhu Nathan**, J Singh, A Asundi, S Bent,* Stanford University

Residential, transportation, and industrial needs have led to a reliance on nonrenewable energy sources, which has contributed to the rising greenhouse gas concentration in the atmosphere and a subsequent rise in global temperature.The scarcity of nonrenewable fossil fuels and the continually growing demand for energy necessitates the search for renewable and carbon neutral energy sources. One promising pathway is to catalytically convert molecules like CO and H_2 (syngas), which can be generated renewably, to fuels like ethanol or other higher oxygenates which produce fewer emissions than traditional fossil fuels.

Modified cobalt nanoparticle catalysts are of interest for this reaction. Cobalt, a prevalent Fischer-Tropsch catalyst, readily converts syngas to linear hydrocarbons. Much work has been done to direct the selectivity of cobalt towards higher oxygenate production, but there has been little success in engineering a practically useful catalyst. Nanoparticle catalyst activity and selectivity are influenced by interaction with the support and any other metal or metal oxide promoters that interact with the metal surface. Atomic layer deposition (ALD) offers the capability of depositing precise amounts of modifying material on catalyst nanoparticles, allowing atomic-level control over surface composition, which in turn enables better understanding of the catalyst surface.

Prior work has shown that modifying Co with ZnO ALD (using diethylzinc and water) causes restructuring of metallic Co to Co_2C on SiO_2-supported catalysts, and further modifies the carbide, resulting in enhanced oxygenate selectivity but significantly lowered activity [1]. In this work, we investigated whether Co/Co_2C activity towards higher oxygenates could be enhanced by varying the support of ZnO-modified Co. The modified Co on most of the tested supports also showed restructuring to Co_2C. However, these alternate support materials did not enhance the oxygenate activity compared to the ZnO-modified Co/SiO_2. In contrast to the other materials, we found that ZnO-modified Co/Al_2O_3 did not carburize, but that the activity of the catalyst was much greater than Co/SiO_2. To combine this activity improvement with the selectivity of Co_2C, Al_2O_3 ALD (using trimethylaluminum and water) was applied to ZnO-modified Co/SiO_2. The additional Al_2O_3 ALD enhanced the activity of the Co/Co_2C catalysts, and an Al_2O_3 ALD support modifier improved the turnover frequency of ZnO-modified Co/SiO_2 by four times. By using ALD modifying layers, the activity of Co/Co_2C catalysts towards higher oxygenates can be improved while retaining enhanced selectivity.

[1] J. A. Singh et al., *ChemCatChem*. **2018**, 10, 799.

9:30am **AA1-TuM-7 Atomic Layer Deposition of Bismuth Vanadate Core-Shell Nanowire Photoanodes***, **Ashley Bielinski**, S Lee, J Brancho, S Esarey, A Gayle, E Kazyak, K Sun, B Bartlett, N Dasgupta,* University of Michigan

Photoelectrochemical (PEC) water splitting is a direct route for capturing solar energy and storing it in the form chemical bonds. Bismuth vanadate (BVO) is one of the most promising photoanode materials for water oxidation. It has a bandgap of 2.4 eV, which enables visible light absorption and its bands are favorably positioned for water oxidation. BVO has demonstrated potential for high anodic photocurrents, but it is limited by electron-hole separation, charge transport, and water oxidation kinetics. The development of an ALD process for BVO enables core-shell architectures that help address the charge transport and carrier separation challenges by decoupling carrier diffusion and light absorption lengths.

In this study we demonstrate the deposition of ALD BVO using $Bi(OCMe_2{}^{i}Pr)_3$ as the bismuth source, vanadium(V) oxytriisopropoxide as the vanadium source, and water as the oxidant [1]. The choice of this Bi precursor provides full control of Bi:V stoichiometry. The BVO films were deposited as a nanolaminate of binary bismuth and vanadium oxides and then post-annealed to achieve the photoactive monoclinic $BiVO_4$ phase. Film composition and photocurrent were investigated as a function of deposition pulse ratio and film thickness. Additionally, we demonstrate 3D nanostructured BVO photoanodes by depositing the BVO on ZnO nanowires with an ALD SnO_2 interlayer.

The photoactivity of the ALD BVO photoanodes was measured in a three-electrode cell under simulated AM1.5G illumination. A planar photoanode of 42 nm thick BVO produced a photocurrent density of 2.24 mA/cm^2 at 1.23 V vs. RHE (reversible hydrogen electrode) and the application of a ZnO nanowire substrate provided a 54% increase in photocurrent to 3.45 mA/cm^2 at 1.23 V vs. RHE. These values are the highest reported to date for any photoanode using an ALD film as the primary light absorber.

[1] A. R. Bielinski, S. Lee, J. Brancho, S. L. Esarey, A. J. Gayle, E. Kazyak, K. Sun, B. M. Bartlett, N. P. Dasgupta *Submitted*

9:45am **AA1-TuM-8 Improved Photocatalytic Efficiency by Depositing Pt and SiO_2 on TiO_2 (P25) using Atomic Layer Deposition in a Fluidized Bed***, **Dominik Benz**, H Nugteren, H Hintzen, M Kreutzer, R van Ommen,* Delft University of Technology, Netherlands

Photocatalysts for water cleaning typically lack efficiency for practical and economical applications. Here we present a new material that was developed using knowledge of working mechanisms of catalysts and the abilities of Atomic Layer Deposition (ALD). The deposition of ultrathin SiO_2 layers on TiO_2 nanoparticles, applying ALD in a fluidized bed reactor, showed in earlier studies in our group their beneficial effects for the photocatalytic degradation of organic pollutants. There we assume that due to the surface modification with SiO_2 the surface becomes more acidic which benefits the hydroxyl radical generation. Furthermore, we have investigated the role of Pt on P25 as an improved photocatalyst. There we found the main reason for the catalytic improvement is adsorbed oxygen on the Pt particles, which is an important reactant in the photocatalytic degradation process of organic pollutants. Having recognized, that the two independent materials, SiO_2:P25 and Pt:P25, have different mechanisms improving the photocatalytic activity gave us the opportunity to combine these two materials into a new material, where we deposited SiO_2 onto P25 followed by deposition of nanoclusters of Pt. Indeed, this new material exceeded the performance of the individual SiO_2:P25 and Pt:P25 catalysts. This unconventional approach shows that by understanding the individual materials' behavior and using ALD as an appropriate deposition technique, new materials can be developed, further improving the (photo-)catalytic activity and moving one step closer to implementation. We will demonstrate that ALD is an attractive technology to produce the catalysts developed by this approach in a precise and scalable way.

ALD Applications

Room Grand Ballroom E-G - Session AA2-TuM

ALD for Batteries I

Moderators: Neil P. Dasgupta, University of Michigan, Noemi Leick, National Renewable Energy Laboratory

10:45am **AA2-TuM-12 Atomic Layer Deposition of Glassy Lithium Borate-Carbonate Electrolytes for Solid-State Lithium Metal Batteries***, E Kazyak, A Davis, S Yu, K Chen, A Sanchez, J Lasso, T Thompson, A Bielinski, D Siegel, **Neil P. Dasgupta**,* University of Michigan

Solid electrolytes could enable significant improvements in the energy density, cycle life, and safety of next-generation battery chemistries. The ability to fabricate thin electrolyte films with high ionic conductivity and electrochemical stability on complex architectures has been a bottleneck to realizing a wide range of 3D structured thin-film and bulk batteries. Recent progress in ALD for solid electrolytes has shown great promise, and there is significant interest in realizing materials with even higher conductivities and stability with Li metal anodes in order to dramatically enhance the energy density of ALD-based batteries. In addition, ALD films with high ionic conductivity and good stability could be used for interfacial engineering of bulk-type solid and liquid based batteries to improve stability and safety.

This work demonstrates a novel ALD process for glassy lithium borate-carbonate thin films with ionic conductivities above 10^{-6} S/cm at 298K [1]. This is the highest reported value to date for any ALD-deposited solid electrolyte. The composition, structure, and stability of the films are characterized with X-ray photoelectron spectroscopy and a range of electrochemical measurements. These experiments are compared with those calculated with Density Functional Theory and Molecular Dynamics to elucidate the origins of the high ionic conductivity and excellent stability.

The film properties are studied as a function of ALD deposition temperature, showing tradeoffs between process conditions and performance, and demonstrating the precise control afforded by the ALD process. The optimized film remains an ionic conductor when in contact with metallic Li, with no measurable changes after several weeks, and displays stable cycling when paired with a thin-film cathode and Li metal anode. This new ALD material and process represents a pathway towards interfacial engineering of both thin-film and bulk solid-state batteries, enabling stable cycling against Li metal anodes.

1) Kazyak, E.; Chen, K. H.; Davis, A. L.; Yu, S.; Sanchez, A. J.; Lasso, J.; Bielinski, A. R.; Thompson, T.; Sakamoto, J.; Siegel, D. J.; Dasgupta, N. P. *J. Mater. Chem. A* **2018**, *6*, 19425–19437.

11:00am **AA2-TuM-13 ALD Interlayers for Stabilization of $Li_{10}GeP_2S_{12}$ Solid Electrolytes Against Li Metal Anodes***, **Andrew Davis**,* University of Michigan*; K Wood,* National Renewable Energy Laboratory*; R Garcia-Mendez, E Kazyak, K Chen, J Sakamoto,* University of Michigan*; G Teeter,* National Renewable Energy Laboratory*; N Dasgupta,* University of Michigan

Solid-state batteries based on high-ionic-conductivity solid electrolytes are a promising technology to increase battery lifetime and capacity, and reduce safety concerns associated with flammability. In recent years, sulfide solid electrolytes such as $Li_{10}GeP_2S_{12}$ (LGPS) have achieved ionic conductivities comparable to or higher than that of traditional liquid electrolytes. Despite these promising breakthroughs, realization of sulfide solid-state batteries with high capacities and energy densities has proved elusive. This can be attributed to the narrow electrochemical stability window of sulfide electrolytes, which leads to undesirable reactions at the electrode/electrolyte interface against both high voltage cathode materials and Li metal anodes. This forms an unstable solid electrolyte interphase (SEI), which dramatically degrades battery performance. Artificial SEIs made of ALD interlayers have recently been explored as a method of increasing stability of the Li metal/solid electrolyte interface. ALD allows for conformal, pinhole free coating of the LGPS which protects the surface from direct contact with lithium metal while facilitating Li-ion transport across the interface.

In this study, we explore the impact of ALD interlayers at the LGPS-Li metal interface, in order to gain a deeper fundamental understanding of the dynamic evolution of the SEI. A multi-modal characterization approach was performed that combined electrochemical measurements*, operando* X-ray photoelectron spectroscopy (XPS), *in-situ* auger spectroscopy, scanning electron microscopy (SEM), and optical microscopy. This allowed for quantitative evaluation of the time-dependent degradation of the interface, which occurs due to the evolution of a variety of decomposition by-products. ALD coated samples exhibited significantly less decomposition of the LGPS interface. *Operando* XPS was used to correlate the distinct decomposition products that correspond to increases in overpotential [1]. Auger, SEM and optical mapping of the surface shows spatial inhomogeneities that lead to preferential Li plating and corresponding $Li_{10}GeP_2S_{12}$ breakdown. These observations were rationalized in the context of bulk solid-state batteries employing Li metal anodes, demonstrating the advantages and challenges associated with ALD modification of solid-state battery interfaces.

K. N. Wood, K. X. Steirer, S. E. Hafner, C. Ban, S. Santhanagopalan, S.-H. Lee, G. Teeter, *Nature Communications* **9**, 2490 (2018).

11:15am **AA2-TuM-14 ALD and MLD on Lithium Metal – A Practical Approach Toward Enabling Safe, Long Lasting, High Energy Density Batteries***, **Andrew Lushington**,* Arradiance*; Y Zhao, L Goncharova, Q Sun, R Li, X Sun,* University of Western Ontario, Canada

Global warming and rising levels of atmospheric CO_2 have resulted in a rapid search for alternative energy sources. Among the possible portable energy storage systems available, lithium-based batteries have the highest theoretical energy density. Unfortunately, current battery technology is approaching its limits and research toward alternative battery chemistries with higher energy density, such as Li-S, Li-O_2 and all solid-state batteries, is required to meet future energy storage demands. However, these next-generation batteries require the use of a pure Li-metal anode .[1] Li-metal has a high specific capacity of 3860 mAh g^{-1}, a value 10x greater than the standard graphite anode (370 mAh g^{-1}) used today. Unfortunately, Li-metal is highly reactive and forms a high surface area mossy-like reaction product with the electrolyte, known as the solid electrolyte interface (SEI). The uncontrolled growth of this SEI rapidly consumes liquid electrolyte, drying up the battery and causing it to quickly fail. This problem is further exacerbated by dendrite growth which can short circuit the battery, posing a significant safety threat.[2] One effective strategy for mitigating these problems is to use Atomic layer deposition (ALD) and molecular layer deposition (MLD) to coat the surface of electrodes. This strategy has been shown to help form a stable SEI layer and improve battery longevity.[3]

Herein we compare the stripping and plating behavior of Li-metal coated using 3 different ALD and MLD films. Galvanostatic cycling revealed that MLD coated electrodes vastly outperform ALD coated ones. We use Gravimetric Intermission Titration Technique (GITT) to carefully analyze the voltage behavior of coated electrodes and disseminate the key MLD film properties that enable the formation of a stable SEI layer. Additionally, electrode morphology was examined using scanning electron microscopy along with Rutherford backscattering spectroscopy to reveal the composition of the SEI. To further demonstrate the practicality of MLD coated Li-metal, full cell batteries using lithium iron phosphate and carbon-sulfur as a cathode was performed. This presentation provides the necessary fundamental understanding of the hurdles that face the commercialization of lithium metal anodes and how ALD/MLD can be used to address these challenges.

1. Lin, D., Liu, Y. & Cui, Y. Reviving the lithium metal anode for high-energy batteries. *Nat. Nanotech.* **12**, 194–206 (2017).

2. Palacín, M. R. & De Guibert, A. Batteries: Why do batteries fail? *Science.***351**, (2016).

3. Zhao, Y. et al. Robust Metallic Lithium Anode Protection by the MLD Technique. *Small Methods.***2(5)**, 1700417 (2018).

11:30am **AA2-TuM-15 Synergistic Effect of 3D Current Collectors and ALD Surface Modification for High Coulombic Efficiency Lithium Metal Anodes***, **Kuan-Hung Chen**, A Sanchez, E Kazyak, A Davis, N Dasgupta,* University of Michigan

Improving the performance of Li metal anodes is a critical bottleneck to enable next-generation battery systems beyond Li-ion. However, stability issues originating from undesirable electrode/electrolyte interactions and Li dendrite formation have impaired long-term cycling of Li metal anodes. In this work, we demonstrate a bottom-up fabrication process using templated electrodeposition of vertically aligned Cu pillars, which are subsequently coated by an ultrathin layer of ZnO by atomic layer deposition (ALD) to form a to form core-shell geometry with precise thickness control [1]. Transmission electron microscopy (TEM) analysis was performed to show the uniform thickness and core-shell geometry on the pillar surface. We demonstrate the application of these core-shell 3-D architectures as an efficient current collector for Li metal electro-deposition and dissolution. By rationally tuning geometric parameters of the 3D current collector architecture, including pillar diameter, spacing, length, and ALD shell thickness, the morphology of Li plating/stripping upon cycling can be controlled.

We further demonstrate the mechanistic role of the ZnO shell on current collector surface, which facilitates the initial Li nucleation, and influences the morphology and reversibility of subsequent cycling. The improved nucleation is correlated with increased wettability of molten Li metal, which is quantitively evaluated using a sessile drop test inside of an argon glovebox. The resulting core-shell pillar architecture allows for the geometry and surface chemistry to be decoupled and individually controlled to optimize the electrode performance. Leveraging the synergistic effects of the optimized 3D geometry and ALD surface modification, we have demonstrated cycling of Li metal anodes with Coulombic efficiency of 99.5%, which is among the highest reported values to date for any Li metal anode. The results from this work thus provide a pathway toward high-efficiency and long-cycle life Li metal batteries with reduced excess Li loading.

[1] K.-H. Chen, A. J. Sanchez, E. Kazyak, A. L. Davis, N. P. Dasgupta, *Adv. Energy Mater*. **9**, 1802534 (2019).

11:45am **AA2-TuM-16 Atomic Layer Deposition FeS@CNT from Elemental Sulfur as an Electrode for Lithium-Ion batteries***, **Hongzheng Zhu**, J Liu,* University of British Columbia, Canada

Iron sulfide (FeS) is regarded as an attractive anode material for high-performance LIBs because of its high lithium storage capability, natural abundance, and ecofriendly. However, FeS suffer from low reversible capacity and large volume change (200%) during charging and discharging process, resulting in mechanical degradation of cracking and loss of electrical connection with current collectors and then rapid capacity loss [1]. In order to overcome these problems, we choose ALD (Atomic Layer Deposition) method to deposit a controllable thin layer on CNT to building 3D nanostructured electrode for Li-ion batteries [2-3]. In this work, ALD method are chosen to realize thickness and size control of FeS, and CNTs are applied for replacing traditional carbon black to further improve the electrical conductivity and excellent physical support for the electrodes. In most of the metal sulfide ALD processes, film was deposited by using H_2S as the source of sulfur. However, H_2S is a flammable, corrosive, and highly toxic gas, and its incorporation in the ALD technology presents several serious technical challenges. Therefore, the aspiration for a new route of FeS by ALD process seems particularly strong. It is known that sulfur-based ALD processes have been reported for copper sulfide thin films recently [4]. But there is no report on FeS sulfur-based ALD process.

Here, we present a simple ALD process for the deposition of FeS thin films by using elemental sulfur as sulfur source, and test its performance in Li-ion batteries, as a highly viable solution to the challenges discussed above. The XPS spectra of the Fe 2p and S 2p regions are shown in figure a and b for FeS thin film with ALD deposited temperature at 180 °C. The Fe 2p3/2 peaks located at 710.6 and 713.0 eV belong to Fe^{2+} of FeS, which is a solid evidence for the existence of FeS. However, the FeS might partially be oxidized to $FeSO_4$. From the S 2p region in figure b, S 2p3/2 at binding energies 169.1 and 170.2 eV are belonging to SO_4^{2-}, which is the proof of FeS oxidation. Figure c shows the growth rate of FeS is ≈5.2 Å per cycle. The cyclic voltammograms (CVs) of the FeS electrode are shown in Figure d. The strong peak at 0.7 V is attributed to the decomposition of the electrolyte and formation of a solid electrolyte interlayer (SEI) in the first cathodic scan. The peak at 1.7 V in the second cathodic scan is related to the reversible interaction of Li^+ with FeS: $2FeS + 2Li + 2e^- = Li_2FeS_2 + Fe$. In the anodic sweep, the oxidation peak appear obviously at 2.5 V is attributed to the oxidation of Fe and the delithiation process of Li_2FeS_2 to form $Li_{2-x}FeS_2$.

ALD Applications
Room Grand Ballroom E-G - Session AA1-TuA
Emerging Applications I

Moderators: Anjana Devi, Ruhr University Bochum, Han-Bo-Ram Lee, Incheon National University

1:30pm **AA1-TuA-1 Atomic Layer Deposition of Indium Gallium Zinc Oxide (IGZO) Semiconductor Thin Films: From Precursor to Thin Film Transistor Application***, **Jin-Seong Park,*** Hanyang University, Republic of Korea **INVITED**

Oxide semiconductor thin film transistors (TFTs) have been extensively researched as a switching device in display industry. Also, the amorphous indium gallium zinc oxide (a-IGZO) have been already adopted for the mass-production of OLED TVs because it showed remarkable performances such as high mobility (>10cm^2/V. sec), low process temperature (<350^{o}C), optical transparency (>3eV) and low-cost fabrication process. Recently, there are a few efforts to fabricate atomic layer deposited (ALD) IGZO thin films and demonstrating their device properties. However, ALD IGZO systems are quite difficult to understand their electrical and chemical properties because each precursor is affected to growth mechanism, crystallinity, and electrical performance.

In this talk, I will show key properties (growth behavior, electrical/chemical properties, and device performances) of indium gallium oxide (IGO) and indium gallium zinc oxide (IGZO) thin films depending on a few In and Ga precursor species. There films are deposited using the concept of “super-cycle” – IGO (n cycle InO_x – m cycle GaO_x) and IGZO (n cycle of InO_x – m cycle of GaO_x – k cycle of ZnO). Then, the bottom gate-top contact (inverted staggered structure) thin film transistors were fabricated by ALD processes. The devices with IGO and IGZO active layers are named Device A (IGO TFT using Indium A precursor), Device B (IGZO TFT using indium B precursor), Device C (IGZO TFT using Indium B precursor), Device D (IGZO TFT using indium B’ precursor).

The representative transfer curves and performance parameters are shown in Figure 1 and Table 1. The IGZO device D exhibited boost mobility of 74.4 cm^2/V.sec. but the IGZO device B and C with different Indium precursors showed different mobilities of devices. It may result from a different growth rate and film composition. Thus, it is believed that ALD IGZO TFT will be very promising for the next generation switching transistor beyond the low-temperature poly-silicon (LTPS) thin film.

2:00pm **AA1-TuA-3 ALD Growth of Ultra-thin Co Layers on the Topological Insulator Sb_2Te_3***, **Emanuele Longo,** R Mantovan, R Cecchini,* CNR-IMM Unit of Agrate Brianza, Italy*; M Overbeek,* Wayne State University*; M Longo,* CNR-IMM Unit of Agrate Brianza, Italy*; L Lazzarini,* CNR-IMEM, Italy*; M Fanciulli,* Università degli Studi di Milano-Bicocca, Italy*; C Winter,* Wayne State University*; C Wiemer,* CNR-IMM Unit of Agrate Brianza, Italy

The coupling between ferromagnetic thin films (FMs) and topological insulators (Tis) is nowadays one of the hottest topics in the context of spintronics. The presence of Dirac-like dispersed surface states in the TI, jointly with the presence of a large spin-orbit coupling, is expected to favor a super-efficient (i.e. low-power) FM’s magnetization manipulation through a large *spin orbit torque* (SOT). The role of the interface between Co and TI is fundamental in driving SOT functionalities, making the choice of the deposition technique crucial and itself often responsible of low-quality interfaces formation. The high conformality, excellent low thickness control and its low energetic character make atomic layer deposition (ALD) an appealing technique for spintronic applications. We present here a pure ALD process to grow few nm-thick Co metal films in direct contact with a granular-TI Sb_2Te_3 thin film grown by Metal Organic Chemical Vapor Deposition (MOCVD). The ALD of Co metal films was performed by alternating a saturative pulsing sequence of bis(1,4-di-tert-butyl-1,3-diazadienyl)cobalt ($Co(^{tBu2}DAD)_2$) (4 s), N_2 purge (10 s), *tert*- butylamine ($tBuNH_2$) (0.1 s) and N_2 purge (10 s) at 180°C. In order to compare the Co growth on the Sb_2Te_3 substrate, we performed simultaneous Co depositions on sputtered Pt substrates (conventionally used as a SOT material), maintaining the same number of cycles. We conducted a thorough chemical-structural characterization of the Co/Sb_2Te_3 and Co/Pt heterostructures by employing X-Ray Diffraction (XRD), X-Ray Reflectivity, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The results demonstrated the possibility to synthesize Co thin films from several tens, down to 4 nm, forming uniform and high-quality Co thin films characterized by a stable and sharp interface with the Sb_2Te_3 substrate. Indeed, XRR showed that the thinner Co films replicate the surface roughness of the Sb_2Te_3 buried layer, proving their conformal growth. The growth rate was found to be higher on Sb_2Te_3 than on Pt. XRD evidenced the substrate selectivity of this growth process, showing the structural continuity of the grown Co layer on the underlying substrate. On Pt, the Co grains were found to adapt to the [111] textured substrate by developing a strained cubic structure. On Sb_2Te_3, Co was shown to grow with hexagonal structure, with out-of-plane grains oriented along the [00l] direction, as the rhombohedric Sb_2Te_3 layer. The distinct magnetic ordering of cubic and hexagonal Co polymorphs, with the possibility to selectively grow Co with different magnetic properties, pave the way towards novel applications in spintronics.

2:15pm **AA1-TuA-4 Modifying Interfacial Chemistry of Cellulose-Reinforced Epoxy Resin Composites using Atomic Layer Deposition (ALD)***, **Jamie Wooding**, Y Li, K Kalaitzidou, M Losego,* Georgia Institute of Technology

Automotive and aerospace industries require new lightweight materials that enhance payload and improve efficiency via vehicle weight reduction. Employing composites, such as fiber-reinforced polymer resins, is a common approach to light-weighting these vehicles. In this talk, we will examine the use of ALD to modify the surface chemistry of cellulosic reinforcements to improve the interfacial adhesion in polymer resin composites. Cellulosic reinforcements offer advantages in sustainable materials sourcing, lower density, and lower cost. However, raw cellulosics are hydrophilic and are immiscible with most non-polar thermosetting polymer resins. In this study, a variety of ALD-derived surface modification schemes are discussed as a means to improve resin permeation within the fibrous structure and to establish better adhesion at the cellulose – polymer matrix interface. Specifically, we consider surface modification with the ALD-precursors trimethylaluminum (TMA) and titanium tetrachloride ($TiCl_4$), as well as with vapor-delivered carboxylic acids and silanes. Surface modification is confirmed with XPS studies and contact angle measurements. All are found to make the cellulose prepreg more hydrophobic, but the $TiCl_4$ – H_2O treatment demonstrates the best permeability for the polymer resin. Composites treated with low cycles of $TiCl_4$ – H_2O are found to have a 30% improvement in the modulus of elasticity and a 38% increase in the tensile strength compared to untreated cellulose – resin composites. Furthermore, the $TiCl_4$ – H_2O surface treatment results in a composite tensile strength equal to that of a 3-aminopropyltriethoxysilane, a widely-used surface modifying agent, treatment while avoiding the disadvantages of using wet chemistry. The structural enhancements in the cellulose – resin composite, as demonstrated via wicking studies and scanning electron microscopy (SEM), inform these improvements in mechanical properties.

2:30pm **AA1-TuA-5 Atomic Layer Deposition of Au Nanoparticles on Titania***, **Fatemeh S.M. Hashemi,*** Delft University of Technology, Netherlands*; F Grillo,* ETH Zurich, Switzerland*; V Ravikumar, D Benz, A Shekhar,* Delft University of Technology, Netherlands*; M Griffiths, S Barry,* Carleton University, Canada*; J van Ommen,* Delft University of Technology, Netherlands

Nanoparticles of Au supported on TiO_2 have various applications in photocatalysis, plasmonics and photovoltaics. These supported materials are commonly synthesized using liquid-based techniques such as sol-gel and deposition-precipitation. These methods, while being low-cost, result in high level of impurities and formation of Au particles with inhomogeneous size and composition. Here we present a vapor-based approach via atomic layer deposition (ALD) for controlled deposition of Au nanoparticles on TiO_2. We also use the designed structures for photocatalytic degradation of pollutants.

We perform a low temperature (105 °C) thermal ALD process using Trimethylphosphino-trimethylgold (III) and two oxidizers (ozone and water) in a fluidized bed reactor under atmospheric pressure condition. While plasma-assisted ALD of Au using Trimethylphosphino-trimethylgold (III) has been previously reported (Griffiths et al., Chemistry of Materials 2016), no studies have looked into the thermal deposition process for this precursor. We investigate the effects of Au precursor saturation and oxidizing reactants on controlling the nucleation, particle size distribution and composition of the Au nanoparticles.

Our studies suggest that ozone and water have an opposite effect on Au particle size distribution. While longer ozone pulse time results in the deposition of smaller Au particles, larger particles are formed when water pulse time is increased. TiO_2 nanoparticles have a high surface area of about 50 m^2/g, thus achieving precursor saturation on them requires long precursor dosage times. However, we show that the growth properties can also be controlled in the under-saturation regime. We also investigated the effects of Au loading and particle size on the photocatalytic activity of

Au/TiO_2 nanoparticles. A 3 fold enhancement in the photocatalytic activity of TiO_2 is achieved when Au/TiO_2 nanoparticles are used for degradation of the model pollutants (Acid Blue 9 and Rhodamine B). This all vapor process provides a highly controlled and efficient method for producing Au/TiO_2 particulates that meet the criteria for various applications.

2:45pm **AA1-TuA-6 Multi-layer Protective Coatings on Silver for Protection of Historic Silver Artifacts***, E Breitung,* Metropolitan Museum of Art*; S Creange,* Rijks Museum, Netherlands*; G Pribil,* J.A. Woollam*; A Bertuch,* ***Ritwik Bhatia****,* Veeco-CNT

Historic silver artifacts are usually protected from tarnish by polymer-based coatings such as nitro-cellulose lacquer [1]. These coatings can be problematic because of uneven application, incomplete coverage and yellowing due to age. This has led to investigation of atomic later deposition of oxide layers as a possible alternative to lacquer based protective coating. It is important that the ALD coatings do not change the appearance (color, luminance) of the artifact. This is particularly challenging since historic silver can have bulk compositional variability as well as differences in surface composition [2].

In this work we start with substrates of silver content between 75% - 99.9% with copper as the major impurity. These substrates are characterized by variable angle spectroscopic ellipsometry to obtain their optical properties across the visible spectrum. It is found that (a) optical properties of the silver substrates depend significantly on composition and surface finish, and (b) a thin (2-11nm) interface layer is required to adequately model the ellipsometric data.

The optical model of the substrates obtained by ellipsometry is used to obtain the reflection spectrum and color of the substrates when coated with various ALD films such as SiO2, Al2O3 and TiO2. The modeled color of the coated substrate is compared to an uncoated substrate using the color difference metric (ΔE_{00}) [3]. Consistent with previous findings [4], we show that pure silver (99.99%) can be coated with SiO2 and Al2O3 without a perceptible color difference ($\Delta E_{00} < 1$) for a wide angle of incidence range (AOI = 0-75°). However, for silver alloys (80-95% silver) there is no coating thicker than 10nm that results in $\Delta E_{00} < 1$. [Figure-1]

The need to find a film stack that worked not just for pure silver but for silver alloys led to a multi-objective optimization problem – minimizing ΔE_{00} for silver substrates of different composition and AOI in 0-60°. A multi-layer film stack was found that showed $\Delta E_{00} < 1.25$ for all substrates for AOI=0-70°.

In addition to the optical characterization, modelling and optimization work mentioned above, we will report on the deposition and color measurement of the ALD films stacks on the silver substrates.

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3:00pm **AA1-TuA-7 Nonlinear Optical Properties of TiO_2-Based ALD Thin Films***, **Theodosia Gougousi**, R Kuis, I Basaldua, P Burkins, J Kropp, A Johnson,* University of Maryland, Baltimore County

Nonlinear materials in thin film form are highly desirable for the development of ultrafast all-optical system on-a-chip platforms, optical frequency converters and optical limiting applications. Conventional nonlinear optical (NLO) materials are usually cut from bulk crystals or are liquids that are not suitable for integration with the contemporary semiconductor industry process flow. The third order nonlinear response of ALD TiO_2-based films is investigated using thermally managed Z-scan technique. Some of the as-deposited films exhibit very high nonlinear response which is orders of magnitude higher than conventional nonlinear optical materials such as silica fibers and CS_2. Thermal treatment of the films at 450°C for 3 hours in an oxygen rich atmosphere affects the films' optical properties and results in the loss of the high nonlinear optical response. TiO_2 films deposited by Physical Vapor Deposition (PVD) from a 99.9% TiO_2 target at room temperature are used as control samples and their nonlinear optical response is found below the detection limit of the Z-scan setup. This extraordinary nonlinear optical behavior of the TiO_2 ALD films is linked to the presence of a very small at. % of TiN bonding in the film. We will present detailed characterization of these films by x-ray photoelectron spectroscopy, x-ray diffraction and UV-Vis absorption. The high level of control of the nonlinear index of refraction, n_2, using the deposition process coupled with the ability of ALD to coat non-planar geometries with atomic level precision and the fact that these processes are CMOS compatible have the potential to provide a breakthrough in optical device design and applications.

3:15pm **AA1-TuA-8 Atomic Layer Deposition to Alter the Wetting and Thermal Properties of Lumber***, **Shawn Gregory**, C McGettigan, E McGuinness, D Rodin, S Yee, M Losego,* Georgia Institute of Technology

This talk will discuss the use of atomic layer deposition (ALD) to modify the surface chemistry of bulk wood to alter its wettability and thermal conductivity. Wood blocks were ALD treated with three different metal oxide chemistries: $TiCl_4$-H_2O, $Al(CH_3)_3$-H_2O, and $Zn(C_2H_5)_2$-H_2O. All treatments consisted of only 1 ALD cycle. The resulting chemical modification of the wood with TiO_2, Al_2O_3, and ZnO was confirmed with energy dispersive X-ray (EDX) spectroscopy. All ALD chemistries made the wood hydrophobic with contact angles ranging from 90° to 130°. However, upon water submersion, it was found that TiO_2 coated wood had the least water uptake. While untreated wood absorbed up to 70 wt% water, the optimized TiO_2 treatment exhibited only a 10 wt% water uptake after 60 minutes. To understand these differences, we have considered the effective Fickian diffusion kinetics in the high-aspect ratio porosity of the wood structure. Measured pressure changes fit to Fickian diffusion models suggest that $Al(CH_3)_3$, and $Zn(C_2H_5)_2$ follow diffusion limited kinetics while $TiCl_4$ follows reaction limited kinetics. The apparent faster gas diffusion of $TiCl_4$ presumably results in more conformal coverage of the wood's structure. These models also suggest that $TiCl_4$ reacts to a greater extent than either Al or Zn precursor in this study. Because water content contributes significantly to the thermal transport of wood, we also measured thermal conductivity using the hot disc technique. Under dry conditions, untreated and TiO_2 coated wood have approximately the same thermal conductivity (~0.2 $W \cdot m^{-1}K^{-1}$). However, whereas the thermal conductivity of untreated wood increases by 50% in our tested wet environments, the thermal conductivity of $TiCl_4$ treated lumber remains nearly constant.

ALD Applications
Room Grand Ballroom E-G - Session AA2-TuA
ALD for Batteries II

Moderator: Yong Qin, Institute of Coal Chemistry, Chinese Academy of Sciences

4:00pm **AA2-TuA-11 Tunable Electrical Properties of Lithium Fluoride Thin Films using Different Fluorine Sources***, **Devika Choudhury**, A Mane, J Elam,* Argonne National Laboratory

Considering that it has one of the largest optical bandgaps, lithium fluoride is probably the most popular material of choice for ultraviolet coatings today, as compared to other metal fluorides like MgF_2 and AlF_3. The low refractive index of 1.39 (at 580nm) also makes it useful as a window material in the UV-region of electromagnetic radiation.[1] Other utilities of LiF include thermoluminescent detector layers for X-rays and extreme UV sensor applications, electron injection layers in LED or photovoltaics etc.[2] Apart from optical applications, LiF may be useful as a protective coating on the cathodes of Li-ion batteries due to its chemical stability and wide electrochemical window. In this regard, LiF can be mixed with other metal fluorides to improve the lithium-ion conductivity while maintaining the chemical stability. Lithium ion conductivities of order 10^{-6} S/cm at room temperature have been reported for Li_3AlF_6 and Li_2NiF_4.[3]

LiF thin films grown by atomic layer deposition have been reported earlier using lithium tert-butoxide and HF-pyridine resulting in a room temperature ionic conductivity of 10^{-14} S/cm.[4] In this work we explore the possibility of growing LiF films with alternate sources of fluorine, WF_6 and MoF_6. *In-situ* quartz crystal microbalance and fourier transform infrared spectroscopy studies are carried out to obtain the growth characteristics of the films. Compositional analysis is obtained from XPS measurements. Impedance spectroscopy measurements are performed to evaluate the effect of LiF concentration in mixed metal fluoride coatings.

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4:15pm **AA2-TuA-12 The Role of Al_2O_3 ALD Precursor Chemistry on the Electrochemical Performance of Lithium Ion Battery Cathode Mmaterials**, ***Donghyeon Kang**, A Mane, J Elam,* Argonne National Laboratory*; R Warburton, J Greeley,* Purdue University

Al_2O_3 coatings prepared by atomic layer deposition (ALD) using trimethyl aluminum (TMA) and H_2O on lithium metal oxide cathode surfaces have been shown to enhance the performance of lithium ion batteries. However, the effects depend on the choice of cathode material. For example, 1-2 TMA/H_2O cycles on lithium cobalt oxide (LCO) dramatically improves cyclability and slightly decreases capacity [1]. In contrast, the same treatment on lithium manganese oxide (LMO) improves capacity but has little effect on cyclability [2]. Furthermore, the TMA surface reactions on LMO are unusual in that they do not involve hydroxyls, ethane is released, and the Mn undergoes redox chemistry. Density functional theory (DFT) calculations reveal that this unique mechanism is driven by the large free energy changes upon methyl loss from TMA [2]. This leads us to speculate that the surface reactions and subsequent electrochemistry might also depend on the choice of Al precursor. To evaluate this hypothesis, we are exploring a range of aluminum precursors including trimethyl aluminum (TMA), tris(dimethylamido) aluminum (Al-TDMA), aluminum trichloride ($AlCl_3$), dimethyl aluminum isopropoxide (DMAI), and aluminum triisopropoxide (ATIP) on a variety of cathode materials such as LCO, LMO, and nickel manganese cobalt (NMC) materials. Our initial results suggest a correlation between cation reduction on the cathode surface and the relative Lewis acidity of the Al precursor ligands. We will elaborate on these findings using results from XPS measurements, DFT calculations, and coin cell cycling studies.

[1] Y. S. Jung et. al., *J. Electrochem. Soc.***157** (1) A75-A81, (2010).

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4:30pm **AA2-TuA-13 Spatial Atomic Layer Deposition of Hybrid Nanolaminates for High Capacity Li-ion Battery Electrodes**, *E Balder, L Haverkate, M Tulodziecki, F van den Bruele, S Unnikrishnan,* ***Paul Poodt**,* TNO/Holst Center, Netherlands

Lithium-ion batteries have become the dominant battery technology in many applications. For future applications, there are still several challenges that need further development, including increasing the energy- and power density, reducing charging time, increasing the lifetime and improving the safety of operation. Solutions to these challenges can be found in combinations of new battery architectures, high performance materials and manufacturing methods.

ALD could be one of these new manufacturing methods, because of its unique characteristics in terms of film quality, uniformity and step coverage. For that reason, ALD is being explored for a wide variety of functional layers inside battery devices. One main drawback of ALD is its low deposition rate, limiting throughput and thereby leading to high manufacturing costs. Atmospheric pressure Spatial ALD could be a solution to this challenge, as it combines all the benefits of ALD with high deposition rates and scalability to large areas. Spatial ALD technology has already been developed for high performance applications in e.g. photovoltaics, roll-to-roll SALD for barrier foils and large-area SALD for OLED displays. This technology can potentially also be used as future manufacturing method of next generation solid state (3D) lithium ion batteries.

A material that is receiving considerable attention as an electrode for lithium-ion batteries is TiO_2, since it offers a potentially cheap, environmentally friendly and stable alternative to the current electrode materials. However, due to its low electronic conductivity and poor Li-ion conductivity it has a poor rate performance. The rate performance of TiO_2 films can be increased by decreasing the thickness, which comes at a cost of capacity. Nanolaminates of TiO_2 films can be used to maximize both the capacity and rate performance, where a stack of a number of thin TiO2 films will have a higher capacity than a monolithic film with the equivalent thickness. We have used Spatial ALD to make a hybrid nanolaminate film composed of thin TiO_2 layers separated by decoupling layers made by Spatial MLD of aminophenol-based titanicones. These decoupling layers have both a sufficient electrical conductivity and ionic conductivity in order for Li ions to penetrate in the underlying TiO_2 layers. When tested in a coin cell configuration, these nanolaminate electrodes demonstrate a 2-3 higher capacity than the reference, bulk $TiO\text{-}_2$ electrodes of the same thickness, a high Coulombic efficiency and a good cycling stability. These results demonstrate the potential of nano-scale engineered high performance electrodes made by high throughput Spatial ALD.

4:45pm **AA2-TuA-14 Lithium Organic Thin Films for Various Battery Components**, ***Juho Heiska**, M Karppinen,* Aalto University, Finland

The field of energy storage is constantly evolving and facing new challenges. The next-generation batteries should be cheap, constitute of abundant elements only, and show electrochemical performances at least on par with the current state-of-the-art lithium-ion batteries. One of the promising new material families is the organic electrode materials; they are composed of light elements and thus possess high gravimetric capacities. Organic electrode materials do however suffer from low electronic conductivity and solubility issues when applied with a liquid electrolyte. Coating the organic materials with a thin passivation or solid-electrolyte layer is an effective way to suppress the dissolution without dramatically affecting the electrochemical properties. An attractive way to deposit these layers in a controlled manner is the atomic/molecular layer deposition (ALD/MLD) method. When organic electrodes are deposited with ALD/MLD the redox mechanisms are easy to experiment on since the system works as such without any conducting carbon or binder making it a simple model system. The deposition of solid electrolytes or protective coatings is also a highly feasible application for ALD/MLD.

In this research, a new ALD/MLD processes were developed for promising organic electrode materials and novel Li-organic coatings. The experimented molecules are related on the known electrode material lithium terephthalate with additional functional groups which alter the electrochemical properties. Since the bulk electrode composition is not standard in literature the comparison of the materials is difficult and prone to error. When the thin films of lithium-2-aminoterephthalate and lithium-2,5-dihydroxyterephtalate (Li_2DHTP) are compared with lithium terephthalate (Li_2TP) the direct comparison of electrochemical performance is possible. We find that both of the films do decrease the redox voltage as expected but also the flat discharge plateau of Li_2TP is lost. In addition, the rate capability and the cycling life of the films were negatively affected. We propose that the functional groups that donate electron density to the π-conjugated system are causing π-π repulsion between adjacent molecules. In addition, it was found hydroxyl groups of Li_2DHTP are lithiated at low potentials vs. Li^+/Li. Also, a novel lithium ethylene glycol ALD/MLD process was developed showing promising properties as a coating material for lithium-ion batteries. This and previous studies demonstrates the feasibility of this approach for developing better batteries and battery materials and highlights the potential of ALD/MLD technique for actual battery applications.

5:00pm **AA2-TuA-15 ALD Infiltration of $LiCoO_2$ for High Rate Lithium Ion Batteries**, ***Ian Povey**, M Modreanu, S O'Brien,* Tyndall National Institute, Ireland*; T Teranishi, Y Yoshikawa, M Yoneda, A Kishimoto,* Okayama University, Japan

Atomic layer deposition (ALD) was selected to deposit Al_2O_3 on cathode active material, $LiCoO_2$, to create a protective barrier layer [1], supress the high potential phase transition and thus reduce the subsequent Co dissolution [2]. However, surprisingly in this study it was found that it also resulted in the reduction of the charge transfer resistance at the cathode-electrolyte interface, thus enhancing the performance of the battery and not just its robustness. Energy-dispersive X-ray spectroscopy, in conjunction with transmission electron microscopy, shows that a discrete Al_2O_3 shell was not formed under the selected growth conditions and that the Al diffused into the bulk $LiCoO_2$ [3]. The resulting active oxide material, which was significantly thicker than the nominally Al_2O_3 ALD growth rate would predict, is proposed to be of the form $LiCoO_2$: Al with amorphous and crystalline regions depending on the Al content. Cells fabricated from the modified electrodes were found to have good cycling stability and discharge capacities of ~110 $mAhg^{-1}$ and ~35 $mAhg^{-1}$ at 50C and 100C respectively. Here we discuss the reasoning behind these observations and through a series of electrode treatments prior to ALD tune the behaviour.

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5:15pm **AA2-TuA-16 ALD Al_2O_3 and MoS_2 Coated TiO_2 Nanotube Layers as Anodes for Lithium Ion Batteries***, H Sopha,* University of Pardubice, Czech Republic*; A Tesfaye,* Ecole Nationale Supérieure des Mines de Saint-Etienne, France*; R Zazpe,* University of Pardubice, Czech Republic*; T Djenizian,* Ecole Nationale Supérieure des Mines de Saint-Etienne, France*; **Jan Macak**,* University of Pardubice, Czech Republic

The miniaturization of Lithium ion batteries (LIBs) as a power source to drive small devices such as smartcards, medical implants, sensors, radio-frequency identification tags etc. has been continuously developed to meet the market requirements of portable applications.[1] In this direction, 3D microbatteries have been considered to satisfy the requirements of these portable devices. Anodic TiO_2 nanotube layers (TNTs) have been recently explored as anodes for LIBs due to their high surface area, low volume expansion, short diffusion lengths for Li^+ ion transport and good capacity retention even at faster kinetics.[2,3]

Recently, various coatings produced by Atomic Layer Deposition (ALD) on electrode materials have been explored extensively in LIBs. For example, Al_2O_3 and TiO_2 coatings act as a protective layer for the suppression of the solid electrolyte interphase (SEI) in various electrode materials.[4,5] But their influence on increasing the electronic conductivity of the electrode material has not been explored in details. In addition, it is also possible to synthesize using ALD the main electrode materials, such as oxides[6] and sulphides.[7] However, high surfacearea and sufficiently conducting support would be beneficial for these ALD derived materials to support an excellent performance of the batteries. The door for various one-dimensional nanomaterials, such as TNTs, is therefore open

In this presentation, we will show ALD synthesis of Al_2O_3[8] and MoS_2[9] coatings on TNTs as new electrode material for lithium-ion batteries. We show an influence of different coating thicknesses on the battery performance, in particular on the charging and discharging capacity.

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ALD Applications
Room Grand Ballroom A-C - Session AA3-TuA
ALD for Memory Applications I

Moderators: Scott B. Clendenning, Intel Corp., Adrien LaVoie, Lam Research Corp.

4:00pm **AA3-TuA-11 Doped Hi-K ALD Films of HfO_x and ZrO_x for Advanced Ferroelectric and Anti-Ferroelectric Memory Device Applications:***, **Niloy Mukherjee**, J Mack, S Rathi,* Eugenus, Inc.*; Z Wang, A Gaskell, N Tasneem, A Khan,* Georgia Institute of Technology*; M Dopita, D Kriegner,* Charles University **INVITED**

The discovery of ferroelectricity in doped hafnium oxide has generated excitement in the solid-state device community in recent years since hafnium oxide is a relatively simple oxide compared to traditional perovskite-based ferro-/anti-ferroelectric materials, and hafnium oxide is already used widely in the semiconductor industry. The discovery has inspired many researchers to study the system in further detail in the past few years. Recently, this group has discovered the ability to obtain anti-ferroelectric ZrOx in as-deposited ALD films alone, without the need for capping metallic electrodes or any post-deposition/post-metallization annealing. Tunability of the anti-ferroelectric behavior of ZrOx is also demonstrated using lanthanum doping and is co-related to changes in unit cell tetragonality with lanthanum doping. Process methods, including precursor delivery schemes and ALD deposition schemes, used to deposit doped HfOx and ZrOx-based ferroelectric and anti-ferroelectric films will be described in detail. Structural and electrical properties of such films will be described in detail and co-related.

[See figure in attachment]

4:30pm **AA3-TuA-13 ALD of La-Doped HfO_2 Films for Ferroelectric Applications***, **Tatiana Ivanova**, P Sippola, M Givens,* ASM, Finland*; H Sprey,* ASM, Belgium*; T Büttner, P Polakowski, K Seidel,* Fraunhofer IPMS-CNT, Germany

Ferroelectric (FE) HfO_2 and its doped compounds [1] have received increasing interest for potential to harness these materials for non-volatile memory applications. ALD HfO_2-based ferroelectrics can provide smooth process integration to silicon based semiconductor technology in contrast to e.g., perovskite FE materials. Especially, La-doped HfO_2 films have been shown to exhibit superior ferroelectric responses with the so far highest reported remanent polarization for doped FE-HfO_2 [2]. Nevertheless, a comprehensive in depth study of this promising material system has not been done.

This research covers highlights of the growth and FE properties of La-doped HfO_2 ALD films. The 10 nm La-doped HfO_2 films were deposited on 300 mm Si wafers in an ASM Pulsar® 3000 ALD reactor over a temperature range of 200-300 ° C. The La-doped HfO_2 ALD process utilized $HfCl_4$ and a novel lanthanum precursor with co-reactant oxidants. Spectroscopic ellipsometer and x-ray photoemission spectroscopy were used to study the film growth and composition properties, respectively. In addition, La-doped HfO_2 crystallization kinetics were studied with in-situ x-ray diffractometry (IS-XRD). The FE properties were studied via fabrication and electrical characterization of planar metal-ferroelectric-metal capacitors (MFMCap).

Control of La-doped HfO_2 in the range of [La] ~ 1-10 % (based on 100*[La]/([La] + [Hf])) was studied by varying the ratio of LaO_x:HfO_2 subcycles during the ALD process. The La-doped HfO_2 growth rate and residual C and Cl impurity concentrations were studied as a function of LaO_x:HfO_2 subcycle ratio and temperature for as-deposited films. IS-XRD analysis during high temperature annealing revealed the presence of the desired high symmetry phase of FE hafnium oxide for low [La] (1-5 %) and lower temperature (200-250 ° C) deposited samples, while samples with higher [La] showed an even stronger stabilization of the film which showed electrically no FE behavior. Crystallization temperatures increased with increasing La content, while it decreased with increasing deposition temperature: e.g. [La]~2 % samples deposited at 200-300 ° C crystallized at 615-470 ° C, respectively. The MFMCap studies confirmed the presence of strong FE responses for the low La content films exhibiting maximum remanent polarization of 26.5 $\mu C/cm^2$ (post cycle conditioning) for [La]~2 % films deposited at 250 ° C.

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4:45pm **AA3-TuA-14 Characterization of Multi-Domain Ferroelectric ZrO_2 Thin Films for Negative Capacitance and Inductive Responses***, **Yu-Tung Yin**, P Cheng, Y Jiang, J Shieh, M Chen,* National Taiwan University, Republic of China

By using a specific plasma-enhanced atomic layer deposition (PEALD) process, an as-deposited nanoscale ferroelectric ZrO_2 (nano-*f*-ZrO_2) thin film has been prepared. A unique periodically arranged crystalline has been observed under nano-beam electron diffraction (EBED) and dark field TEM images, indicating the presence of multi-domain structure in nano-*f*-ZrO_2. From the large-signal RLC oscillations in time domain analysis, the existence of positive imaginary part of the impedance, enhancement of small-signal capacitance of the series-connected capacitances, and the sub-60mV/dec subthreshold swing in nanoscale transistors, the multi-domain nano-*f*-ZrO_2 has provided the experimental observation for the inductive behavior and negative capacitance induced by the net polarization switching. According to the theoretical calculation, the net polarization switching of multi-domain nano-*f*-ZrO_2 produces an effective electromotive force which is similar in behavior with Lenz's law, leading to the inductive responses and the negative capacitance effect. Since the as-deposited multi-domain nano-*f*-ZrO_2 thin film provides a significant inductance behavior compared to conventional inductors, the PEALD deposited nano-*f*-ZrO_2 would become a promising material in a variety of applications including nanoscale transistors, filters, oscillators, and radio-frequency integrated circuits.

5:00pm **AA3-TuA-15 Scaling Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ on Metal-Ferroelectric-Metal (MFM) and Metal-Ferroelectric-Insulator-Semiconductor (MFIS) Structures***, **Jaidah Mohan**, H Hernandez-Arriaga, H Kim, A Khosravi, A Sahota,* The University of Texas at Dallas*; R Wallace,* University of Texas at Dallas*; J Kim,* The University of Texas at Dallas

Ferroelectricity in Hafnium Zirconate (HZO) has recently garnered interest due to the possibility of achieving sub-60mV/decade Subthreshold swing (SS) at room temperatures [1]. Such steep slope behavior could lead to various advantages like reducing static power dissipation and lowering operating voltages. “Negative Capacitance” is the currently proposed mechanism for such behavior but substantial claims and controversies are still being reported. Big mystery questions remain unsolved, (i) can hysteresis free switching continue to get steeper even at GHz frequencies? (ii) Can negative capacitance really be stabilized Nevertheless, various observations of sub-60 SS swing have been reported using a ferroelectric material as the gate dielectric [2][3]. In this work, we study scaling of HZO on Metal-Ferroelectric-Metal (MFM) and Metal-Ferroelectric-Insulator-Semiconductor (MFIS) structures which can further aid in reducing the operating voltages.

In this study, the ferroelectric properties of HZO was studied on MIM and MFIS structures, scaling down to 3nm. HZO was deposited using TDMA-hafnium ($Hf[N(CH_3)_2]_4$), TDMA-zirconium ($Zr[N(CH_3)_2]_4$), and O_3 as the Hf-precursor, Zr-precursor and oxygen source respectively at 250°C. Blanket TiN (90 nm thick) electrodes were deposited after the HZO deposition as the stress given by the TiN electrode helps in crystallizing HZO into the ferroelectric phase. Then, rapid thermal annealing was done at 450^{o}C in an N_2 atmosphere for 60s to crystallize the HZO films. A conventional photolithography/etching process was used to make capacitors of different diameters. Grazing Incidence X-ray Diffraction (GIXRD) confirms that the ferroelectric orthorhombic phase is stable for HZO deposited on top of HF treated Silicon. The ferroelectric HZO film was scaled up to 5nm on top of Silicon and showed significant ferroelectric properties while 4nm and 3nm HZO showed very high leakage properties. Effects or reannealing to increase the grain size and hence the ferroelectric behavior was also studied. It was also observed that as the ferroelectric thickness decreases or the SiO_2 thickness increases, there is an increase in the ferroelectric dipole relaxation, i.e. the ferroelectric domains are naturally tend to orient themselves in a particular direction.

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5:15pm **AA3-TuA-16 Interface Characteristics of MIM Capacitors using Vanadium Nitride Electrode and ALD-grown ZrO_2 High-k Dielectric Film***, **Jae Hyoung Choi**, Y Kim, H Lee, H Lim, K Hwang, S Nam, H Kang,* Samsung Electronics, Republic of Korea

One of the most critical challenges for DRAM (Dynamic Random Access Memory) downscaling is cell capacitor technology, and so far ZrO_2 and TiN film have been adopted as a high-k dielectric and an electrode material respectively, for the capacitor application [1]. ZrO_2 film has been spotlighted in TiN/Insulator/TiN (TIT) capacitor due to its high dielectric constant, wide band gap, and thermal stability [2].

A wide variety of DRAM capacitor electrodes are currently being evaluated as replacements for TiN including VN, HfN, and Ru. Ru-base electrode has advantage of high work function but also has cost and integration problem. Thermally robust HfN/HfO_2 gate stack structure was reported with scaling down of equivalent oxide thickness (Toxeq.) less than 10Å and several attempts to prepare HfN films by metal organic chemical vapor deposition (MOCVD) have been continued [3,4]. Even though Vanadium Nitride (VN) exhibits high melting point, chemical inertness, low resistivity, and high work function from 5.05 to 5.15eV, very little is known about its qualities as DRAM capacitor electrode [5].

In this study, we fabricated new MIM (Metal/Insulator/Metal) capacitor using VN electrode and ALD-ZrO_2 dielectric for DRAM capacitor. VN films (100~1,000Å) were deposited at different temperatures ranging from 25 to 500^{o}C by reactive magnetron sputtering. ZrO_2 films were used as a dielectric by atomic layer deposition (ALD) method with Tetra-Ethyl-Methyl-Amino-Zirconium (TEMAZ) liquid precursor and O_3 reactant at the temperature of 250℃. ALD-ZrO_2 films were progressed to post deposition anneal (PDA) in N_2 atmosphere to crystallize the dielectric layer. Electrical properties of MIM capacitor with VN/ZrO_2 combination such as capacitance, leakage current density and dielectric constant were compared with TiN/ZrO_2 stack. Resistivity, composition, interfacial reaction, and crystalline structure of VN and ZrO_2 films were analyzed by 4-point probe, Rutherford backscattering spectroscopy (RBS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and transmission electron microscopy (TEM). Furthermore, the VN/ZrO_2 interface effects on the electrical properties will be discussed in detail.

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ALD Applications

Room Evergreen Ballroom & Foyer - Session AA1-TuP

Energy Harvesting and Storage Poster Session

AA1-TuP-1 Study on Atomic Layer Deposited Al_2O_3, TiO_2 and ZnO for the Application in Silicon Photovoltaics*, **Arun Haridas**, M Sreenivasan,* Hind High Vacuum Company Pvt. Ltd., India*; A Antony,* Indian Institute of Technology Bombay, India

We have fabricated a thermal atomic layer deposition (ALD) system with a substrate size of 150 mm diameter. Non-uniformity of 95 nm Al_2O_3 films deposited over polished (100) Si substrate at a temperature of 200°C is ± 0.41 % over 150 mm diameter as measured using ellipsometry. The optical properties, i.e. n & k values were found to be very uniform indicating the uniformity of the growth and the quality of the layer over large area. Passivation quality of the Al_2O_3 films over the Silicon substrate is studied by measuring the minority carrier life-time and photoluminescence. Application possibility of ALD grown TiO_2 and ZnO films have been examined as carrier selective layer for Silicon.

Highly uniform Atomic layer deposition of Al_2O_3 thin film using trimethyl Aluminium and H_2O as counter reactant has been achieved. Surface recombination is a major loss factor in the Si solar cells. These losses can be reduced with good quality chemical passivation or field effect passivation. Al_2O_3 is a promising high quality passivation material for p-type Si, because of its ability to act as a field effect passivator for the charge carriers. Crucial parameter of this layer is thickness and uniformity that can be precisely controlled using ALD.

The material quality and doping level by the oxygen vacancies of the metal oxide layer plays a crucial role in the performance of the carrier-selective silicon solar cells. High quality films of TiO_2 using Titanium isopropoxide and H_2O, as well as ZnO using diethyl Zinc and H_2O are investigated for carrier selectivity. ALD has very good potential as effective tool for depositing ultra thin carrier-selective layers for solar cells.

In this work we are exploring the advantages of the ALD technique to grow pinhole free, conformal and extremely uniform films for improving the performance of Silicon solar cells.

AA1-TuP-2 Nitrogen-Doped TiO_2 Film Deposited using Plasma-Enhanced Atomic Layer Deposition to Improve the Electrical Conductivity for Surface Passivation of Crystalline Silicon*, E Song,* Korea Institute of Materials Science, Republic of Korea*; J Ahn,* Korea Maritime and Ocean University, Republic of Korea*; **Jung-Dae Kwon**,* Korea Institute of Materials Science, Republic of Korea

For surface passivation with improved electrical conductivity, we investigate nitrogen doped TiO_2 film by combining the TiO_2, TiN sub-cycles using plasma-enhanced atomic layer deposition. For composition control of the TiON films, a super-cycle was adopted which was composed of one cycle of TiO_2 and x-cycles of TiN. The thickness of the TiON films as the nitrogen doping concentration linearly increases with the number of super-cycles. We confirm the chemical states, crystalline phase and interface characteristics of these TiON films through the XPS, XRD and C-V analysis. When the nitrogen was doped in the TiO_2 thin film, the carrier lifetime was increased from 30 to 243 µs and the resistivity decreased from 3.1E+08 to 7.1E-01 Ω·cm for the TiO_2:TiN=1:20 film.

AA1-TuP-3 Multilayer Encapsulation for Highly Stable Perovskite Solar Cells with Atomic Layer Deposited Al_2O_3 and Chemical Vapor Deposited Flowable Oxide*, **Jungwoo Kim**, H Hwangbo, S Kim, J Jang, H Tran Vo, H Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Perovskite solar cells (PVSCs) are known to be easily deteriorated in atmospheric environment. Many researchers have studied encapsulation technique to protect PVSCs. However, few researchers reported long term stability under severe conditions such as 85 °C with 85% relative humidity (RH). Atomic layer deposited metal oxides are considered to be effective to thin film encapsulation. However, PVSCs can be easily damaged by oxygen radicals during the metal oxide deposition process. In this work, we introduced flowable oxide inter layer for the cell protection before spatially-resolved plasma atomic layer deposition (ALD) process. The flowable oxide layer prevent oxygen radicals generated in N_2O plasma during Al_2O_3 process and the power conversion efficiencies (PCEs) of PVSCs were almost preserved. With flowable oxide and Al_2O_3 double layer, 45% in efficiency drop was observed after 1000 hours in 85 °C/35% RH condition. The PSVCs with multiple stacked flowable oxide/Al_2O_3 layer with glass encapsulation showed less than 10% of efficiency degradation after 1000 hours in 85 °C/85% RH. The multilayer with flowable oxide protection layer and Al_2O_3 moisture barrier layer structure is expected to provide long term stability in ambient condition.

AA1-TuP-5 Oxide Buffer Layers for Perovskite Solar Cells Grown with a 200 mm Commercial ALD System Using Low-Temperature Process*, P Rajbhandari, **Tara Dhakal**,* Binghamton University

Organic materials provide a very small thermal budget for any post-fabrication treatment or for a subsequent layer in device fabrication. The demand for the low-temperature process has driven the focus of our study to obtain atomic layer deposited oxide buffer layer at temperatures suitable for a perovskite solar cell. The buffer layer will assist in blocking holes, effectively extract electrons, provide better shunt protection and act as a sputter protection layer covering the organic perovskite films from sputter damage from a subsequent layer, such as a transparent conductor. Three different oxide layers, Al_2O3, ZnO, and TiO_2 are grown at 100°C and studied for this purpose using **Synchronous Modulated Flow Draw ALD (SMFD-ALD)** technology optimized in commercial 200 mm ALD reactor from Sundew Technologies. It allows greater precursor utilization and shorter deposition cycle times that in turn reduces thermal processing time compared to traditional ALD processes. These thin films have shown to enhance the fill factor (FF) and high charge extraction from the solar cell. Three oxides are compared on all aspect, among which ZnO (4 nm) along with Al_2O_3 (1 nm) as a buffer layer has shown excellent performance improvement in the device up to 20% power conversion efficiency. In this presentation, ALD growth details of the oxide layers and the resulting perovskite solar cell results will be discussed.

AA1-TuP-6 Ultra-thin Nickel Films for Energy Harvesting Applications*, **Ken Bosnick**, P Motamedi,* National Research Council Canada, Canada*; K Cadien,* University of Alberta, Canada*; K Harris, J Cho,* National Research Council Canada, Canada

The harvesting of ambient heat and light could potentially lead to useful power for driving off-grid, internet-of-things sensors. Recent theoretical predictions suggest that ultra-thin Ni films can show thickness dependent optical properties that can lead to enhanced solar absorptance. The maximum solar absorptance is predicted to occur at a very thin layer thickness of ~12 nm and is attributed to an impedance matching effect [N. Ahmad, *et. al, Nano Energy* **1**, 777 (2012)]. Light absorptance in ultra-thin Ni films can be further enhanced by patterning the Ni films and depositing multi-layer structures. Atomic layer deposition (ALD) produces conformal films with a high level of control and uniformity with respect to the film thickness. While ALD is most widely known for depositing ultra-thin dielectric materials for advanced electronics applications, we have successfully used the technique to deposit ultra-thin Ni films [P. Motamedi, *et al., ACS Appl. Mater. Interfaces* **9**(29), 24722 (2017); P. Motamedi, *et al., Adv. Mater. Interfaces* **5**(24), 1800957 (2018)].

In this study, ALD Ni films are deposited with varying thicknesses onto fused silica and sapphire substrates. Structural characterization indicates that the films are continuous, polycrystalline Ni films with a relatively low degree of roughness and are suitable for comparison with the theoretical predictions. Optical absorptance is measured using an integrating sphere as a function of film thickness and compared with theory. An optimum thickness is found but the experimentally determined absorptance maximum is less significant than theoretically predicted. Possible explanations include surface roughness or deviations from the refractive index of bulk Ni. Nevertheless, the thickness for optimum absorptance is found to be around 10 nm for planar ALD Ni films.

Glancing angle deposition (GLAD) is used to produce quasi-periodic silica pillars on fused silica wafers and ALD Ni films are deposited conformally onto the GLAD pillars. It is hypothesized that the GLAD films with ultra-thin ALD Ni coatings will act similarly to lithographically patterned gratings and lead to enhanced optical absorptance. Optical absorptance measurements reveal a low reflectance at all wavelengths, but an extremely high absorptance in the UV / visible range that decreases to very low values in the NIR. The spectra are seen to have a strong dependence on the ALD Ni thickness but to be less sensitive to changes in the GLAD deposition parameters. Structural characterization, further control experiments, and theoretical modeling are planned to understand these optical results.

AA1-TuP-7 MoNx-Deposited on High-surface N-doped Carbon Coated-Carbon Cloth Substrates: The Best Possible Option for ALD in View of Energy Storage Application*, S Sawant, D Nandi, R Rahul, S Kim, **Moo Hwan Cho**,* Yeungnam University, Republic of Korea

Molybdenum [https://www.sciencedirect.com/topics/chemistry/nitride] (MoN_x) was directly grown on 3-dimensional nitrogen doped-carbon coated carbon cloth (NC-CC) at a relatively low temperature of 250 °C by atomic layer deposition (ALD) and then tested as an electrode for supercapacitive charge storage. The charge storage performance of NC-CC and MoN_x deposited CC have also been evaluated for the comparative studies. The successful formation of MoN_x@NC-CC and MoN_x@CC composite was confirmed by several characterization techniques. The scanning and [https://www.sciencedirect.com/topics/chemistry/transmission-electron-microscopy] analyses showed the extremely uniform and conformal coating of the MoN_x on NC-CC. The 3D and porous texture of NC provided the excessive surface area for MoN_x coating and also granted easy access for the electrolyte penetration. The high areal capacitance of 911 mF/cm^2 was achieved at a current density of 4 mA/cm^2 which is 1.3 times higher than that of NC-CC. The negligible charge storage capacity of 7 mA/cm^2 obtained for MoN_x@CC highlighted the significance of NC deposition on CC prior to the loading of MoN_x. The ultra -high stability of MoN_x@NC-CC (108% capacity retention after 50,000 cycles) further confirmed its exceptional supercapacitive charge storage performance.

AA1-TuP-8 ALD Coatings for Nano Imprint Masks*, Thomas Seidel,* Seitek50

Nano Imprint Lithography (NIL) usage has been limited by mask defects during fill and release process steps. Additionally, as for any process step, it is desirable to improve throughput. The optical intensity in the features of quartz imprint masks with high index conformal coatings was simulated using Maxwell solver software.[1] The index of refraction of the coatings, exposure wavelength, aspect ratio, film thickness and feature size were varied parameters. The simulations indicate the optical intensity may be increased within the mask features using coatings of higher index films relative to the uncoated reference quartz mask for physical feature sizes below 7nm, indicating the possibility of improved productivity.[2] Defectivity is proposed to be addressed by the application of *fractional* fluorine terminated monolayers of a fluro-hydrocarbon (FHC) film at the mask feature surface. This approach is intended to address the dichotomy of fill and release type defects in the imprint feature.[1,2] In addition, ALD conformal films may be used to reduce the critical feature size below that achievable with the state-of-the-art electron beam processes. A matrix of candidate ALD precursors and processes for higher index coating films (Al_2O_3, TiO_2 and Si) relative to quartz, as well as monolayer FHC precursors are reviewed with considerations of quality and throughput. Various ALD wafer systems are considered for process deposition for square mask quartz plates of 6in. x 6in. x 0.25in. geometry.

The support of Nayoa Hayashi and Nobuhito Toyama of Dia Nippon Printing is acknowledged for the simulations.

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AA1-TuP-9 The Investigation of Al_2O_3 Passivation Characteristics in the Condition of Growth Temperature and Ozone Concentration*, Young Joon Cho, H Chang,* Chungnam National University, Republic of Korea

The surface passivation for high efficiency c-Si solar cell is a prerequisite for the achievement of high efficiency solar cell. The capability of Al_2O_3 passivation using trimethlyaluminium(TMA, $Al(CH_3)_3$) precursor and H2O oxidant was presented. Aluminum oxide (Al_2O_3) grown by atomic layer deposition (ALD) was showed excellent passivation performance as good as obtained by thermally grown SiO_2. A superior property of the ALD- Al_2O_3 film appeared to be the field-effect passivation induced by negative fixed charges and the high level of chemical passivation resulting from a low interfacial defect density. ALD- Al_2O_3 film using ozone oxidant showed better thermal stability and no-blistering because of excluding hydroxyl group in ozone oxidant. Therefore, more detail study is required about the effect of growth temperature and ozone concentration on ALD- Al_2O_3 passivation.

Al_2O_3 were deposited on 8 inch p-type crystalline semiconductor Si(100) wafers of 10 Ω-cm resistivity and 710 ~ 740 μm wafer thickness. Al_2O_3 films of about 20 nm thickness were deposited in the range of 150°C and 300°C with trimethlyaluminium ($Al(CH_3)_3$) (TMA) precursor and ozone oxidant at the concentraion of 200g/Nm^3 and 330g/Nm^3 after RCA cleaning. Comparing H_2O oxidant, ozone oxidant has several advantages, such as its higher activity for ligand elimination relative to H_2O, significantly less amount of defect states like Al–Al and OH bonds compared with those prepared with H_2O. Ozone concentration was controlled by MKS ozone generator at 150g/Nm3 (~10wt%) and 330g/Nm3(~20wt%).

As a result, the lifetime and implied Voc for the as-deposited Al_2O_3 shows the maximum at growth temperature 250°C and for both of ozone concentration 200g/Nm^3 and 330g/Nm^3. After annealing, the lifetime and implied Voc has a similar tendency with the as-deposited Al_2O_3. We investigated the reason that the lifetime and implied Voc have a maximum at 250°C before and after annealing through SIMS(secondary ion mass spectroscopy), XPS(X-ray photoelectron spectroscopy), TEM(tunneling electron microscopy), etc.

AA1-TuP-10 Effect of Al2O3 Passivation on n-type Si Solar Cell with Passivated Emitter and Rear Cell (PERC)*, Kiryun Kim, H Chang,* Chungnam National University, Republic of Korea

N-type solar cells are immune to LID (Light Induced Degradation) effect, because of the absence of the boron-oxygen defect. However, The fabrication process of n-type PERC includes more steps and makes a solar cell more expensive. Therefore, newer technologies will be needed efficient process steps and structures.

In this study, we investigated n type-PERC cell formed by double-sided Al2O3 deposition using ALD. Al2O3 films as a passivation layer were grown by ALD at 300℃. After double-sided Al2O3 deposition, UV laser ablation with ns pulse performed to make a electrode contact-patterning. Finally, we evaluated passivation performance as a function of emitter sheet resistance and electrode open ratio. In addition, we have evaluated the passivation characteristics affected by electrode materials such as Cu and Al.

The passivation performance of the Al2O3 layer was compared with the emitter saturation current (J0) and the implied Voc through Quasi-Steady-State Photoconductance (QSSPC). As a result, We have achieved iVoc of 680 mV through the optimization process.

AA1-TuP-11 High Quality CaF_2 from a New ALD Process: Enabling New Approaches in Battery Technology and Optical Applications*, Max Gebhard, A Mane, J Elam,* Argonne National Laboratory

Calcium fluoride (CaF_2) is highly transparent over a broad range of the electromagnetic spectrum, covering ultra-violet (UV), visible, and infrared (IR) wavelengths. Its high transparency between 150 nm – 12,000 nm and its extremely low refractive index *n* (~1.43 at λ = 500 nm - 600 nm) makes it a well-known candidate for optical applications. In combination with materials exhibiting a higher refractive index, CaF_2 coatings find application in anti-reflective coatings and band pass filters. Like other fluorides, such as MgF_2 and LaF_3, the ionic bonding situation in CaF_2 enables applications even below 200 nm (*e.g.* photolithography). Recently, metal fluoride materials were also suggested to be incorporated in Lithium-Ion-Batteries, acting either as the solid electrolyte or electrode material.[1]

In both cases, *i.e.* optical applications (such as lenses and three-dimensional structures for optical filters) and coatings in Li-ion batteries, the respective thin film must be of high purity and thickness control is of utmost importance. In consequence, the fabrication of CaF_2*via* ALD is the method of choice. Different ALD processes for CaF_2 have been reported in the past, using $Ca(thd)_2$[2,3] and $Ca(hfac)_2$[4] as metal source and NH_4F,[2] TiF_2,[3] and Hhfac[4] as fluorine precursor.[2] These processes showed best results at temperatures around 300 °C.

Herein, we present a new and straight-forward ALD process for CaF_2 thin films using the $[Ca(amd)_2]_2$–dimer and HF-pyridine as precursor, working at temperatures as low as 175 °C. The process was monitored and optimized employing *in-situ* diagnostics such as FTIR and QCM, and thin films were characterized in terms of their composition (XPS), structure (TEM, XRD, PDF) and optical properties (UVVis, ellipsometry). The process was applied to cathode powers used in Li-ion-batteries and the performance of the respective materials was investigated.

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AA1-TuP-12 Properties of Molybdenum Oxide Deposited by Plasma Enhanced Atomic Layer Deposition for High Efficiency Solar Cells*, Taewan Lim, H Chang,* Chungnam National University, Republic of Korea

Transition Metal Oxides (TMO) are applied as a carrier selective contact layer in silicon hetero junction (SHJ) solar cells. MoO_x has high work function (> 6 eV) and wide band gap (~ 3 eV). It is well known that molybdenum oxide exhibits good optical and electrical properties when deposited on Crystalline Silicon (c-Si). But, MoO_x is sensitive to temperature, plasma, and air exposure, and for this reason the work function of MoO_x is degraded and its properties are reduced.

In this study, MoO_x is deposited by plasma-enhanced atomic layer deposition (PE-ALD)using Molybdenum hexacarbonyl ($Mo(CO)_6$) is selected as precursor for Mo and O_2 is adopted as precursor for plasma. Argon was used as a carrier gas of $Mo(CO)_6$ and the gas line and canister temperature was maintained to 40˚C and 45˚,respectively. To obtain the best passivation performance, the plasma power was varied between 10W and 500W at PE-ALD process. To investigate the effect of temperature, the sample was annealed at temperature range from 250 ˚C to 500 ˚C.

X-ray photoelectron spectroscopy (XPS) analysis confirmed the chemical state of the MoO_x film. The growth per cycle(GPC) of MoO_x film and MoO_x/c-Si interface was investigated by transmission electron microscopy (TEM). The GPC of MoO_x film deposited by PE-ALD was found to be 0.25 Å. The life time and V_{oc} were measured by quasi steady state photoconductivity (QSSPC).

AA1-TuP-13 Understanding and Mitigating F Migration in ALD Nanocomposite Coatings

Anil Mane, *M Gebhard, J Elam,* Argonne National Laboratory*; M Popecki, T Cremer,* Incom Inc.*; M Minot,* incom

We have developed atomic layer deposition (ALD) processes to synthesize metal-dielectric oxide nanocomposite coatings comprised of conducting, metallic nanoparticles (M) embedded in an amorphous dielectric matrix, nominally Alumina (Al_2O_3), and where the metallic component is selected from either tungsten (W) or molybdenum (Mo). The nanocomposite layers are prepared using alternating exposures to trimethyl aluminum (TMA) and H_2O for the Al_2O_3 ALD and alternating metal hexafluoride / disilane (MF_6/Si_2H_6) or metal hexafluoride TMA (MF_6/TMA) exposures for the metal ALD component. By varying the ratio of M:Al_2O_3 ALD cycles and the order of precursor dosing for the two components, we can tune the composition enabling a wide range of mechanical, electrical, and optical properties of these nanocomposites. We have applied these nanocomposites to a variety of applications, but I will focus this presentation on their use as resistive layers for glass capillary array microchannel plates (GCA-MCPs). These ALD nanocomposite coatings contain residual fluorine (F) from the metal hexafluoride precursor in the form of AlF_3. Although we can modulate the F content by adjusting the W nucleation conditions, it is not possible to eliminate the F and this can introduce challenges for device fabrication and integration. For instance, we often deposit ALD magnesium oxide (MgO) following the ALD resistive coating to improve the secondary electron emission (SEE) of the surface. In these cases, we find that residual F can diffuse from the resistive layer into the MgO forming MgF_2 and affecting MCP performance. In this presentation, I will describe several strategies we have developed to minimize F migration. I will conclude by showing the enhanced performance and stability of ALD-GCA-MCPs achieved with this technology.

AA1-TuP-14 Ultrathin Metal Oxide Passivation by Atomic Layer Deposition Enhances Stability and Performance of Visible Solar Water Splitting on Solution-Processed Organic Semiconductor Thin Films

L Wang, D Yan, Stony Brook University*; D Shaffer,* Brookhaven National Laboratory*; X Ye,* Stony Brook University*; B Layne, J Concepcion, M Liu,* ***Chang-Yong Nam***, Brookhaven National Laboratory

Solution-processable organic semiconductors have potentials for visible photoelectrochemical (PEC) solar water splitting because of their tunable small band gaps and electronic energy levels. However, the poor stability and photocatalytic activity of organic semiconductors have been posing persistent challenges. Here, we demonstrate that the application of ultrathin metal oxide passivation by low-temperature atomic layer deposition (ALD) enables the direct, visible PEC water oxidation on solution-processed organic semiconductor thin films with enhanced stability and performance. N-type fullerene-derivative thin films passivated by sub-2 nm ALD ZnO allowed the visible PEC water oxidation at wavelengths longer than 600 nm in harsh alkaline electrolyte environments with up to 30 μA/cm^2 photocurrents at the thermodynamic water-oxidation equilibrium potential, which is accompanied by the photoanode half-lifetime extended to ∼1000 s. The investigation shows that the enhanced water oxidation catalytic activity is afforded by the ALD ZnO passivation, and the hole transfer through the passivation layer governs the charge collection process. Further improved PEC water splitting performances were realized by improving the bottom ohmic contact to the organic semiconductor, again via the ZnO interlayer implemented by ALD, ultimately achieving ∼60 μA/cm^2 water oxidation photocurrent at the equilibrium potential, the highest value reported for organic semiconductor thin films to our knowledge. The results not only highlight the significant utility of ALD on improving the stability and performance of organic-semiconductor-based solar water splitting but also provide important design guidelines for optimal ultrathin passivation on organic semiconductor photoelectrodes.

AA1-TuP-15 Enhancement of Photovoltaic Efficiency using a Novel Nickel-4 Mercaptophenol Hybrid Interfacial Layer

S Mo, ***Jinseon Park****, N Long, H Thu,* Hanyang University, Republic of Korea

In this work, we introduced a novel Ni-4 mercaptophenol (Ni4MP) as an interfacial layer in Sb_2S_3-sensitized mesoporous TiO_2 solar cells. Ni4MP thin films with controllable thickness were prepared by an integrated approach via atomic/molecular layer deposition techniques and were systematically characterized. Introduction of the Ni4MP interlayer significantly enhanced the photovoltaic performance and the interfacial charge transfer kinetics of Sb_2S_3-sensitized solar cells. The augmentation of open circuit voltage and short circuit density due to the insertion of a Ni4MP interlayer enhanced the power conversion efficiency of the solar cells from 2.07% to 2.79%, corresponding to a 35% increase in efficiency. This improvement in device performance was discussed based on the energy band diagram. We found that the Ni4MP interlayer can effectively extract the photo-generated holes from the Sb_2S_3 sensitizer due to the excellent band matching and hole scavenging characteristics, thus enhancing the charge transport and suppressing the recombination.

AA1-TuP-16 Enhancement of Photovoltaic Properties of Metal/III-V Schottky Solar Cells using Al2O3 Anti-Reflection and Passivation Layer

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The metal-semiconductor (M-S) Schottky junction structure is gaining traction in photovoltaic device applications compared to *p-n* junction structure, due to simplicity in device processing, possibility of development of high efficiency multi-junction structures, and also cost-effective large-scale device fabrication[1]. III-V compound semiconductors with direct bandgap and short absorption depth are suitable candidates for fabrication of high efficiency solar cells. Schottky solar cells based on Au/$Al_{0.3}Ga_{0.7}As$/GaAs heterostructure have been designed and fabricated, resulting into short-circuit current density and power conversion efficiency of 20.46 mA/cm^2 and 4.84%, accordingly[2].

One of the main issues regarding the M-S structures for solar cells remains about the high reflectivity from the top metal surface. This leads to significant reduction in photon absorption in the active layer of solar cell and, therefore, lowered photo-generated current. Graphene and indium-tin-oxide (ITO), with transmission of more than 80% in the visible region, have been used in conjunction with *n*-GaAs to create Schottky solar cells, leading to short circuit current density and power conversion efficiency of up to 19 mA/cm^2 and 11.1%, respectively[3,4].

Anti-reflection coating (ARC), such as aluminum oxide (Al_2O_3), has been used to reduce the reflection from top surface of M-S Schottky solar cells, and enhance the photovoltaic properties of these devices. In this work, an 80 nm Al_2O_3 has been grown on the whole top surface of the Ag/*n*-GaAs Schottky solar cell using atomic layer deposition (ALD) technique at 200̊C, Figure 1 (attachment). The initial optical measurements show the reduction of reflection from the solar cells from 48% (without ARC) to 16% (with ARC), indicating the improvement in photon absorption, Figure 2. *J-V* and EQE measurements will be performed to extract the photovoltaic properties of these devices and investigate the effect of ARC on M-S structure.

Moreover, the effect of Al_2O_3 as passivation layer will be studied in the full paper. Initial measurements have indicated a decrease in leakage current between the metal contacts, leading to enhancement of shunt resistance from 3×10^4 W to 1×10^5 W. This will be further investigated, and changes in photovoltaic properties of the solar cells, including filling factor, reverse saturation current, and power conversion efficiency, will be reported.

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AA1-TuP-17 Investigation of ALD-grown i-ZnO Buffer Layer Properties for CIGS Solar Cell Application

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Zinc oxide (ZnO) is a wide bandgap (3.4 eV) n-type semiconductor material that can be mostly used in various optoelectronic applications from thin film transistors (TFTs) to solar cells due to its excellent optical and electrical properties [1]. In the CIGS solar cell device structure, the i-ZnO thin film acts as a buffer layer that reduces the leakage of shunt current paths and also it improves p-n hetero-junction quality. In the present study, we deposited the i-ZnO thin films from 80°C to 180°C onto both Si (100) and soda lime glass (SLG) by using atomic layer deposition (ALD) method. The as-grown films were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction, UV-Vis-NIR spectroscopy, and Hall effect measurements. The thickness of as-grown ZnO films is independent of the growth temperatures from 100°C to 180°C. All samples exhibit the optimal bandgap of 3.24 eV. The ZnO buffers show the electrical resistivity of 6 Ω×cm, 0.29 Ω×cm, and 0.0058 Ω×cm for the films-grown at 80°C, 100°C, and 150°C, respectively. In addition, we investigated the J-V characteristics of the fabricated CIGS solar cells using ALD-grown i-ZnO buffers prepared at 80°C, 100°C, and 150°C. The solar cell fabricated with i-ZnO buffer grown at 100°C exhibits the best power conversion efficiency (η) of 8.59% with V_{oc} of 470 mV, J_{sc} of 28.84 mA/cm^2, and *FF* of 63.48%.

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Acknowledgment:

This research was supported by the Technology Development Program to Solve Climate Changes of the National Research Foundation (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2017M1A2A2087577) and (NRF-2016M1A2A2936759), also, this research was financially supported by the Ministry of Trade, Industry and Energy (MOTIE) and Korea Institute for Advancement of Technology (KIAT) through the National Innovation Cluster R&D program (P0006704).

**AA1-TuP-18 Atomic Layer Deposited Zirconium-doped ZnO Transparent Conductive Oxides for Silicon Solar Cells*, Geedhika Kallidil Poduval,* *M Hossain, B Hoex,* University of New South Wales, Australia

Transparent conductive oxides (TCOs) are intensively investigated due to their ability to conduct charge carriers and transparency in the visible light in various fields ranging from large scale displays to photovoltaic devices. Currently, the most widely used TCO is indium tin oxide (ITO) which simultaneously offers high optical transparency and high electrical conductivity. Limited reserves, increasing indium prices, and free carrier absorption due to relative high carrier concentration have been the motivation to explore other TCO materials. Some of the alternatives to ITO are, doped ZnO, SnO_2, Cu_2O, and TiO_2.

Among the various kinds of silicon solar cell architectures, heterojunction (HET) silicon solar cells consisting of crystalline silicon absorber and amorphous silicon (a-Si) surface passivation and doped a-Si as the electron and hole selective layers implement TCOs to improve the lateral conductivity of collected carriers. As a-Si degrades at temperatures >200°C and sputtering of ITO damages the interface, leading to increased absorption and recombination, a surface sensitive low-temperature self-limiting process such as atomic layer deposition is very appealing.

In this work, Zr is used as a dopant to increase the mobility and reduce parasitic absorption of earth-abundant ZnO. The recipe for ZrO_2 growth using Tetrakis(dimethylamido) zirconium(IV) (TDMAZ) was developed and optimized on a Fiji G2 plasma enhanced ALD tool. The growth properties were studied by *in-situ* spectroscopic ellipsometry. The effects of doping (0-29 at.% Zr) were investigated for 40 nm thick films. ZnO and ZrO_2 supercycles at different ratios were carried out, and their influence on optical and electrical properties was investigated. A slight increase in mobility of ~5% up to 19 cm^{2}V^{-1}s^{-1} was observed by doping ZnO with 2.4% Zr, and the mobility reduces with increased doping. The optical band gap of ZnO increases with doping level up to a value of 3.42 eV at 10% Zr and reduces for higher Zr concentrations. First-principles density functional theory (DFT) calculations reveal the formation of defects states in the conduction band resulting from the substitutional replacement of Zn by Zr. XPS results indicate that the Zr ions in ZnO are in the Zr^{+4} oxidation state thereby contributing two additional electrons to the lattice. This results in an increase in carrier concentration from $2x10^{19}$ cm^{-3} to $1.2x10^{20}$ cm^{-3}. Elemental depth profiling using Tof-SIMS is currently ongoing and will be shown at the time of the conference. The improvement in TCO properties of ZnO upon doping with Zr opens the possibility for applications in silicon solar cells as well as thin film solar cells.

**AA1-TuP-19 Atomic Layer Deposition of Few-Atom Cluster Arrays for Solar Fuel Catalysis*, David Mandia,* *N Guisinger, A Martinson,* Argonne National Laboratory

Solar fuels catalysis is vital to developing new technologies for creating value-added products from alternative feedstocks, such as carbon dioxide and water. Inhomogeneities in typical "state-of-the-art" synthesis techniques for heterogeneous catalysts severely limit the accuracy of determining the chemical composition of active sites and elucidating mechanistic details for catalysis. In the present work, we synthesize discrete, few-atom metal oxide cluster arrays to gain insight into the relationship between cluster size/shape and catalytic activity/efficiency. Clusters are synthesized with exquisite synthetic control via atomic layer deposition (ALD) on chemically modified epitaxial graphene (EG) on SiC. Metal oxide/nitride/sulfide ALD thin film growth is strongly inhibited on graphene. Understanding the factors contributing to unintentional and intentional nucleation and growth on EG will benefit from the use of an accurate, precise imaging technique such as STM. Furthermore, we employ an *in-situ* plasma treatment (H_2, N_2, O_2) of EG to create attachment points for intentional cluster nucleation via ALD. Discrete, few-atom clusters will be synthesized and cluster size, morphology, distribution, and density of states will be determined via STM/XPS/AFM/Raman mapping. We will correlate these parameters to catalytic activity and efficiency for solar fuels catalysis.

ALD Applications
Room Evergreen Ballroom & Foyer - Session AA2-TuP
Microelectronics Poster Session

**AA2-TuP-1 Chemically and Mechanically Activated Carbonaceous Materials for Supercapacitor*, D Lam, J Kim, Seung-Mo Lee,* Korea Institute of Machinery and Materials, South Korea

Carbothermic reduction in the chemistry of metal extraction (MO(s) + C(s) → M(s) + CO(g)) using carbon as a sacrificial agent has been used to smelt metals from diverse oxide ores since ancient times. Here, we paid attention to a new aspect of the carbothermic reduction remained unnoticed till now to prepare activated carbon textile for high rate-performance supercapacitors. On the basis of thermodynamic reducibility of metal oxides reported by Ellingham, we employed not carbon, but metal oxide as a sacrificial agent in order to prepare activated carbon textile. We conformally coated ZnO on bare cotton textile using atomic layer deposition (ALD), followed by pyrolysis at high temperature (C(s) + ZnO(s) → C′(s) + Zn(g) + CO(g)). We figured out that it leads to concurrent carbonization and activation in a chemical as well as mechanical way. Particularly, the combined effects of mechanical buckling and fracture occurred between ZnO and cotton were turned out to play an important role in carbonizing and activating cotton textile, thereby significantly increasing surface area (nearly 10 times) compared with the cotton textile prepared without ZnO. The carbon textiles prepared by carbothermic reduction showed impressive combination properties of high power and energy densities (over 20 times increase) together with high cyclic stability.

AA2-TuP-2 Diamond Field Effect Transistors with Different Gate Lengths of HfO_2 Deposited by Atomic Layer Deposition*, Changzhi Gu,* Institute of Physics, Chinese Academy of Sciences, China

The single crystal diamond was treated in hydrogen plasma formed by microwave plasma chemical vapor deposition equipment, and the normally-off hydrogen terminal diamond field effect transistors with different gate lengths were prepared by atomic layer deposition of HfO_2 as gate oxide. We studied the effect of hydrogen treatment time and HfO_2 gate oxide on hydrogen terminal diamond field effect transistor. The experimental results showed that the HfO_2 gate oxide was suitable to fabricate hydrogen terminal diamond field effect transistor and exhibited a normally-off characteristic, which is advantageous for the fabrication of power devices. Furthermore, with increasing the gate length, the drive current density, threshold voltage and transconductance of the diamond device decreased.

AA2-TuP-3 Atomic Layer Deposition of IGZO Thin Films for BEOL Applications*, Shóna Doyle,* Tyndall National Institute, Ireland

In the drive for scaling of electronic devices one approach has been the integration of functionality into the back end of line (BEOL). Thin film transitors (TFT) are one such component with high quality devices being realised by PVD indium-gallium-zinc oxide (IGZO). However, the limitations of the PVD deposition process in terms of reliability and coverage in complex 3D topologies is of concern, where uniform sub nanometre films that demonstrate high mobility are required.

Here we have used atomic layer deposition (ALD) to deposit both nano-crystalline/amorphous ZnO and IGZO based laminate structures to generate high mobility thin film materials with sub-nm thickness control. Materials were grown using both thermal and plasma processes on a 200 mm Picosun R200 ALD system. Characterisation, in terms of morphology and composition, were achieved through electron microscopy, x-ray diffraction and x-ray photoelectron spectroscopy. Electrical properties were assessed via 4-point probe and both AC and DC Hall measurements.

AA2-TuP-4 Preparation and Electrical Properties of Polymer-based High-density MIM Capacitors by Plasma-Enhanced Atomic Layer Deposition

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Due to its unique flexibility, efficient and low-cost manufacturing process, and broad application prospects in the information and energy fields, flexible electronic technology has drawn more and more tremendous attentions. Among them, polymer-based high density metal/insulator/metal (MIM) capacitors have triggered a massive amount of research efforts in searching for the most applicable materials and fabrication processing.

In this work, we reported the fabrication and electrical properties of Hf-Ti-O and Hf-Sn-Ti-O MIM capacitors on polymer substrates (PET, PI and epoxy) by plasma-enhanced atomic layer deposition (PEALD). The effect of precursor and cycle ratio on electrical properties of MIM capacitors has been investigated. Organic tetradimethylaminohafnium (TDMAH), inorganic $TiCl_4$ and $SnCl_4$, or tetradimethylaminotitanium (TDMAT) and tetradimethylaminotin (TDMASn) were used as Hf, Ti, Sn metal sources, respectively, with plasma O_2 as O source. The deposition temperature was set to 80~100 ^{o}C. By tuning the pulse cycle ratio and cycle number of PEALD, the electrical properties of the Hf-Ti-O and Hf-Sn-Ti-O MIM capacitors were optimized. When the cycle ratio of HfO_2: TiO_2 was 2: 4, the sample of $Hf_{0.82}Ti_{0.23}O_2$ on polymer substrates with total 210 cycles showed larger capacitance density of 7.5 fF/μm^2 and leakage current density of 1.9×10^{-4} A/cm^2 at -3 V. When the cycle ratio of HfO_2: SnO_2: TiO_2 was 6: 5: 4, $Hf_{0.81}Sn_{0.06}Ti_{0.18}O_2$ capacitor on polymer substrates with total 300 cycles exhibited better electrical properties of capacitance density of 8.0 fF/μm^2 and leakage current density of 1.9×10^{-5} A/cm^2 at -3 V. When the bending radius was no less than 8.2 mm, polymer-based MIM capacitors displayed stable electrical properties without significant change. These results indicate that PEALD Hf-Sn-Ti-O dielectrics on polymers are promising candidate for flexible high-density MIM capacitors application.

AA2-TuP-5 High Voltage MIM Capacitor based on ALD Deposited Crystalline $HfAlO_x$ Film

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MIM capacitor was developed herein with ALD-fabricated $HfAlO_x$ dielectric layer. MIM capacitor is a key building element in modern CMOS platforms. It may occupy a significant part of the chip area. The high-k dielectric materials were introduced in the advanced production to minimize the footprint area of MIM: HfO_2-based materials grown by ALD replaced conventional dielectrics SiO_2 and Si_3N_4. To prevent the uncontrolled crystallization of amorphous HfO_2 film in a monoclinic phase that degrades its electrical parameters, some dopants (i.e. alumina) are introduced in deposited HfO_2 layer: the composite HfO_2/Al_2O_3 remains amorphous at deposition and during BEOL annealing processes.[1] Thus, amorphous materials are usually used in MIM capacitors located in BEOL. Hafnia doping enhances the composite crystallization (T≥600˚C) into metastable phases of higher symmetry having significantly higher k-value (30-40).[2] Crystalline HfAlOx dielectric has been employed in low voltage capacitors used in DRAM. Some CMOS applications (RF, CIS) require HV MIM capacitor (operating voltage 2.5-3.3V) located as DRAM in IMD0, to benefit from the attractive properties exhibited by crystalline HfAlOx. The increased operational voltage of HV MIM entails thicker dielectric layers compared to those used in DRAM. To take advantage of crystallinity of the HfAlOx film, engineering of the film growth and its crystallization parameters should be optimized for the required film thickness of the HV MIM capacitor. The developed capacitor with EOT≤2nm shows excellent dielectric integrity (V_{BVD}≥8V) along with the low leakage current.

Table 1 presents the plan of experiment where HfO_2-Al_2O_3 laminated stack (12:1) was deposited by ALD in the same run on two types of substrates: Si/SiO2/TiN(70nm) – structure A (MIM) and p-Si/thermal SiO_2(6.4nm) – structure B (MOS). The stack thickness is 14nm. Both pre-deposition (PreDA) and post-deposition (PDA) annealing were performed at the same conditions (T>600˚C). The RTA processing of structure A samples (MIM) was applied in three different flows to distinguish between the effects produced by RTA on the TiN bottom electrode and on the $HfAlO_x$ dielectric layer. Fig.1 shows the scheme of MIM capacitor. The results of electrical characterization are presented in Fig.2 and Table 2. The difference in electrical parameters of MIM capacitors were compared with the detailed structural study of samples 1, 2 and 3 performed by XRD (Fig.3) and TEM/STEM (Fig.5) techniques. Surface characteristics of the TiN electrode was shown in Fig.4. PreDA process allows to prevent the void formation at the TiN/HfAlOx interface and to improve electrical integrity of sample 2.

AA2-TuP-6 Improved Performance of GaN Metal-Oxide-Semiconductor Capacitors byPplasma ALD of AlN Interlayer

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High quality metal-oxide-semiconductor (MOS) gate stacks with stable threshold voltage are required for future GaN-based power transistors [1]. Here, we report a route to the realization of GaN MOS-capacitors (MOSCAPs) with an ALD AlN interlayer between GaN and Al_2O_3 using a FlexAL ALD system. AlN was grown using plasma enhanced ALD at 300^0C using TMA and N_2 and H_2 plasma. The GaN samples were first exposed to an N_2 150W 5min plasma pre-treatment followed by in-situ ALD of approximately 2nm of AlN. A 20nm Al_2O_3 was then deposited in-situ using thermal ALD at 200^0C using TMA and H_2O. The results from these samples were then compared with MOSCAPs that had only an N_2 150W 5min plasma pre-treatment followed by a 20nm thermal ALD Al_2O_3 layer.

20nm Pt/ 200nm Au contacts were deposited ex-situ as the gate contact and the MOSCAPs were measured at room temperature using capacitance-voltage (C-V) and current-voltage (I-V) measurements. The C-V measurements were used to calculate the hysteresis and frequency dispersion of these samples. The hysteresis included the flat band voltage difference between the forward and backward sweep of the C-V curve when swept from -5 to +5V and back to -5V at 1MHz. The frequency dispersion gives the maximum difference in the flat band voltage for C-V curves measured at various frequencies ranging from 1MHz to 1kHz (1MHz, 500kHz, 100kHz, 10kHz and 1kHz).A flat band voltage hysteresis and a frequency dispersion of 200mV was observed for samples that only had an Al_2O_3 gate dielectric while the insertion of an AlN interlayer resulted in a hysteresis and a dispersion of 50mV.

The I-V measurements produced a leakage of 0.016mA/cm^2 at 1V for the sample with only Al_2O_3 while the one with the interlayer produced a leakage of 0.0096 mA/cm^2 at 1V. These positive improvements with the insertion of an AlN interlayer could result due to the prevention of GaO_x sub-oxide formation at the GaN-Al_2O_3 interface [2].

In summary, the insertion of a PE-ALD AlN interlayer between an N_2 plasma treated GaN surface and ALD Al_2O_3 gate dielectric reduces the C-V hysteresis and frequency dispersion by 75% and decreases the leakage current by 40%. Both of these are encouraging for the realisation of high performance GaN power transistors.

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AA2-TuP-7 2-Dimensional Perovskite Oxide Thin Films Deposited by ALD for High-k Application

*J Ahn, **Seung-Won Lee**,* Korea Maritime and Ocean University, Republic of Korea*; C Kim, S Kwon,* Pusan National University, Republic of Korea

As the size of the DRAM is scaled down, the new high-k dielectric materials have received considerable attention. Among high-k materials, the dielectrics based on Zr- and Hf- have extensively been used in semiconductor industry. However, there is a limitation to obtaining an equivalent oxide thickness of under 0.5nm. Therefore, to replace the high-k material based on Zr- or Hf-, new high-k materials, such as rutile-TiO_2 and perovskite oxide, have attracted a candidate in next generation DRAM devices. Meanwhile, 2-D perovskite oxide films made by Langmuir-Blodgett method were reported that the permittivity was measured over 200.[1] However, Langmuir-Blodgett method can’t be applied to electronic applications, especially on the substrate with a high aspect ratio.

Therefore, in this paper, $Sr_xNb_yO_z$ (SNO) thin films with 2-D perovskite structure were deposited on TiN and $SrRuO_3$ substrate using atomic layer deposition (ALD). Then, rapid thermal annealing and laser annealing were performed for crystallization of thin films. Finally, we analyzed physical and electrical properties by RBS, TEM, XRD and semiconductor parameter analyzer.

AA2-TuP-8 High Performance Atomic Layer Deposition (ALD) of Gate Dielectrics for 4H-SiC Power Device Application, *B Lee, M Kang,* North Carolina State University; ***Adam Bertuch,*** Veeco-CNT; *V Misra,* North Carolina State University

Silicon carbide is one of most promising substrates for the power Metal Oxide Semiconductor Field Effect Transistor (MOSFET) and other power electronic devices. Due to high density of interface states (D_{it}) at SiO2/SiC interface, the mobility of Si-face (0001) 4H-SiC MOSFETs remains extremely low. Incorporations of nitrogen and phosphorous into the thermal oxide through a high temperature anneal are proven to be effective to suppress the D_{it}. Although the presence of nitrogen or phosphorous improves the mobility, achieved mobility values remain low when compared to the bulk SiC mobility. Additionally, nitrogen and phosphorous incorporations lead to negative threshold voltage (V_T) shift and makes even normally on devices. A positive enough threshold voltage is necessary for safe and reliable operation of power devices. Therefore, to deal with this trade-off between mobility and threshold voltage, deposited dielectrics on 4H-SiC have attracted more research interest to replace the thermal oxide. With deposited gate dielectrics, the substrate consumption is minimized and thus the carbon related defects associated with thermal oxidation can be avoided. Using deposited dielectrics also enables interface engineering to control interface properties independently. Among various deposition method, the atomic layer deposition (ALD) technique has proven to provide good film quality, low substrate damage, precise thickness control, and low temperature processing. This work first evaluates device electrical characteristics and reliability of SiO_2grown by either thermal or plasma ALD. $SiO_2$is the most suitable dielectric due to its large bandgap as well as a high conduction band offset to SiC resulting in suppression of electron tunneling current in SiC MOS devices. It was found that the channel mobility is similar between thermal and plasma ALD SiO_2but thermal ALD oxide shows lower threshold voltage compared to the plasma ALD oxide. Although ALD SiO_2provides positive threshold voltage and good gate insulating property, the SiC/SiO_2interface requires further treatment to enhance the mobility. We have recently demonstrated a novel interface engineering technique to improve the MOSFET mobility by combining ultrathin lanthanum oxide (LaO) at the SiC/dielectric interface and ALD SiO_2. In this study, we deposited ultrathin 1nm LaO followed by 30nm SiO_2using ALD tool without breaking the vacuum. It was found that the channel mobility is enhanced with the incorporation of 1nm LaO between SiC and SiO_2as compared to the device without LaO layer. This combination of ultrathin LaO and SiO_2provides an effective solution to challenges of SiC MOSFETs for power applications.

AA2-TuP-9 Atomic Layer Deposted TiO_2-Based Memristors using In-situ Fabricated Al Doped ZnO Thin Film as Electrodes, ***Kai Zhang,*** *P Lin,* Old Dominion University; *A Pradhan,* Advance Material Solution LLC; *H Baumgart,* Old Dominion University

Memristor is a nonlinear and two-terminal passive device, which has ability to change the resistance between high resistive states and low resistive states by applying bias voltage. This property called resistive switching makes the memristors suitable for a wide range of applications in nonvolatile random access memory, dynamic random access memory and flash memory. In recent years, Metal-oxide based memory devices have drawn significant attention due to their high-density integration, high endurance, fast switching behavior, low power consumption and simple structure. In addition, among the promising binary transition metal oxide materials, such as nickel oxide, zirconium oxide, zinc oxide, hafnium oxide, and titanium oxide, TiO_2 films are extensively used to fabricate the nonvolatile memristor devices due to its simple structure and compatible with CMOS integration process. Recently, ZnO has been widely used for various applications due to its good electrical conductivity, wide band gape (3.37 eV), high exciton binding energy (~60 meV), low cost, nontoxicity, high mechanical and thermal stability. When doped with Aluminum ZnO grown via atomic layer deposition (ALD) has been reported to show resistivity values ranging from insulating to on the order of 10^{-3} Ω·cm, which is suitable for memory device electrodes.

Currently, the most common methods used were magnetron sputtering, pulsed laser deposition, thermal oxidation, electrodeposition, chemical vapor deposition, sol gel chemical reaction, and atomic layer deposition. The ALD is a self-limiting technique that allows atomic layer growth each time. ALD can precisely control the film layer thickness, stoichiometry, composition, uniformity, and sharp interface. ALD also shows perfect conformal coverage when it deposits thin film on complex surface structures. Therefore, ALD is considered as a novel and competitive method to deposit MIM memory structures. To create such devices, transparent Al:ZnO film was grown on Si wafers as an transparent electrode followed by an active layer of TiO_2 film, then the other layer of Al:ZnO was deposited *in-situ* on the TiO_2 layer to form memristor structures. All the thin films in the structures were synthesized by the ALD system sequentially.

Several physical characterization techniques have been employed to determine the ALD films of memory devices. The crystal structure was analyzed by X-ray diffraction. The film morphology was determined by field emission scanning electron microscopy. The surface roughness was analyzed by atomic force microscopy. The electric properties were measured by semiconductor analyzer. The results demonstrate a fairly good memristive device.

AA2-TuP-10 Homogeneously Doped Atomic Layer Deposition Zinc Tin Oxide Thin Films for Improving Contact Resistance in Semiconductor Device Applications, ***Alex Ma,*** University of Alberta, Canada; *T Muneshwar,* Synthergy Inc., Canada; *D Barlage, K Cadien,* University of Alberta, Canada

For thin film semiconductor device applications, the formation of high quality contacts is critical. Currently, it is difficult to realize ohmic contacts on zinc oxide (ZnO) thin films especially for applications that require more resistive active layers e.g. thin film transistors (TFTs) and Schottky diodes. In this work, we investigate the contact resistance in thin film devices that employ ZnO active layers grown by low temperature plasma-enhanced atomic layer deposition (ALD) with the gated transmission length method (TLM). The contact performance in intrinsic ZnO devices are compared to identical devices but with a homogeneously doped ALD zinc tin oxide (ZTO) interlayer inserted between the semiconductor body and metal contact. By incorporating a small percentage of tin (Sn) in the ZnO during ALD growth, we observed an increase in the film's electron concentration resulting in lowered contact resistance.

AA2-TuP-11 AlGaN/GaN Layers Obtained by Atomic Layer Deposition Targeting Thin Film HEMT, ***Joaquin Alvarado,*** *M Chávez,* Benemérita Universidad Autónoma de Puebla, Mexico; *S Gallardo,* CINVESTAV-IPN, Mexico; *Y Sheng, D Muenstermann,* Lancaster University, UK

$Al_xGa_{1-x}N$ and GaN films were obtained using Plasma enhanced Atomic Layer Deposition (PE-ALD) at 300 °C, we study the effect of Al content variation on the optical and structural and electrical performance. XRD measurements show the hexagonal structure, SIMS profile signals reveals the main components of $Al_xGa_{1-x}N$.

Experimental

AlGaN thin films were deposited on silicon wafers via atomic layer deposition using a mega cycle which consists of sub cycles of AlN and GaN to obtain the $Al_xGa_{1-x}N$ alloy. The AlN sub cycle consist of (1) pulse of Trimethyl Alluminium (TMA), (2) Ar purge, (3) H_2/N_2 plasma and (4) Ar purge, the growth ratio is (0.5Å/cycle) at 300°C, the total number of megacycles were 215. GaN sub cycles consist of (1) pulse of Trimethyl Galliu (TMGa), (2) Ar purge, (3) H_2/N_2 plasma and (4) Ar purge, the growth ratio is (0.2Å/cycle) at 300 °C, the total number of megacycles were 131. The number of megacycles were calculated in order to obtain ~20 nm.

Results

The XRD patterns of $Al_xGa_{1-x}N$ on silicon substrates growth with 0.3 and 0.6 Al content were performed. Two peaks were observed in the sample $Al_{0.3}Ga_{0.7}N$ the peak located at 2θ=34.5° (002) is assigned to hexagonal phase of GaN and a second peak at 2θ=32.3° (100) correspond to the hexagonal phase of AlN. The sample $Al_{0.6}Ga_{0.4}N$ show peaks at 2θ=32.3° , 34.3° ,37.0° assigned (100), (002), (100) AlN. Furthermore, from photoluminescence characterizations it is possible to observe in the $Al_{0.3}Ga_{0.7}N$ sample a yellow luminescence band situated at 2.32 eV, which is related to Gallium and N vacancies, carbon defects, as well as to the high concentrations carriers 10^{19} cm^{-3} [1]. The peak observed at 2.2 eV is associated to dislocations defects [2]. However, a sample which contains higher content of Al didn't show PL signal.

On the other hand, by SIMS sputtering time profile it is possible to observed that the sample with $Al_{0.3}Ga_{0.7}N$ show a non-uniform Al content, although $Al_{0.6}Ga_{0.4}N$ show a better Al distribution film. Electrical characterizations of the deposited films will be also included.

AA2-TuP-12 High-Temperature Thermal Stability of ALD-TiN Metal Gate on *In-situ* Al_2O_3/Y_2O_3/(In)GaAs(001): Toward the Self-Aligned Gate-First Process*, Lawrence Boyu Young*, *H Wan, J Huang, K Lin, J Liu, Y Lin,* National Taiwan University, Republic of China*; J Kwo,* National Tsing Hua University, Republic of China*; M Hong,* National Taiwan University, Republic of China

High-k metal gate (HKMG) technology has been introduced since the 45-nm node complementary metal oxide semiconductor (CMOS). The gate-first process was replaced by the gate-last process because of the threshold voltage pinning caused by the subsequent high-temperature process[1]. The gate-first process provides a capability to reduce the process complexity, and is more economic than the gate-last process. To realize high-performance MOS field-effect transistors (MOSFETs) using self-aligned gate-first process, the thermal stability of MOS structure must be excellent to sustain the subsequent high temperature process. With the higher electron mobility, GaAs-based III-V semiconductors have potential to replace the current Si-based CMOS technologies. However, the reported thermal stability between high-k/III-V was limited to 500~600ºC caused by the inter-diffusion. In our previous study, ultra-high thermal stability above 850ºC between in-situ grown oxide/III-V interface was attained[2,3], critical for the present study of atomic layer deposition (ALD)-TiN/oxide/(In)GaAs thermal stability at temperatures ranging from 850 to 950°C. Here, we have studied the samples with different post-metallization annealing (PMA) using transmission electron microscopy (TEM), J-E, and C-V characteristics of the MOS capacitors (MOSCAPs). The samples were prepared in a ultra-high vacuum (UHV) multi-chamber growth/analysis system (Fig. 1). The detailed fabrication process and the schematic structure of the MOSCAPs are shown in Fig. 2 . The TEM shows the smoothness in an atomic scale of the ALD-TiN/high-k/(In)GaAs interfaces. The interface remained intact without degradation after 800ºC 5s in He ambient (Fig. 3). From the J-E curves (Fig. 4), the leakage current densities of the MOSCAP with different PMA in N_2 show no degradation after 900ºC annealing for 10s. The leakage current density of the MOSCAPs maintained below 10^{-7} A/cm^2 at electric fields of ± 4 MV/cm, which is the same with that of the MOSCAP without PMA. A different behavior was found in the MOSCAP with PMA in He. The leakage current density raised sharply in the negative bias region, probably resulted from the generation of nitrogen vacancies during the high temperature annealing in He. Similar features were found in the C-V characteristics (Fig. 5). With the PMA in N_2, the C-Vs showed no degradation after 900-950ºC annealing, while the MOSCAP was too leaky to measure the C-Vs for the MOSCAP with PMA in He with temperatures above 900ºC. The excellent electrical and thermal stability of the MOS structures with TiN gate are vital to realize high performance GaAs inversion channel MOSFETs using a gate-first process.

AA2-TuP-13 Identification of Interfacial Defect in ALD Grown Al_2O_3/GeO_x/Ge Gate Stack*, Jinjuan Xiang*, *L Zhou, X Wang, X Ma, T Li, W Wang,* Institute of Microelectronics of Chinese Academy of Sciences, China

Germanium (Ge) has attracted tremendous interest as a channel material for high performance complementary metal-oxide-semiconductor (CMOS) devices. The interfacial cfixed charges are detrimental to the performance promotion of Ge MOSFET devices as they can form Coulomb scattering center to reduce channel carrier mobility and device reliability. Thus we experimentally investigate the interfacial defect in the GeO_x/Al_2O_3 gate stack grwon by ALD using X-ray photoelectron spectroscope (XPS) and electrical charateristics by capacitance-voltage (*C-V*) measurement. For GeO_x interlayer by ozone oxidation, oxygen vacancies exist and show positive charges at the Ge/GeO interface. The O_2 annealing is helpful to decrease the oxygen vacancy defect. For the GeO_x/Al_2O_3 interface, oxygen dangling bonds exist, and show negative charges. This work can be effectively applied to engineer the interface promotion and enhance the performance of Ge-based devices.

AA2-TuP-14 Modifications of the Electrical Properties of MOS Capacitors Based on Bilayer Gate Metallization - WC_xN_y Capped by CVD Molybdenum on SiO_2 and on ALD Al_2O_3*, Ekaterina Zoubenko,* Technion - Israel Institute of Technology, Israel*; I Fisher, S Thombare, P Van-Cleemput, M Danek,* Lam Research Corp.*; M Eizenberg,* Technion - Israel Institute of Technology, Israel

Refractory metal nitrides and carbides, deposited by ALD, are attractive for gate metallization of 3D metal-oxide-semiconductor (MOS) devices, due to the good thermal and chemical stability and metal effective work function (EWF) variation capability. However, obtaining low resistivity of the gate metallization is challenging. Therefore, a bilayer approach, where a thin refractory metal carbide/nitride liner capped by a pure metal, is implemented. The liner determines the EWF and serves as a nucleation layer and a diffusion barrier for the contact metal. Currently, Tungsten is commonly used as a local interconnect conductor. Due to its resistivity and device performance challenges, Molybdenum is considered as an alternative capping layer.

The objective of the current research is to investigate the structural and the electrical properties of a bilayer metallization: thermal-ALD tungsten carbo-nitride, WCN (WC_xN_y), liner with thicknesses of 10/20/30Å covered by 100Å CVD-Mo cap. The evolution of the properties upon annealing at 750ºC in forming gas (FG -10%H_2, 90%Ar) and vacuum (10^{-6}torr) is correlated with the values of the EWF on thermal SiO_2 and on ALD Al_2O_3/SiO_2. The metal stack structure and composition were studied by XRD, STEM-EDS, and ToF-SIMS. The sheet resistance was measured by the four-point probe technique. The EWF of the WCN/1kÅ Mo metal stack on SiO_2 and on Al_2O_3 was studied using capacitance-voltage measurements of MOS devices by plotting the flat-band voltage versus the effective oxide thickness.

It was found that the lowest sheet resistance of as-deposited samples was obtained for the metal stack on the 10Å WCN liner (26Ω/□); annealing at FG led to sheet resistance decrease up to 11Ω/□. The EWF of the as-deposited samples is determined by the WCN layer: a value of 4.8eV on SiO_2, as was obtained by a 30Å WCN/W reference sample, and a value of 5.35eV on Al_2O_3/SiO_2, demonstrating a difference of ~0.4eV attributed to a dipole at the Al_2O_3 /SiO_2 interface, earlier obtained in our group. Both thermal treatments induced Mo diffusion towards the interface with the dielectric, but the annealing ambient effect on metal crystallinity and Mo diffusion rate is different. Annealing at vacuum caused grain growth of the cubic W_2N phase and stabilization of the EWF to a value of 4.8eV on SiO_2. FG annealing led to BCC-Mo grain growth, significant Mo diffusion towards the interface, and EWF on SiO_2 decrease of 0.2eV. Similar EWF decrease due to FG annealing was observed on Al_2O_3. This, combined with the low resistivity, makes WCN/Mo stack a good candidate for many applications, e.g. FDSOI devices.

AA2-TuP-15 Effect of Metal-insulator Interface on Dielectric Properties of Ultrathin Al_2O_3 and MgO Fabricated using *In-situ* Sputtering and Atomic Layer Deposition*, Jagaran Acharya,* *J Wilt, R Goul, B Liu, J Wu,* The University of Kansas

We have investigated the properties of ultrathin $Al_2O_3$and MgO in metal-insulator-metal (M-I-M) trilayers fabricated using *in situ* integrated sputtering and atomic layer deposition (ALD). The quality of ultrathin Al_2O_3 was found to be significantly dependent on the pre-ALD conditions which lead to extremely different M-I interface. After optimization of ALD processing parameters, M-I interfacial layer (IL) was reduced to a negligible level obtaining a dielectric constant (ε_r) up to 8.9 on the Al_2O_3films in a thickness range between 3.3-4.4 nm, corresponding to an effective oxide thickness (EOT)~1.4-1.9 nm respectively comparable to high-K dielectrics. While ε_r decreases at a smaller Al_2O_3 thickness, the hard-type dielectric breakdown 32 MV/cm and in situ scanning tunneling spectroscopy (STS) revealed band gap ~2.63 eV confirming high quality dielectric as good as an epitaxial Al_2O_3 film. This result suggests that the IL is unlikely a dominant reason for the reduced ε_r at the Al_2O_3 thickness of 1.1-2.2 nm and is due to electron tunneling as supported by transport current-voltage measurement. However, non-optimal conditions result in the growth of significant IL with drastically reduced ε_r~0.5-3.3. The properties of MgO with and without 5C-ALD Al_2O_3 studied in the thickness range 2.5-5 nm point out significance of seed layer in fabrication of high-quality dielectrics, approaching ε_r~9 for 5C-ALD-Al_2O_3/ALD-MgO at thickness 3.8-4.9 nm corresponding to EOT~1.6-2.1 nm respectively. But, 40C-ALD MgO without seed layer has unexpectedly lower ε_r~3-4 possibly due to poor nucleation forming an interfacial layer, and correspondingly increase in the leakage current. The similar decreasing trend in ε_r with decrease in MgO thickness is observed but at thickness greater than that of Al_2O_3, due to higher leakage current observed for MgO dielectrics and also confirmed by in situ STS analysis. Our results demonstrate the significance of controlling the nucleation in ALD to achieve better M-I interface in order to fulfill the demand for leak-free and defect-free high-quality ultrathin dielectrics an alternative for low-cost gate dielectric for CMOS, and tunnel junction for quantum computing and memory applications.

AA2-TuP-16 Thermal and Plasma ALD Al_2O_3 Gate Insulator for GaN Electronic Devices Characterized by CV-Stress Measurements*, Nicole Bickel,* *E Bahat Treidel, I Ostermay, O Hilt, O Krüger,* Ferdinand-Braun-Institut, Germany*; F Naumann, H Gargouri,* SENTECH Instruments GmbH, Germany*; J Würfl, G Tränkle,* Ferdinand-Braun-Institut, Germany

The technology of atomic layer deposited (ALD) Al_2O_3 films is ideally suited for fabrication of high quality GaN MISFET's gate insulator especially in vertical GaN n-channel transistor technology (Fig. 1). The gate oxide technology is a very crucial process step as it influences transistor functionality such as normally-OFF operation, hysteresis and low positive threshold voltage drift. Furthermore, dependent on the transistor design the gate oxide/channel interface may also determine ON-OFF-ratio. For qualifying and characterizing the gate insulator film technology, circular-planar MIS-capacitors were formed on a *n*-GaN layer (Fig. 2). The 25 nm thick Al_2O_3 films were deposited by plasma enhanced atomic layer deposition (PEALD) and thermal atomic layer deposition (ThALD) in SENTECH ALD system SI PEALD. Different in-situ surface pre-treatment conditions such as NH_3-plasma, NH_3-flow and without any pre-treatment were tested to optimize the GaN/Al_2O_3 interface. After top electrode metallization the capacitors were annealed at 350°C in N_2-ambient to achieve a large $\Delta C_{ON\text{-}OFF}$. Accumulated capacitance-voltage-(CV)-scans were performed to evaluate the insulator charging effects, to identify possible shifts in the CV-profile and to gain insight into bulk and interface charging phenomena (see Figs. 3 and 4). While measuring the accumulated bidirectional scans the maximum positive stress bias voltage was increased in 2 V steps from 0 V to 16 V after each bias sweep. The capacitance was measured at 1 MHz and 1 V AC amplitude. According to Figs. 3 and 4 a negative bias down to -15 V has turned out to be sufficient to empty the interface traps. PEALD and NH_3-plasma treated samples show a significant broadening of the positive bias stress CV-profile. Furthermore the flat band voltage shifts up to 7.2 V (Fig. 5). In contrast, the ThALD films with NH_3-plasma pre-treatment show a reduced broadening with a flat band voltage shift of only 2.9 V. When using NH_3-plasma pre-treatment, the calculated maximum negative fixed-oxide charges are less for ThALD ($-\Delta N_{OX}$ 5.1 × 10^{12} cm^{-2}) as compared to PEALD ($-\Delta N_{OX}$ 1.1 × 10^{13} cm^{-2}), see Fig. 6. Therefore thermal ALD in combination with NH_3-plasma pre-treatment is very suitable for GaN MISFET technology.

AA2-TuP-17 Variable Morphology Highly-Conformal Diffusion Barriers for Advanced Memory and Logic Applications*, **Hae Young Kim**, S Rathi, B Nie, N Naghibolashrafi, Y Okuyama, S Chugh, J Heo, S Jung, J Mack, N Mukherjee,* Eugenus, Inc.

Atomic layer deposition (ALD) of metallic ternary TiSiN films is associated with a variety of morphological and structural variations. Among these phenomena are the thickness and stoichiometric-dependent amorphous to crystalline phase transitions, film density changes, surface roughness and film resistivity variations. In the case of TiSiN films deposited via thermal ALD at temperatures of about T<600° C, using chlorine-based Si precursors, titanium tetrachloride and ammonia, the film structure is highly dependent on the total Si incorporated in the film. In this work, we demonstrate the tunability of crystalline phase in highly conformal TiSiN films with varied Si content. TiSiN films were deposited on high aspect ratio structures using a Eugenus 300mm commercial QXP mini-batch system. Film thickness and Si content were varied, and corresponding structural analysis was performed using multiple characterization techniques. X-ray diffraction and reflectivity studies of these films showed a reduction in film density and transition from nano-crystalline to pure amorphous phase with increase in Si fraction. Cross-section high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) pattern analyses corroborates with the X-ray analysis that high-Si TiSiN films exhibit a fully amorphous structure. Moreover, control of Si fraction in the film enables tuning of the morphology from polycrystalline to fully amorphous; in all cases, excellent step coverage on high aspect ratio structures were obtained.

AA2-TuP-18 Room Temperature Deposition of Hafnium Oxide by Atomic Layer Deposition for Gating Applications*, **Pragya Shekhar**, S Shamim, S Hartinger, J Kleinlein, R Schlereth, H Buhmann, L Molenkamp,* University of Wuerzburg, Germany

The advancement of fabrication techniques for nanostructures devices has led to technological breakthrough in semiconductor industries. Apart from the lithographic developments, high-κ materials like ZrO_2 and HfO_2 have been employed as gate dielectric for efficient control of the carrier density. In this regard, atomic layer deposition (ALD) has been used to grow these insulators as it produces highly uniform and conformal layer with precise thickness. Previous works to grow HfO_2 by ALD require higher temperature (>100 ^{o}C) for microelectronic devices has been done. However, many devices and materials have additional constraints that their properties degrade at higher temperatures. This limits the operating temperature at which the various fabrication processes can be carried out. For our research in the field of topological physics, mercury telluride (HgTe) topological insulators (Tis) are significant due to its versatility and tunability from trivial to 2D TI to 3D TI to Weyl by tuning the thickness and applied strain (compressive or tensile). However, the transport properties degrade when the HgTe wafer are heated above 80 ^{o}C . To overcome this problem, we have developed a room temperature ALD process for growing HfO_2. A comprehensive study of structural and transport properties of devices containing HfO_2 gate dielectrics was carried out and results has been compared to device containing coventional SiO_2/ Si_3N_4 multilayers insulator films grown by plasma enhanced chemical vapour deposition (PECVD).This comparison demonstrates that our ALD grown insulator is superior in terms of structural properties. We have already shown that microstructures fabricated with ALD grown insulator shows quantum spin hall effect for 2D HgTe based devices. This capability is critical for understanding the properties of microscopic devices and may provide new insights in the field topological insulators. Our process is not just limited to HgTe (e.g. we use Si for process control) but can be easily adapted to other material systems which also require low temperature lithography process in order to retain the intrinsic property of material.

AA2-TuP-19 Influence of Surface Cleaning Process on Initial Growth of ALD-Al_2O_3 and Electrical Properties of Pt/Al_2O_3/*β*-Ga_2O_3 MOS Capacitors*, **Masafumi Hirose**,* Shibaura Institute of Technology, Japan*; T Nabatame,* National Institute for Materials Science, Japan*; E Maeda,* Shibaura Institute of Technology, Japan*; A Ohi, N Ikeda, Y Irokawa, Y Koide,* National Institute for Materials Science, Japan*; H Kiyono,* Shibaura Institute of Technology, Japan

β-Ga_2O_3 power device with metal-oxide-semiconductor (MOS) structure have been widely investigated. Al_2O_3 is the leading candidate as gate insulator because of relatively stable amorphous structure, a high dielectric constant (*k*) of 8 - 9 and a large bandgap of 6.5 - 6.8 eV. Al_2O_3 films are generally formed by atomic layer deposition (ALD). However, it remains big issues such as an abnormal flatband voltage (V_{fb}) shift and a large interface state density (D_{it}). To improve these electrical properties, various surface cleaning techniques of the substrate have been considered. In this study, we investigate how the surface cleaning technique affects to morphology of the surface of *β*-Ga_2O_3 and electrical properties of Pt/Al_2O_3/*β*-Ga_2O_3 MOS capacitors.

At first, n-*β*-Ga_2O_3 epilayer (2.0 × 10^{16} cm^{-3}) / n^+-*β*-Ga_2O_3 (3.7 × 10^{18} cm^{-3}) substrates (n-*β*-Ga_2O_3) were cleaned under four conditions: just a SPM for 5min, and SPM for 5 min (SPM), followed by BHF for 1 (BHF1), 10 (BHF10), and 30 min (BHF30). 25-nm-thick Al_2O_3 films were deposited on n-*β*-Ga_2O_3 substrates by ALD at 300 °C using TMA precursor and H_2O gas. Finally, Pt gate electrodes and Ti/Pt ohmic electrode were deposited.

The minimum root mean square (RMS) value (0.36 nm) of the n-*β*-Ga_2O_3 substrate was observed after SPM treatment. The RMS values (~ 0.6 nm) increased drastically when BHF treatment carried out even for 1 min and the value was unchanged even if treatment time was longer. In addition, the n-*β*-Ga_2O_3 substrate was etched by 0.9 nm for the BHF30. This is because the increase of the surface roughness is due to the heterogeneous etching of the n-*β*-Ga_2O_3 substrate. The Al_{2p} XPS intensities of the Al_2O_3 films after ALD 5 cycles for the BHF10 and BHF30 decreased by about 25 % compared to the SPM and BHF1, suggesting that the surface roughness affects to the initial growth of the Al_2O_3.

The MOS capacitor exhibited similar *J-V* properties regardless of the surface treatment techniques, indicating that the characteristic of the Al_2O_3 films was unchanged. On the other hand, the V_{fb} hysteresis ($V_{fb\ hys}$) due to the trapped/detrapped electrons increased as the BHF treatment time increases. The D_{it} energy distribution due to the fixed charge, which was calculated using conductance method, increased with increasing the BHF treatment time. These $V_{fb\ hys}$ and D_{it} behaviors are in good agreement with the data of the surface roughness of the n-*β*-Ga_2O_3 substrate. Considering to these data, note that the fixed charge and trapped/detrapped electrons occur at the Al_2O_3/n-type *β*-Ga_2O_3 interface. Therefore, the BHF surface treatment technique is not necessary promising from the viewpoint of the interface characteristics.

AA2-TuP-20 Reliable Gate Stack Development Employing Plasma Assisted Atomic Layer Deposited HfO_xN_y on InGaAs Substrate*, **Sukeun Eom**, M Kong, K Seo,* Seoul National University, Republic of Korea

We developed an advanced plasma-assisted atomic-layer-deposited (PA-ALD) HfO_xN_y process targeted on InGaAs substrate. The developed ALD process is consisted of isopropyl oxidant precursor and in-situ cyclic N2 plasma nitridation that improves both interface and dielectric bulk quality as well. The interface chemistry and capacitance-voltage characteristics of HfO_xN_y / InGaAs MOS devices are investigated. Clear oxide related elements were eliminated using our ALD process confirmed by XPS and STEM measurements. The IPA-based HfO_xN_y/n-$In_{0.53}Ga_{0.47}As$ MOS capacitor exhibited a significant decrease of interface trap density, D_{it}, of 4.5×10^{11} eV^{-}

^{1}cm^{-2} at E_c - E_t = 0.3 eV and outstanding inversion behaviors. Morevover, substantial improvement was found not only in n-type substrates but also in p-type substrates as well. The significant mid-gap D_{it} decrease is responsiblefor this inversion behavior. The improvement mechanism of the proposed technology is assumed to be that nitrogen incorporation reduces oxygen vacancies which act as oxygen diffusion paths and with the use of IPA oxidant the interface would be strongly protected during pre- and post-dielectric deposition. Detailed electrical characteristics such as positive-bias-temperature-instabiltiy characteristics were investigated.

ALD Applications

Room Evergreen Ballroom & Foyer - Session AA3-TuP

Catalysis and Sensor Applications Poster Session

AA3-TuP-1 Highly Dispersed Uniform Pt Catalysts on Carbon Support by Atomic Layer Deposition with Fluidized Bed Reactor(FBR)., ***Jung-Yeon Park***, *W Hong, S Oh,* Hyundai Motor Group, Republic of Korea*; W Lee, S Kwon,* Pusan National University, Republic of Korea

One of the key issues for fuel cell study is to increase the active surface area by controlling the size of Pt catalyst and reduce Pt loading to achieve high performance and cost savings. Atomic layer deposition (ALD) has recently received attention as an effective method for synthesis of nano catalyst since it allows precise control at the atomic level. In this study, Pt catalyst is synthesized using ALD directly on the surface of porous carbon support floated by fluidizing bed reactor (FBR). The oxygen functional group introduced on carbon surface through acid solution treatment provides reaction site of Pt precursor. In initial cycle, nucleation occurs on carbon surface, and high density 1-2 nm size uniform nanoparticle is formed. The Pt precursor adheres to the surface of already generated Pt and grows the Pt nanoparticle. Because of this growth mechanism, the size distribution of the particle is slightly wider at high cycles, but the size of the particle is controlled by the cycle and grows up to about 4 nm in 30 cycles. About 1 nm size particles have the highest active surface area, but in terms of catalyst performance, about 3 nm size particles show the best results under the Pt loading fixed condition. When the size of particle is not less than 3 nm, Pt exhibit physical properties as a catalyst and agglomeration of particles can be suppressed. To evaluate the catalyst performance of new processes , MEA optimization is important and this remains as a future plan.

AA3-TuP-3 Stabilizing Ultrasmall Colloidal Platinum Diphosphide (PtP_2) Nanocrystals with Atomic Layer Deposition Oxide for Neutral H_2O_2 Electrosynthesis, ***Hui Li***, *S Geyer,* Wake Forest University

Despite recent demonstrations of various electrocatalysts for small amount hydrogen peroxide (H_2O_2) production with rotating ring-disk electrode technique, it is still a great challenge to develop an efficient, selective, and stable O_2-to-H_2O_2 electrocatalyst for realizing continuous on-site production of neutral hydrogen peroxide. Here we synthesize ultrasmall and monodisperse colloidal PtP_2 NCs which achieves nearly zero-overpotential and unit H_2O_2 selectivity at 0.27 V vs. RHE for ORR. DFT calculation suggests that the P play a key role in promoting associative hydrogenation of OOH* to H_2O_2 and suppressing the dissociative OOH* to O*. With precise ALD Al_2O_3 overcoat and activation, the proton-exchange membrane fuel cell (PEMFC) with $42Al_2O_3/PtP_2$-600 catalyst achieves a maximum r(H_2O_2) of 2.26 mmol h^{-1} cm^{-2} and a highest current efficiency of 78.8% for 120 h. Under recycle mode, the accumulated neutral H_2O_2 concentration reaches up to 3wt% for 65 h and 1.21 mol L^{-1} for 120 h, and which can be readily used for medical, food, and environmental applications.

AA3-TuP-5 Synthesis of Core Shell Nanocatalysts using Atomic Layer Deposition with Fluidized Bed Reactor for PEMFC, ***Seung-Jeong Oh***, *W Hong, J Park,* Hyundai Motor Group, Republic of Korea*; W Lee, S Kwon,* Pusan National University, Republic of Korea

Proton Exchange Membrane Fuel Cells(PEMFC) have attracted significant interest as sources of renewable energy due to higher energy conversion efficiency than conventional internal combustion engines and zero-emission characteristics. Despite its great advantages, it is difficult to commercialize due to high stack cost. Among the parts, Platinum(Pt) catalyst is expensive and scarce, so it is important to maximize the catalyst activity with minimal usage. Many researchers have significantly focused on core shell nanocatalysts due to their great activity, selectivity and stability with reducing the Pt loading. To optimize the characteristics of core shell nanocatalysts, it is necessary to precisely control shell composition and thickness. With the Atomic Layer Deposition(ALD) process, the size of nanocatalysts and shell thickness could be finely tuned at atomic scale. In order to uniformly deposit the nanocatalysts on the porous carbon support with large surface area, ALD with Fluidized Bed Reactor(ALD-FBR) offers the solution. By dispersing the carbon powder in the chamber, particle agglomeration is prevented and nanocatalysts can be uniformly deposited.

In this work, we synthesized core shell nanocatalysts using ALD-FBR. We utilize Nickel(Ni), Ruthenium(Ru) for the core materials, and Pt for the shell material. Ni(1-dimethylamino-2-methyl-2-butanolate)$_2$, η^4-1,3-cyclohexadiene ruthenium tricarbonyl, and Trimethyl(methylcyclopentadienyl)platinum(IV) are used as Ni, Ru and Pt precursor, respectively. The size of nanocatalysts and shell thickness is controlled by changing each ALD cycles. TGA, XRD and HRTEM are used to examine the structural and chemical properties of core shell nanocatalysts. From EDX line profile analysis, shell material(Pt) is preferentially deposited on core nanoparticles(Ni, Ru). Electrochemical Surface Area(ECSA) and cell performance were measured by Cyclic Voltammetry(CV) and MEA test. Core shell nanocatalysts by ALD-FBR show higher ECSA and cell performance than commercial catalyst.

AA3-TuP-6 Porous Nanomembranes Grown by Atomic Layer Deposition: Self-Rolling in Solvent and their Sensing Applications, *F Ma, Y Zhao, G Huang,* ***Yong Feng Mei***, Fudan University, China

Tubular microstructures of various materials have emerged as active agents for large-scale detoxification, sensing, and many other promising applications [1]. Generally, for sensing application, binding of specific recognition sites on tubular structures for targets molecule is engaged to achieve capture and detection of certain molecular [2]. The rolled-up technology [3,4] provide the possibility of producing microtubular structures with desired geometries and surface decoration on surface, which should be of great importance for real-time bio-sensing. In this study, porous nanomembranes were fabricated with high productivity by depositing active material on the surface of 3D polymer porous template with rough surface via atomic layer deposition technique [5]. The free-standing porous ZnO nanomembranes were obtained after the sacrificial template was removed at high temperature in oxygen. The rough surface of the template and the high temperature treatment make the surface of the nanomembrane with porous microstructure. Self-rolled porous ZnO nanomembranes were then prepared by sonication in chemical solvent. The porous surface was used as cysteine recognition sites for effective and selective binding of neurotransmitter compounds like dopamine (DA). Such selective binding is significantly enhanced by the high surface-to-volume-ratio of the porous structure . For sensing applications, dispersion solution containing rolled-up structures was dropped on the surface of glassy carbon electrode, and then cysteine recognition sites was self-assembled on porous ZnO nanomembrane to capture target DA molecules which induces concentration-dependent electrical signals. Detailed analyses demonstrate that increased mass transfer leads to the enhanced sensitivity for DA. The current strategy provides an opportunity to develop 3D biosensor for high-affinity capture-based detection of nerve agents and can be extended to environmental contamination field.

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AA3-TuP-7 Fabrication and Characterization of Atomic Layer Deposited ZnO-based Ultra-thin Films for Hydrogen Sensing, ***Yan-Qiang Cao***, *A Li,* Nanjing University, China

As a high-energy density, non-polluting renewable energy source, hydrogen is widely used in many fields such as industrial synthesis, fuel cells, and rocket propulsion. It is of great importance to develop reliable, fast, and precise hydrogen sensors so as to avoid possible explosion risks and harm. Due to the low cost, chemically and thermally stability, extremely abundant nanostructures and simple fabrication technique, ZnO as n-type semiconductor is widely used to detect reductive gases, such as hydrogen. Usually thin film-based sensor is more effective for improved gas sensing performance due to its small size, larger surface to volume ratio, and feasibility in integrated circuits. To date, research on ZnO ultra-thin film-based H_2 sensor is still lacking.

In this work, the ZnO ultra-thin films with varied thicknesses from 5 nm to 30 nm were grown on SiO_2 substrate at 200 ℃ using diethyl zinc (DEZ) and H_2O by atomic layer deposition (ALD), which could precisely control the thickness of the films down to values comparable to the Debye length. The effect of ZnO thickness and post-anneal on H_2 sensing, such as detection concentration, work temperature, and sensitivity has been carefully investigated. It is found that H_2 sensor based on 10 nm-thick ZnO ultrathin film exhibits better room temperature sensing performance with R_{air}/R_{gas} of 29 in 4000 ppm H_2. We also attempted to prepare Pt nanoparticles-decorated ZnO ultra-thin films by ALD. The impact of Pt NCs size and areal density on enhanced H_2 sensing of ZnO film sensor has been evaluated. The improved mechanism has been proposed.

ALD Applications
Room Evergreen Ballroom & Foyer - Session AA4-TuP
Protective Coatings, Barrier Films, Membranes and Flexible Substrates Poster Session

AA4-TuP-1 ALD for Membrane Applications, ***Matthieu Weber***, *M Bechelany,* Institut Européen des Membranes, France

Atomic layer deposition (ALD) is a technology allowing for the preparation of conformal ultrathin films with a sub-nanometer thickness control, a unique capability. Therefore, this route is particularly suited for the structural modification and pore tailoring of porous structures. ALD can be advantageously applied to the area of membranes by fine-tuning their surface properties, and by controlling the diameter and the aspect ratio of the pores with (sub)nanometer precision. The precise control over the chemical and physical nature of the pore surface provided by ALD makes this route extremely valuable for membrane science. Thus, ALD coatings have been prepared on a wide variety of membrane substrates, from inorganic templated substrates to porous polymers.

This presentation aims to provide a summary of the advances of ALD applied to membranes. Based on a wide literature data survey including some of our recent data,[1–3] the application of ALD for different types of membranes will be described and illustrated using relevant examples, and the main challenges and opportunities of the ALD route will also be assessed.

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AA4-TuP-2 Nano-Hardness of ALD Films, ***James Daubert***, *W Sweet, J Kelliher,* Northrop Grumman

In this presentation, we will explore different films (Al_2O_3, ZrO_2, Ta_2O_5) deposited using atomic layer deposition (ALD) to compare how the processing conditions (i.e. deposition temperature, material interfaces, and annealing temperatures) effect hardness. The mechanical and electrical performance of materials used in microelectronics are often dependent on the processing conditions of material, but extensive testing after device manufacturing is often required to determine these relationships. Bulk, macroscale measurements, such as thickness, index of refraction, and sheet resistance can easily be measured, but often do not translate well to the performance of the final device, because the devices are often dependent on nanoscale properties of the materials (i.e. defects). If the nanoscale properties of the materials can be measured before final device fabrication, then correlations can be established linking material processing conditions with device performance.

One method to measure nanoscale properties of materials is through nano-identation. Nano-indentation is a method to measure the hardness of materials using atomic force microscopy (AFM) that allows one to see differences in hardness on the nanoscale. Measuring the hardness of a material on the nanoscale allows you to elucidate variations in hardness that results from polycrystallinity of the material. We report on how the hardness is impacted by film thickness (50-1000 Å) and the underlying material. We also show how crystallinity produced by deposition or anneal temperature influences hardness of ALD films.

AA4-TuP-3 High Acid Corrosion Resistance of Nb_2O_5 Thin Film Deposited by Room Temperature ALD, ***Kazuki Yoshida***, *K Saito, M Miura, K Kanomata, B Ahmmad, S Kubota, F Hirose,* Yamagata University, Japan

Metal oxide thin films like aluminum oxide (Al_2O_3), silicon oxide (SiO_2), and titanium oxide (TiO_2) have been well known as gas barrier materials for moisture. For acid corrosion, Al_2O_3 exhibits a slight deliquescence against hydrochloric acid. On the other hand, niobium pentoxide (Nb_2O_5) has been studied as a cathode protective layer of a fuel cell and a corrosive barrier film for metal. By laminating Nb_2O_5 on Al_2O_3 using thermal ALD, the corrosion resistance was enhanced to a certain degree. However, the deposition temperature was over 200℃ although the high-temperature process is not acceptable for not heat-tolerant flexible electronics. In this study, a laminated film of Al_2O_3 and Nb_2O_5 was deposited by room temperature atomic layer deposition (RT-ALD) and we report the improved acid corrosion resistance.

We used plasma excited humidified Ar as an oxidizing gas, trimethylaluminum (TMA) and tert -butylimidotris-(ethylmethylamido)niobium (TBTEMN) as precursors of Al_2O_3 and Nb_2O_5, respectively. The RT-ALD system is shown in Figure 1. We prepared SUS 304 plates with a size of 20 × 50 mm^2 as samples. The SUS plates were cleaned by ultrasonic cleaning with using acetone, isopropyl alcohol, and deionized water to remove organic impurities. The surface was slightly etched with dilute hydrochloric acid to remove the surface scratches, For the corrosion resistance test, we immersed substrates into the concentrated hydrochloric (36 wt%).

Figure 2 shows the anti-corrosion film coated substrate immersed in concentrated hydrochloric acid for 30 minutes. Al_2O_3 thin films were deposited 30 nm both (a) and (c). The Nb_2O_5 was deposited with a thickness of 5nm both the substrate(b) and (c). The substrate (c) is laminated Nb_2O_5 on Al_2O_3. As we can see from Fig.2, the corrosion resistance for hydrochloric acid is clearly improved by laminating Nb_2O_5. We consider the RT deposited Nb_2O_5 is applicable for not heat tolerant flexible and MEMS application.

AA4-TuP-4 Effects of Composition Ratios on Mechanical and Electrical Properties of AZO – Zincone Composite Thin Film Deposited on Transparent Polyimide Film Using Atomic and Molecular Layer Depositions., ***Seung Hak Song***, *B Choi,* Korea University, Republic of Korea

The combination of ALD and MLD techniques enables the fabrication of various functional organic – inorganic composite thin film structures. It is possible to fabricate thin films with various mechanical and electrical properties by adjusting the ratio of organic / inorganic components. In this study, a composite thin film composed of Al-doped zinc oxide (AZO) and the zincone organic film were deposited on a transparent polyimide substrate using diethylzinc (DEZ) with H_2O and hydroquinone (HQ) precursors. The characteristics of the hybrid thin film are varied significantly with the change of composition ratios, so the change of mechanical and electrical properties of the thin films according to the ratio of zincone organic film were measured. Various nano-structures of hybrid thin film were fabricated by controlling the composition ratio and process conditions, and their morphology and characteristics were analyzed. To investigate the ratio of thin films with high durability and electrical conductivity, the variation of electrical resistivity of thin films according to bending was measured.

AA4-TuP-5 Room-temperature Atomic Layer Deposition of Aluminosilicate Thin Film on Flexible Films, ***Yoshiharu Mori***, *K Yoshida, K Kanomata, M Miura, B Ahmmad Arima, S Kubota, F Hirose,* Yamagata University, Japan

In recent years, aluminosilicate thin films are applied in various fields such as ion absorbers. Aluminosilicate is generally prepared by hydrothermal synthesis. However, it is based on high temperature and pressure processes. It is also not suited for the fabrication on electronic devices. To solve these problems, we newly developed room temperature ALD of aluminosilicate using tris [dimethylamino] silane (TDMAS), trimethylaluminum (TMA) and plasma excited humidified argon. We realized deposition of aluminosilicate on flexible films at room temperature as shown in Fig.1. Fig.2 shows a wide scan XPS spectrum measured from the RT grown aluminosilicate on a PEN film. We confirmed significant peaks of Si, Al and O. The aluminosilicate film thickness was measured by spectroscopic ellipsometry that exhibited the growth per cycle of 0.16 nm/cycle at room temperature. This suggest the possibility of the film thickness control with a precision of nanometer. We confirmed the ion absorption ability of the film. It was confirmed that Na and K cations were effectively absorbed on the film. The ion exchange properties from Na to K was also confirmed. The present RT-ALD offers the ion exchange function on flexible films. This research is expected to be applied as heavy metal ion filters and ion sensitive field effect transistors.

AA4-TuP-6 ALD Layers for Reduced Wear on Micro Cutting Tools*, T Junghans,* ***Hans-Dieter Schnabel,*** Westsächsische Hochschule Zwickau, Germany

In modern life, the usage of electronics is increasing day by day. Therefore, many circuit boards need to be machined. One of the major problems in circuit board manufacturing is the wear of micro cutting tools used for it. Hard and corrosion resistant coatings might be a good opportunity to reduce the wear of these tools [1,2]. Due to the small size of the tools, with diameters of 300 µm and 3 mm, most traditionally used coating techniques are unable to produce conformal coatings on them [3]. This is why the works presented in a poster aimed for thin wear reducing films generated with atomic layer deposition.

The materials used were Al_2O_3 and TiN in various thicknesses from 20 nanometer to 150 nanometer. Those were used because of their properties, like hardness and corrosion resistance [1,4] and the well-established ALD-processes. In order to achieve dense films and low deposition temperatures the processes were plasma enhanced. Al_2O_3 was deposited with TMA as precursor in combination with an oxygen-argon plasma. The TiN films were generated by reacting TDMAT with an ammonia-argon plasma.

The poster shows that Al_2O_3 and TiN do not differ in wear behavior. Therefore, the focus is on Al_2O_3, due to the more stable and less time-consuming process. As the film thickness becomes bigger than 50 nm the Al_2O_3-layers are spalling off of the tools. Therefore, a lower or none reduction of wear was achievable with films as thick as or thicker than 50 nm. The work also shows that especially thin films of about 20 nm thickness achieved high reduction in tool wear. This shows that ALD-layers have promising properties in the field of wear reducing coatings for micro cutting tools.

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AA4-TuP-7 Fabrication of Atomic Layer Deposited Alumina as Protective Coating of Silver*,* ***Gwon Deok Han****, J Park, J Koo, J Shim,* Korea University, Republic of Korea

Silver is one of the precious metals widely used in human life. Silver has the disadvantage of being easily corroded or discolored when exposed to moisture and oxygen. Protective coatings of thin oxide films are effective in preventing corrosion and discoloration of silver products such as cookware, coins and jewelry. It is especially important to make a thin, uniform protective coating to protect the silver products from external environments. In this respect, atomic layer deposition (ALD) is considered the best technique for forming a protective oxide layer. ALD has an excellent function to form a uniform film without pinholes even in a complex three-dimensional (3D) structure with a high aspect ratio.

In this study, we evaluated the anti-corrosion performance of ALD alumina coatings for silver products [1]. The protection stability of the alumina coating layer was tested using an artificial sweat solution. The stability of the protective layer was evaluated by depositing alumina layers of changing thicknesses of 20-80 nm on silver samples and immersing the coated samples in artificial sweat solutions. We have demonstrated that a relatively thick alumina layer is effective in protecting the original properties of silver samples. In this meeting, we will discuss the protection performance of ALD alumina including its microstructure, optical properties and corrosion resistance.

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AA4-TuP-8 Characterization of Laminated Thin Films for Encapsulation using Single Si Precursor by PEALD*,* ***Joong Jin Park****, S Lee, H Lim, S Jang, S Kim, G Park, S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

OLEDs(Organic Light-Emitting Diodes) are used in display devices such as mobile and TV, and next-generation OLED displays should be flexible and foldable. Flexible and foldable OLED displays require curvature radius less than 2.5R. In addition, a good encapsulation property is required in a thin thickness. Therefore, it is essential for OLED to realize these characteristics through laminated thin film rather than single thin film. The laminated thin film can reduce the diffuse reflection by generating the antireflection film effect due to the difference of the refractive index of each single layer film. It is also effective in reducing stress in the film and blocking ultraviolet rays. [1, 2]

Recently, the ALD process has been applied as a method of depositing thin films with excellent film quality. These ALD methods are used to develop thin film encapsulation technology because of the self-limiting surface reaction and the advantages of the reaction fraction.

In this paper, structure of the SiO2 / SiNx stack films were fabricated by using PEALD(Plasma Enhanced Atomic Layer Deposition) method at low temperature (90 ℃) using a single precursor, NSi-01. The thickness and refractive index of the thin film were measured using a Woollam M2000D spectroscopic ellipsometer. In addition, WVTR (Water Vapor Transmission Rate) was measured by using MOCON Aquatran 2 for thin films deposited on polyethylene naphthalate (PEN). In the structure of the SiO2 / SiNx stack film, the refractive index was measured to be 1.47 / 1.85, confirming the possibility of antireflection effect through the multilayer. The WVTR characteristics were measured over 100 hours according to the thickness of the thin film. At a thickness of less than 150 Å, the SiO_2 thin film or SiNx thin film had poor WVTR characteristics. In order to overcome this problem, SiO2 / SiNx structure was deposited. It is also expected that 2 to 3% of carbon in the deposited SiNx film will lower the film stress and maintain the flexibility of the entire film (Figure 1). The SiO2/SiNx/SiO2 laminated thin films exhibited excellent WVTR characteristics with the prevention of destruction of the encapsulation characteristics at a thin thickness(Figure 2). From this work, we confirmed the possibility of a laminated thin film consisting of a silicon oxide film and a nitride film by PEALD in one chamber using one precursor. In particular, the production of a laminated thin film can prevent both reflection and moisture absorption, and it is expected that the next generation OLED encapsulation will be applicable.

AA4-TuP-9 Low-cost Fabrication of Flexible Transparent Electrodes based on Sprayed Nanocomposites Silver Nanowires and Al Doped ZnO Deposited by Spatial ALD*, V Nguyen, J Resende, D Papanastasiou, C Jimenez, D Bellet,* LMGP Grenoble INP/CNRS, France*; S Aghazadehchors,* LMGP, France*; N Nguyen,* Université de Liège*;* ***David Muñoz-Rojas,*** LMGP Grenoble INP/CNRS, France

We report the study of nanocomposite transparent electrodes based on Aluminium doped Zinc Oxide (ZnO:Al) thin films and silver nanowire (AgNW) networks. The electrodes are fully fabricated by low-cost, open-air techniques, namely, atmospheric pressure spatial atomic layer deposition and spray coating. We show that the transparency and the conductivity of the ZnO:Al/AgNW nanocomposites can be tuned by controlling the AgNW network density. We also demonstrate that the thermal, electrical and mechanical stabilities of the composites are superior to those of AgNW networks or ZnO:Al thin films separately. We have also developed a theoretical model to explain the relationship between the conductivity of the composites and the AgNW network density. Our results provide a means to predicting the physical properties of such nanocomposites for applications in solar cells and other optoelectronic devices. Finally, the deposition methods used open the way towards stable, low-cost flexible and transparent electrodes for industrial application.

AA4-TuP-10 Nanomechanical Properties of Crystalline Anatase Titanium Oxide Films Synthesized using Atomic Layer Deposition*,* ***Yousuf Mohammed****, P Lin, K Zhang, H Baumgart, A Elmustafa,* Old Dominion University

Titanium dioxides (TiO_2) thin films have received significantly attentions due to their remarkable biocompatibility, stability, nontoxicity, and excellent photocatalytic properties. TiO_2 films are used in artificial heart valves, photocatalyst in solar cells. The photocatalytic activity of titanium dioxide is exhibited in both the anatase and the rutile phases. Likewise, the photocatalytic properties of TiO_2 thin film coatings are noticeable in medical applications in bactericidal coatings of wound care gauze or in coatings of surgical instruments to be sterilized and for antimicrobial surfaces in hospitals. Fabrication of TiO_2 films has intensified in the last two decades due to their notable optical and electronic properties and their excellent potential applications for gas sensing. Another application for anatase TiO_2 in photovoltaics, when their team realized impressive photovoltaic performance advances with perovskite/ TiO_2 heterojunction solar cells, which were fabricated with pure phase anatase TiO_2 nanosheets with dominant (001) facets serving as the electron collector.

Several deposition techniques have been used in the past to deposit TiO_2 films on silicon substrates, including reactive DC sputtering, RF magnetron sputtering, ion beam induced chemical vapor deposition, metal-organic chemical vapor deposition, chemical vapor deposition, mist CVD and the atomic layer deposition (ALD). The ALD has emerged as a modern chemical reaction based technique to deposit monolayers of inorganic compounds. ALD possesses unique film deposition uniformity and exact composition control with atomic precision and absolute conformality.

Crystalline TiO_2 films of 500 nm thickness were synthesized using ALD on p-type Si (100) substrates. The crystal structures of the TiO_2 thin films were characterized by the X-ray diffraction (XRD). The film thickness and surface morphology were inspected using field emission scanning electron microscopy (FE-SEM) and AFM. The nanomechanical properties were measured using a nanoindenter equipped with a three-sided Berkovich diamond tip to evaluate the hardness and modulus of the TiO_2 thin films. Due to low temperature ALD deposition, the X-ray diffraction revealed a single-phase TiO_2 anatase growth and the FE-SEM images indicate columnar grain structure growth with primarily vertical directions of the polycrystalline TiO_2 films. The measured hardness of the anatase ALD TiO_2 films at 20% film thickness has been measured as 5 Gpa, which is considerably softer compared to the reported benchmark values of the better known rutile phase of ~ 12 Gpa. The elastic modulus of the TiO_2 thin films was estimated as 138 and 145 Gpa.

AA4-TuP-11 Encapsulation of Magnetic Nanostructures by ALD for Improved Stability and Performance*, **Devika Choudhury**, Y Zhang, K Gao, A Mane, J Elam,* Argonne National Laboratory

Morphology of magnetic nanoparticles is an important aspect responsible for controlling the optical, electrical and magnetic properties. Their interesting shapes and sizes result in novel properties significantly different from their bulk counterparts. For example, 1D magnetic nanostructures often exhibit significantly modified properties and enhanced coercivity as compared to the their bulk magnets thus making them attractive for wide range of applications. These materials are not only extensively used in high-density magnetic data-storage mediums, magnetic sensors and spintronic devices, but also suitable for valuable biomedical applications as well.

Metal alloys such as PtCo, SmCo, FeNi and FeCo are well known for their desirable magnetic properties and use. However, due to their nanosize scale, these materials readily oxidize under ambient conditions. Poor chemical stability results in diminished magnetic properties thus limiting their practical usage.

Atomic Layer Deposition (ALD) has emerged as one of the most widely accepted techniques to provide conformal coating of controlled thickness on high curvature structures and a popular method for encapsulation of various type of microstructures. In this work, we report the coating of magnetic metallic alloys using ALD method to improve stability and performance of the nanostructures. Different chemistries are used for the deposition of a variety of protecting layers. Comparison on the effectiveness of the coatings are drawn from the stability and their magnetic properties such magnetic saturation values obtained from SQUID measurements.

AA4-TuP-12 Diffusion Barrier Properties of ALD TiSiN Films*, **Jerry Mack**, J Heo, S Chugh, H Kim, S Rathi, N Mukherjee,* Eugenus, Inc.

The decreasing feature sizes and increasing aspect ratios in semiconductor process flows have imposed stringent requirements on the physical and electrical properties of metal-to-semiconductor interfaces. This has resulted in fundamental material challenges for low-resistance contacts and ultra-thin diffusion-barrier films. Physical vapor deposition (PVD) based TiN film is a widely used diffusion barrier layer. However, deposition of ultra-thin TiN exhibits pronounced islanding which leads to rough film with polycrystalline grain structure. Furthermore, inhomogeneities due to grain boundaries offer diffusion pathways and lead to device degradation. In the current study, we present our findings on the diffusion barrier properties of amorphous ternary alloy films composed of Ti, Si and N (TiSiN), an excellent alternative to TiN films. These films were grown using Atomic Layer Deposition (ALD) technique on the Eugenus 300mm QXP commercial mini-batch reactor. In one set of experiments, TiSiN films were deposited on highly-doped polycrystalline Si:B films followed by diffusion studies of boron. In another set of experiments, fluorine precursor based CVD Wsi_x film was deposited on TiSiN, followed by diffusion studies of fluorine. Secondary Ion Mass Spectrometry (SIMS) and High-resolution electron energy loss spectroscopy (HREELS) were utilized to detect the effectiveness of the barrier film to prevent boron and fluorine diffusion.

ALD Applications

Room Evergreen Ballroom & Foyer - Session AA5-TuP

Emerging Applications Poster Session

AA5-TuP-1 Bottom up Stabilization of Perovskite Quantum Dots LED via Atomic Layer Deposition*, **Rong Chen**, K Cao, Q Xiang, B Zhou,* Huazhong University of Science and Technology, China

Flexible displays are becoming the most promising and attractive techiques in the future. Quantum dots(QDs) have attracted great attentions due to their excellent optical properties, such as tunable wavelength, narrow emission, long carrier diffusion length, and high photoluminescence quantum efficiency. These properties make QDs the most promising optical materials for flexibles displays. However, as the instability of QDs based light emitting diodes limits their practical applications, QDs based LEDs are still under laboratory developments.

In this talk, we will discuss ALD based protection approaches from nanoscale QDs passivation to macroscopic encapsulation to improve the stability and boost its performance of QD-LEDs. First, the low-temperature selective ALD method has been developed for defects elimination. This protection method can preserve QDs monomers without damaging surface ligands and improving the quantum efficiency. For the QD light emitting layers, voids are formed during the stacking which may induce instability from electric, heat transfer. The ALD based filling process has been developed to improve charge transport within the layer. To study the surface interaction mechanisms of ALD precursors with the QDs layer, in-situ characterizations such as quartz crystal microbalance (QCM), infrared spectrometer (IR) are utilized to monitor the ALD process and the interactions with QDs layers. The oxides filling between quantum dots could reduce the carrier transport barrier and enhance carrier injection. Finally, it is imperative to develop efficient and ultrathin encapsulation to improve the stability towards ambient environments and flexibility of displays. Ultrathin multi-stacking films are designed and fabricated based on the combination of spatial ALD, molecule layer deposition and chemical vapor deposition. Such composite films could greatly enhance the water and oxygen resistance, while retain low stress and flexibility of the devices. It has demonstrated that the ALD approaches are versatile and useful for several fabricating steps in flexible QDs displays.

AA5-TuP-2 ALD Bilayers for X-ray Windows with Long Lifetime*, **Agnieszka Kurek**, Y Shu,* Oxford Instruments Plasma Technology*; H Knoops,* Oxford Instruments Plasma Technology, UK*; A O'Mahony, O Thomas, R Gunn,* Oxford Instruments Plasma Technology*; Y Alivov, C McKenzie, B Grigsby, A Degtyaryov,* Oxford Instruments X-ray Technology

X-ray-emitting devices require a window transparent to low energy X-rays while keeping the device at vacuum. Polycrystalline Be windows are often used since they have high X-ray transparency due to the low atomic number of Be. However, Be is sensitive to environmental moisture and shows degradation over time via two routes. Firstly, ambient gas can penetrate the Be window through the crystalline grain boundaries deteriorating the vacuum. Secondly, water vapour reacts with Be material causing corrosion and forming an oxide layer which can delaminate and reduce the window thickness over time. The window can become so thin it can no longer hold a vacuum inside the X-ray device – effectively ending the lifetime of the tube. Here, we show how the application of conformal, pinhole-free ALD bilayer coatings can extend the lifetime of X-ray windows more than five times with negligible influence on X-ray transmittance.

We have developed and patented (US20180061608A1) a robust solution using a combination of Al_2O_3 and TiO_2 less than 200 nm in thickness. The ALD coatings were deposited in an Oxford Instruments Plasma Technology FlexAL™ system at 350 °C. Thermal Al_2O_3 (~40 nm) was used as an adhesion layer, followed by in-situ deposition of thermal TiO_2 (~80 nm) as a harder, protective layer, using trimethylaluminum and tetrakis(dimethylamino)titanium, respectively. The relatively low atomic numbers of Al and Ti mean that the maximum allowed film thickness to maintain clarity of the X-ray spectra is 800-1000 nm, which is much higher than the used thickness. This window coating is an effective moisture barrier and attenuates the transmitting X-rays by less than 5 % compared to the attenuation of an uncoated window. Importantly, the ALD coating does not contaminate the output X-ray spectra. No fluorescence contamination of Al and Ti could be detected. The lifetimes of ALD coated windows were compared with that of uncoated window by determining how long they could sustain ultra-high vacuum. For all sixteen coated samples, the windows survived the test at least 5 times longer and, in many cases, >15 times longer.

The ALD coating of the X-ray windows increases lifetime of X-ray emitting equipment by more than five times minimising specialist maintenance. The excellent conformality of ALD is furthermore expected to help close off grain boundaries present in the Be windows which can be up to 100 nm deep and could otherwise be pathways for gas diffusion into the vacuum of the system. Future options include making the coating conductive as a further advantage for X-ray equipment.

AA5-TuP-3 ALD for 3D Nano MEMS Applications*, Dorothee Dietz,* Fraunhofer Institute for Microelectronic Circuits and Systems IMS, Germany

In the area of MEMS and nano sensor structures, the ALD becomes ever more important. Because of the highly isotropic and highly conformal deposition method, ALD is the best choice for structures with large aspect ratios or structures with complex cross sections. Moreover it is possible to deposit several different materials in the same tool, so that the functionality of the material can be tuned by stacks or doping as good as possible. Because of the low deposition temperature, ALD can be applied in post-CMOS-processes.

ALD techniques enable the fabrication of free standing 3D structures as follows: In a first step, a sacrificial layer is deposited onto a (CMOS-) substrate. Small holes or trenches are etched through it as pillars and an ALD layer is deposited and structured. In the end, the sacrificial layer is removed. This technique can be used e.g. for the processing of different gas sensors or for realizing 3D multi electrode arrays (MEA).

The first type of gas sensor, which is based on conductometric semiconductor gas sensing, operates with metal oxide (MOx) nano wires, 350 nm in width and 150 µm in length. The metal oxide (e.g. ZnO or SnO_2) is used as a functional layer but also for forming the 3D structure. Because the metal oxides need to be heated for gas sensitivity, a heater is realized with the same technology as described above. In this case, Ru, TiN or TiAlCN, is used as heater material, deposited also by ALD.

The second gas sensor is acting as a nano pellistor. The heater has to be a free standing 3D structure, because the sensor has to be thermally decoupled from the substrate underneath. All materials are deposited with ALD to achieve the high aspect ratio and because of the material properties. The heater consists of Ru, the surrounding isolation layer can be Al_2O_3 and the catalytic layer is made of Ru again.

To increase the sensitivity of the sensor, the surface of the catalyst can be increased by using a porous Al_2O_3 layer instead of a solid one. A porous Al_2O_3 layer can be achieved by doping it during the ALD in a first step e.g. with ZnO and by a selective etching of the doping material in a second step.

Another application for using this technology is processing 3D MEA. They can penetrate biological cell membranes for measuring intracellular electrical signals directly. As a conductive and biocompatible material, Ru is used for these electrodes. They are 200 nm in diameter and a few microns in height. With an additional step, the diameter at the tips can be reduced so that they can penetrate membranes easier, without the risk of destroying them.

AA5-TuP-4 Tribological Properties of Plasma Enhanced Atomic Layer Deposition TiMoN*, Mark Sowa,* Veeco-CNT*; A Kozen,* U.S. Naval Research Laboratory*; B Krick, N Strandwitz,* Lehigh University

In our previous study, we demonstrated a tertiary plasma enhanced atomic layer deposited transition metal nitride (TiVN) with exceptional wear rates and friction coefficients. We have extended that work with an investigation of another tertiary transition metal nitride system, $Ti_xMo_yN_z$. For films deposited at 250°C and 300W on a Veeco CNT G2 Fiji PEALD system, we have demonstrated how the ratio of TiN:MoN cycles (1:0, 3:1, 1:1, 1:3, 0:1) provides linear control of the Ti:Mo in the resulting film. Through application of an 13.56MHz RF substrate bias (0-250V) during the plasma step, ion bombardment energy of the substrate can be varied, providing a means for tweaking the films physical and chemical characteristics which in turn are shown to impact the resulting film's tribological properties. As PEALD metal nitrides have broader interest than wear layers and to gain insights on the interrelationships of the mechanical properties, the processing details, and other film properties, we also report on the resulting film composition/impurities, density, crystallinity, optical properties, resistivity, and morphology.

AA5-TuP-5 Thickness Optimization of Alumina Thin Film for Microchannel Plate Detector*, Baojun Yan, S Liu,* Institute of High Energy Physics, Chinese Academy of Sciences, China

Conventional lead glass microchannel plate (MCP) detector has been used in a variety of applications. The MCP performance can be improved by coating high secondary electron emissive layers, such as alumina (Al_2O_3) and magnesium oxide (MgO), via atomic layer deposition (ALD). In this poster, the alumina thin films with varied thicknesses were deposited by ALD on polished Si substrates and MCPs, respectively. The secondary electron yield (SEY) of the alumina thin films on silicon substrate were measured by pulsing electron beam. The MCPs used in our experiment had a high length to diameter ratio ~80:1 and worked in photon counting mode. The optimal thickness of alumina was obtained through comparative study the MCP performance before and after coating. In addition, the DC gain variation as a function of total charge per unit area Q (C/cm^2) were investigated.

AA5-TuP-6 Optical Coatings Deposited on Nonlinear Crystals by Atomic Layer Deposition*, Ramutis Drazdys, R Buzelis, M Drazdys,* Center for Physical Sciences and Technology, Lithuania

Growing requirements for optical coatings deposited on temperature and environment sensitive crystals force to look for alternatives to conventional physical vapor deposition technologies. KDP, DKDP, $LiNbO_3$ are nonlinear optical materials that have been difficult to coat due to specifics of surface adhesion and thermal properties. Atomic layer deposition (ALD) is widely used in nanotechnology and semiconductor devices [1] and recently attracted more interest in manufacturing of optical components [2,3]. The main goal of our research was to develop antireflection (AR) coatings on nonlinear crystals with high laser induced damage threshold (LIDT). HfO_2 and Al_2O_3 thin layers deposited using TDMAH and TMA precursors and H_2O as oxidant by Savannah 200 system from Ultratech at low temperature (<100°C) were investigated. Experimental deposition processes of HfO_2 and Al_2O_3 thin film 150 nm thickness single layers were made at temperatures from 40°C to 100°C with different pulse and purge time duration parameters. To prevent the HfO_2 layer crystallinity we used the nanolaminate concept [4] where each HfO_2 layer with thickness of 20 nm incorporate a certain number of Al_2O_3 monolayers. Growth rates, dependency on precursor pulse and chamber purge durations were determined by using quartz crystal monitoring and optical spectra data. Refractive index and absorption dispersions were determined. Setup with the Nd:YAG laser (from EKSPLA co.) generating pulses with repetition rate 15 Hz, pulse duration ~3 ns was used for LIDT measurements. The investigation of the optical transmission and reflection of produced thin layers allowed to determine optical loses in UV region. These results gave us the possibility to choose optimal technological parameters for AR coating formation on nonlinear crystals substrates. The following design of experimental AR coating was selected: substrate / 75nm HfO_2 / 200nm Al_2O_3. In previous investigations determined growth rates per pulse cycle were used for layers thickness control. The same coating design was used to manufacture AR coatings by IBS and e-beam evaporation. The LIDT measurements of AR coatings demonstrated comparable or higher damage levels for ALD coatings.

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AA5-TuP-7 Atomic Layer Deposition of Nickel and Nickel Oxide Thin-Films for Astronomical X-ray Optics Applications*, Hossein Salami, A Uy, A Vadapalli,* University of Maryland*; V Dwivedi,* NASA Goddard Space Flight Center*; R Adomaitis,* University of Maryland

Nickel and nickel oxide films have optical, electrical and magnetic properties that when combined with good chemical stability makes them attractive for many applications. Nickel oxide is a p-type semiconductor that can be used as a transparent electrode, or in manufacturing nonvolatile resistance random access memories, or for chemical sensing purposes. In its pure form, nickel film can be used as adhesion layer for copper interconnects [1]. Because of its X-ray reflecting property, another application of pure nickel film is in multi layer coatings for X-ray optics [2,3].

In this talk, we will discuss atomic layer deposition process for Ni and NiO thin-films using two different metal precursors, nickelocene and nickel acetylacetonate, in combination with ozone as the oxygen source. We will present two different routes to depositing metallic Ni: direct metal deposition or metal-oxide deposition with a subsequent reduction step. Our initial results confirm the deposition of NiO film and its reduction using molecular hydrogen predicted by thermodynamic analysis. Advantages of each route and their effect on the properties of the final product will be presented. Furthermore, specifically for astronomical applications, roughness and X-ray reflectivity of the prepared thin-films and the conformal coating of high aspect-ratio X-ray optics will be discussed in detail.

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AA5-TuP-8 Atomic Layer Deposition and Chemical Vapor Deposition of Zirconium Boride for Various Applications: New Work Function, Barrier Metal, Hard Mask and Area Selective Deposition*, **Jun-Hee Cho**, J Park, W Chae, J Park, S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

Zirconium boride is an attractive material for microelectronic, hard coating, and other applications. Because, it has high melting point (3040 °C), a high mechanical hardness, excellent wear properties, and excellent corrosion resistance toward molten metals [1]. In this work, we talk about new applications of ZrB$_x$ for new work function, barrier metal, hard mask and area selective deposition (ASD). ZrB$_x$ film have been deposited both by sputtering and chemical vapor deposition (CVD) routes. An inherent shortcoming of sputtering is its non-conformal nature. In conventional CVD of ZrB$_x$ films, the ZrCl$_4$ and BCl$_3$ precursors are reduced with H$_2$, but the incorporation of residual chlorine atoms has proven to be detrimental to film properties. In addition, thermal atomic layer deposition (ALD) was not studied in detail [2, 3]. In this study, ZrB$_x$ films have been deposited by thermal ALD and CVD process using single precursor Zr(BH$_4$)$_4$ for new work function, barrier metal, hard mask and ASD. The work function of deposited ZrB$_x$ film by ALD at 250 to 350 ℃ is 3.93 to 3.96 in the bulk and 3.86 to 3.64 in the surface respectively (Fig. 1). The step coverage was showed 100 % in aspect ratio 19:1 pattern at 250 ℃(Fig. 2). The resistivity of ZrB$_x$ film was about 450 μΩ ㎝ and showed amorphous structure.

The deposited ZrB$_x$ film on Si(100) by CVD is sufficient to prevent copper diffusion into silicon during a 600 °C anneal for 30 min (Fig. 3, 4). The ZrB$_x$ film on SiO$_2$ by CVD has a very slow etch rate for CF$_x$, while a very fast etch rate for BCl$_3$ (Fig. 5). The wet etch was not showed in 0.5% HF solution (Fig. 5). The ZrB$_x$ film has resistance to oxygen. ASD of Zr(BH$_4$)$_4$ was showed selectivity of W metal and SiO$_2$ substrate for ZrB$_x$ film (Fig. 6). The deposited ZrB$_x$ films were showed amorphous phase. The possibility of applying a new work function, barrier metal, hard mask and ASD is expected.

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AA5-TuP-9 Comparative Study of Mo$_{1-x}$W$_x$S$_2$ Alloy Gas Sensor by Atomic Layer Deposition*, **Minjoo Lee**, Y Kim, J Park, H Kim,* Yonsei University, Republic of Korea

Two-dimensional (2D) Transition metal dichalcogenides (TMDCs) are a layered structure, which stacked via weak van der Waals interaction. 2D TMDCs have attracted great attention because of their remarkable electronic and optoelectronic properties such as indirect-to-direct bandgap transition with reducing layers, superior electrical properties and strong spin-orbit coupling. Furthermore, recently the 2D TMDCs have shown the potential as a gas sensing material due to their very large surface-to-volume ratio, semiconducting property, and low power consumption. Thus, the WS$_2$ or MoS$_2$ that is the one of the most popular TMDCs has been studied for its gas sensing properties and demonstrated an excellent response to various gas molecules, such as nitrogen dioxide (NO$_2$), ammonia (NH$_3$), acetone, etc. However, due to the difficulty of uniform synthesis of 2D TMDCs and the highly sensitive characteristic of these TMDCs gas sensors, there are few researches about direct comparative study of each materials. Although only a theoretically calculated studies were reported, the result is often different according to adapted model.

In this study, layer controlled 2D MoS$_2$ and WS$_2$ synthesized with Mo(CO)$_6$ and W(CO)$_6$ and H$_2$S gas as precursors and a reactant using ALD in same equipment under similar conditions. Furthermore, we synthesized Mo$_{1-x}$W$_x$S$_2$ alloys using ALD super-cycle and confirmed that W composition in alloys can be controlled by changing super-cycle configuration. Synthesized 2D TMDCs were fabricated for gas sensors for comparison of gas sensing property and It showed different response and response time according to composition in alloy.

AA5-TuP-10 Fabrication of High-Aspect-Ratio Nanometric Gold Gratings*, O Makarova,* Creatv MicroTech Inc*; **Ralu Divan**, L Stan,* Argonne National Laboratory*; C Tang,* Creatv MicroTech Inc

High-aspect-ratio gold gratings have broad applications in x-ray optics, and their quality and aspect ratio strongly affect the quality of the generated images. To fabricate the gratings, two key technological challenges must be addressed: (i) creating a high-aspect-ratio trenches with smooth vertical walls, and (ii) filling the trenches uniformly with gold.

We report fabrication of 450 nm half-pitch gold gratings with an aspect ratio of 26 using laser interference lithography (LIL), reactive etching (RIE), atomic layer deposition (ALD), and gold electroplating techniques. In the first step, gratings are patterned on the resist/chromium coated silicon wafer *via* LIL. Then, the chromium, which served as a hard mask for silicon etching is etched using RIE. This step is followed by cryogenic RIE to create deep trenches in silicon. Then, a platinum seed layer is deposited by ALD, and finally the mold is electroplated with gold.

RIE of high-aspect-ratio dense and narrow trench/wall structures of gratings imposes significantly more difficulties than the etching of isolated narrow lines or trenches, since the undercut and the negative taper can damage the thin walls. High-aspect-ratio nanoscale silicon gratings were obtained by carefully tuning all etching parameters (Figure 1a).

A continuous, conductive and conformal seed layer is essential for uniform electroplating. We performed ALD of platinum as a seed layer. To improve platinum adherence, a 10 nm alumina adhesion layer was deposited by ALD as well. The high-exposure platinum ALD was optimized to assure conformal coating of the high-aspect-ratio trenches. The nanometric trenches were filled with gold *via* conformal electroplating, when plating occurred from all surfaces. The method has an advantage of much shorter electroplating time, compare to bottom-up plating technique. However, it is challenging to avoid voids formation due to prematurely trench sealing. and achieve uniform plating over the entire trench depth because of the gold ions depletion inside the narrow and deep trenches (Figure 1b).

Use of the Center for Nanoscale Materials, an Office of Science user facility, was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

ALD Applications
Room Grand Ballroom H-K - Session AA1-WeM

ALD for Memory Applications II

Moderators: Seung Wook Ryu, SK Hynix, Myung Mo Sung, Hanyang University

8:00am **AA1-WeM-1 ALD/ALE Process in Commercially Available Leading-Edge Logic and Memory Devices***, **Rajesh Krishnamurthy,*** TechInsights **INVITED**

In 2018, we saw the introduction of a new generation of logic products, featuring FinFET transistors from Intel with their 10 nm generation microprocessor, followed by 7nm devices from competing foundries, primarily targeting high-end application processors in mobile devices. We also saw memory product manufacturers Samsung, Hynix, Toshiba and Micron introducing 64- or 72- stacked layer 3D-NAND devices, and move into 1x generation DRAM devices.

As a supplier of competitive intelligence to the semiconductor and electronics industries, TechInsights performed structural analyses to examine the features and manufacturing processes of all of these innovative devices.

This presentation will examine some of the different structures we have seen through the evolution of these technologies, in particular 7nm and 10-nm logic, 3D-NAND and DRAM parts, that have been introduced. We will also look at several historical applications of ALD/ALE technology that have been observed through reverse engineering. We will highlight the importance of ALD/ALE process in advanced logic and memory devices. In many cases, the technology could not have advanced without the implementation of ALD technology

8:30am **AA1-WeM-3 Atomic Layer Deposited Crystalline Zinc Oxide for Silver-based Ultra-Steep Threshold Switching Selector***, **Harrison Sejoon Kim**, A Sahota, J Mohan, H Hernandez-Arriaga, J Kim,* The University of Texas at Dallas

Along with the growth of emerging non-volatile memory (NVM), developing an outperforming selector is also required to pave the way for realization of neuromorphic networks. Ideally, when cointegrated with the memory element, the role of a selector is to prevent the sneak-current from neighboring devices in a cross-point array [1]. To thrust the emerging NVM at the technological cutting edge, various kinds of selectors have been developed so far [1]. Also, different deposition techniques have been employed to deposit the selector layer. Atomic layer deposition (ALD) provides excellent atomic thickness controllability, thus amongst them, it is the most favorable technique for fabricating the selectors having their switching threshold dependent on the electric field. Electric field dependent conduction mechanism is significant as threshold voltage (V_{th}, voltage that turns on the selector) can be controlled by changing the physical thickness of switching layer. Controllability of V_{th} makes the selector highly compatible with the memory element. Ag or Cu-based threshold switching (TS) selectors are exemplary for the electric field driven selectors, and moreover, they possess superior characteristics over many kinds of the selectors developed so far [2].

In this work, we demonstrate Ag-based TS selectors fabricated with ALD grown crystalline zinc oxide (ZnO) unlike the most prevalent cases where switching layers have been deposited amorphously. The selector device has simple metal-insulator-metal (MIM) structure. Stacked Ag electrodes are assumed to act as the reservoir for providing Ag metal atoms to form metallic filament within insulating ZnO layer (Fig. 1a). As a result, we have obtained robust TS behavior using ALD ZnO with high selectivity ($>10^7$), ultra-low off-state leakage current (~ pA), high on-state current density (> 0.01 MA/cm^2), and ultra-steep slope (< 10 mV/decade) (Fig. 1b). To suppress cycle-to-cycle variability found in Ag-based TS selectors, we have proposed “Ag delta-doping” concept (Ag-doped ZnO) for minimizing the stochastic issue (Fig. 2). Here, we expect crystalline ZnO would benefit reducing randomness providing better controllability on Ag diffusion (as illustrated in Fig. 2). This will be achieved through a technique so called “super-cycle ALD”, followed by further investigation on the reliability of Ag-doped ZnO switching layer.

The authors thank Semiconductor Research Corporation (SRC) for providing financial support in this work.

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8:45am **AA1-WeM-4 ALD Ge-Se-Te OTS Selectors with Controlled Composition for PCM Applications***, **Valerio Adinolfi**, L Cheng, R Clarke, S Balatti, K Littau,* Intermolecular, Inc.

The increasing need for faster high-capacity NV-memories have led researchers to explore chalcogenide materials as a solution to fabricate PCM memories and OTS selectors. Memories and selectors are vertically integrated in X-point arrays to produce storage devices. In order to meet the stringent requirements on integration chalcogenide stacks will have to be integrated in 3D structures (as is currently happening for FLASH NANDs). 3D architectures can be enabled exclusively by ALD depositions – providing the necessary conformality and film quality – of the active layers. A limited number of ALD chalcogenide films have been demonstrated but, despite intense efforts, these processes fail in controlling the film composition – fine control over the composition of chalcogenide systems is indispensable for producing performing OTS and PCM devices.

Here we present, for the first time, ALD of binary and ternary films of Ge – Te – Se with controlled composition evaluated in devices as two terminal threshold switches. A unique process involving $HClGe_3$, btms -Te(Se), and Te ethoxide was developed by alternating semiconducting GeTe(Se) and metallic Te/Se layers. Nucleation and growth mechanisms are thoroughly investigated by means of an in-situ ellipsometer. We demonstrate the ability to cover a large part of the ternary triangle plot (see figure attached) by using RBS, XPS, and calibrated XRF. X-SEM and AFM reveal smooth surfaces and compact films. Conformality is assessed by uniformly filling trench structures with a high aspect ratio (40:1).

Finally we electrically characterized $Ge_xTe_ySe_z$ thin films contacted with tungsten and TiN bottom plugs and top contacts (respectively). Different compositions produce dramatically different devices; germanium rich compositions exhibit resistive or PCM behaviors while Te – Se rich compositions produce OTS selectors (see figure attached). DC current-voltage (IV) measurements, transient IVs, and threshold voltage characterizations are performed over a large number of devices and a statistical analysis is presented.

This work shows for the first time ternary ALD chalcogenide films with controllable composition and their electrical operation as memory devices (PCM and OTS); this novel ALD process poses the foundation for the imminent development of chalcogenide based 3D X-point memory arrays.

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9:00am **AA1-WeM-5 Pulsed CVD of Amorphous GeSe for Application as OTS Selector***, **Ali Haider**,* IMEC, Belgium*; S Deng,* ASM, Belgium*; E Schapmans,* IMEC, Belgium*; J Maes,* ASM, Belgium*; J Girard,* Air Liqude Advanced Materials, France*; G Khalil,* imec*; G Kar, L Goux, R Delhougne,* IMEC*; M Caymax,* IMEC, Belgium

Alongside advances in RRAM structural design to scale down the memory, the problem of sneak currents, which frustrate the accurate reading/writing of data in each cell, remained a critical issue. An attractive approach is to add a selection device operating for example by means of the Ovonic threshold switching (OTS) mechanism to each memory element that suppresses sneak currents through highly nonlinear current-voltage (IV) characteristics. Amorphous germanium selenide (GeSe) is a well-known candidate for OTS selector which so far has only been grown by physical vapor deposition (PVD) for planar RRAM devices. The 3D RRAM approach, which has the advantage of ultra-high storage density with low cost, calls for a uniform and highly conformal deposition technique to deposit this amorphous GeSe selector material on 3D structures.

Here, we report pulsed chemical vapor deposition (CVD) of amorphous GeSe using germanium chloride and alkylsilylselenide precursors. We learned from a study of precursor chemisorption kinetics based on Total Reflection X-ray Fluorescence (TXRF) that both precursors cover the wafer surface only quite slowly. The same measurements also show that Se precursors need Cl sites (from the Ge precursor) for precursor ligand exchange reactions. Further investigation reveals that higher GPC is obtained in pulsed CVD mode (so, no purge steps between the pulses). Based on this basic understanding, we developed a pulsed CVD growth process (GPC=0.3 Å/cycle) of GeSe using $GeCl_2.C_4H_8O_2$ and $(TMS)_2Se$ as Ge and Se source, respectively. TEM images reveal that ~20 nm grown GeSe layer is amorphous while EDX and RBS measurements revealed stoichiometric GeSe films with traces of Cl impurities. EDX mapping revealed uniform Ge and Se distribution throughout the film. Elastic recoil detection (ERD) measurements show ~5 % carbon inside the grown GeSe film. AFM images show an RMS surface roughness of 1.7-1.9 nm. GeSe grown on 3D test structures showed excellent film conformality.

Currently work is ongoing to apply conformally grown GeSe layers as OTS selector devices in electrical test vehicles. We will report electrical switching and endurance characteristics of conformal, pulsed CVD grown OTS GeSe selector layers and bench mark these with PVD grown GeSe layers.

9:15am **AA1-WeM-6 Thin Film Challenges in 3D NAND Scaling**, ***Jessica Kachian**, D Pavlopoulos, D Kioussis,* Intel Corporation **INVITED**

In today's datacentric society, 3D NAND has become a storage architecture of focus through increased bit density, relative to 2D architectures. Continuing bit density increase through 3D NAND scaling requires clever manufacturing strategies, centered on discovery and patterning of target materials. Thin film deposition steps face daunting aspect ratios with unforgiving quality specs. The inherent conformality afforded by ALD makes it an attractive process for 3D NAND. However, many relevant ALD processes do not deliver film quality as-deposited. This talk focuses on general material and patterning requirements for key steps in 3D NAND fabrication and considers how ALD may address these challenges, with attention to target properties towards performance.

ALD Applications
Room Grand Ballroom H-K - Session AA2-WeM

ALD for ULSI Applications I

Moderators: Ravindra Kanjolia, EMD Performance Materials, Han-Jin Lim, Samsung Electronics

10:45am **AA2-WeM-12 The Journey of ALD High-k Metal Gate from Research to High Volume Manufacturing**, ***Dina Triyoso**, R Clark, S Consiglio, K Tapily, C Wajda, G Leusink,* TEL Technology Center, America, LLC **INVITED**

In the early days of the search to find a replacement for SiO_2-based gate oxides the goal was to find a material with a very high k value which could be incorporated into CMOS production for multiple technology nodes. A historical overview of the many promising high k materials considered for SiO_2 replacement leading to the selection of ALD HfO_2 as "the winner" will be presented. ALD HfO_2 has successfully been implemented in CMOS production for over a decade, starting at the 45nm node. There are two general integration approaches for implementing ALD High-k/Metal Gate stacks (HKMG) in production: gate first and gate last. Challenges with each integration approach, leading to the wider adoption of gate last will be discussed. Furthermore, as the dielectric constant of HfO_2 is only ~20 and a thin SiO_2-base interface was still required to maintain mobility and reliability, HfO_2 provided essentially a one-time scaling benefit. Further thinning of HfO_2 resulted in unacceptable leakage and thus to continue transistor scaling fully depleted devices such as FINFET and Ultra Thin Planar SOI (FDSOI) were pursued. High volume manufacturing flows for FINFET (with gate last integration) and FDSOI (with gate first integration) come with their own unique challenges. For example, with FINFET maintaining gate height uniformity is crucial for Vt targeting and control. With FDSOI, maintaining gatestack stability at high temperature is key. To continue future scaling, new device architectures (e.g. GAA, Vertical FETs, etc.) will pose further challenges for gate stack integration. Recent and historical progress in HfO_2 growth, interface control, selective deposition, morphology and etching will be discussed with respect to the possibility for future gate stack engineering.

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11:15am **AA2-WeM-14 Effects of Er Doping on Structural and Electrical Properties of HfO_2 Grown by Atomic Layer Deposition.**, ***Soo Hwan Min**, B Park, C Lee,* Yonsei University, Republic of Korea*; W Noh,* Air Liquide Laboratories Korea, South Korea*; I Oh,* Yonsei University, Republic of Korea*; W Kim,* Hanyang University, Republic of Korea*; H Kim,* Yonsei University, Republic of Korea

Gate dielectric materials with high-*k* are required for further scaling down in future years. As an alternative of conventional high-*k* materials such as HfO_2, the addition of elements to host high-*k* materials has attracted attention. Among various elements, rare-earth elements, such as Y, La, Dy, or Er has been known to transform the crystal structure of HfO_2 from the first-principles study. The theoretical study showed that the doping into HfO_2 can energetically stabilize the cubic or tetragonal phase at lower temperature than thermodynamic conditions of pure HfO_2. Since cubic (*k*~29) or tetragonal (*k*~70) HfO_2 has much higher dielectric constant than that of amorphous (*k*~16-19) and monoclinic (*k*~20-25) phases, it is noteworthy that the structural modulation by doping of rare-earth elements can enhance the electrical properties of HfO_2.

In this work, Er doping into HfO_2 was experimentally carried out using atomic layer deposition (ALD) super-cycle process with $Er(MeCp)_2(N\text{-}iPr\text{-}amd)$, $HfCl_4$, and H_2O co-reactant. ALD Er-doped HfO_2 with a variety of Er/(Er+Hf) compositions were systematically examined, mainly focusing on structural and electrical properties. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) were utilized to investigate the film composition and crystal structure. In addition, MOS capacitors were fabricated with various compositions to evaluate the electrical properties from capacitive-voltage (C-V) and current-voltage (I-V) measurements. In specific ratio, the dielectric constant and the interface trap density of Er-doped HfO_2 were found to have significantly improved compared to undoped HfO_2. Structural and electrical characterization revealed that the addition of Er to HfO_2 induces phase transformations from the monoclinic to the cubic or tetragonal phases, even at low post-annealing temperatures of 600°C. This study identifies optimum conditions to improve the electrical properties of Er-doped HfO_2 films which have potential applications in future nanoscale devices.

11:30am **AA2-WeM-15 Improvement of Electrical Performances of Atomic Layer Deposited ZrO_2 MIM Capacitors with Ru Bottom Electrode**, ***Jaehwan Lee**, B Park,* Yonsei University, Republic of Korea*; W Noh,* Air Liquide Laboratories Korea, South Korea*; I Oh,* Yonsei University, Republic of Korea*; W Kim,* Hanyang University, Republic of Korea*; H Kim,* Yonsei University, Republic of Korea

With accelerated scaling down and three-dimensional structuring of integrated circuits, it becomes very challenging to fabricate metal-insulator-metal (MIM) capacitors with low leakage current and high capacitance density. Specifically, the introduction of high-k dielectrics in conjunction with TiN electrodes has improved electrical properties in sub-100 nm processes. Various high-k dielectrics layers combined with TiN electrodes in MIM capacitors were studied for further improvement of MIM capacitors. Controlling an interfacial layer formation between dielectric layer and metal electrode is essential for depositing high-k dielectric thin film on a TiN electrode. When high-k dielectric films were placed on the TiN, interfacial layer was formed due to high reactivity of TiN. The interfacial layer acts as charge traps causing degradation of electrical properties. Surface treatment like plasma treatment on the TiN has been known to help suppress formation of an interfacial layer, but it would be hard to apply for mass-production of DRAM process due to difficulty of uniform treatment without damage caused by energetic species such as ions and radicals on the devices formed inside deep trenches with high aspect ratio.

Alternatively, selection of stable metal electrodes with high work function is required to improve electrical properties. Among several metals, Ru electrode can be appropriate option due to its good thermal and chemical stability, low resistivity, high work function. In this paper, we investigated effects of bottom electrodes on the thin film properties of atomic layer deposited (ALD) ZrO_2, concentrating on correlation between interfacial layer formation and electrical properties. Transmission electron microscopy (TEM) showed thinner thickness of the interfacial layer on the Ru electrode than TiN electrode. Chemical composition of the interfacial layer was analyzed by X-ray photoelectron spectroscopy (XPS) analysis, and ZrO_2 on Ru was less intermixed with bottom electrode due to good thermal and chemical stability of Ru electrode. Introducing Ru electrode improved symmetry of the normalized C-V characteristics. Simultaneously, the introduction of Ru electrode affects decrease of leakage current density from ~10^{-5} A/cm^2 to ~10^{-7} A/cm^2 in I-V characteristics. These results are very meaningful capacitor with Ru electrode can be a very promising device for MIM capacitor in DRAM production.

11:45am **AA2-WeM-16 Perfecting ALD-Y_2O_3/GaAs(001) Interface with Ultra-High Vacuum Annealing**, ***Keng-Yung Lin***, *Y Lin, W Chen, H Wan, L Young,* National Taiwan University, 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

High-performance metal-oxide-semiconductor field-effect transistors (MOSFETs) require the semiconductor/high-κ interface with high-temperature thermal stability and a low interfacial trap density (D_{it}). Previously, *in-situ* atomic layer deposition (ALD) or molecular beam epitaxy (MBE) Y_2O_3 has effectively passivated GaAs(001) surface.[1,2] The growth was achieved in an integrated ALD/MBE ultra-high vacuum (UHV) system. Despite the difference in deposition, both Y_2O_3/GaAs interfaces withstand 900 °C annealing, and the D_{it}'s lie below 5×10^{11} $eV^{-1}cm^{-2}$. MOS capacitors (MOSCAPs) with such interface outperform those with *ex-situ* deposited Al_2O_3.[3] By *in-situ* synchrotron radiation photoemission study on ALD-Y_2O_3/GaAs(001)-4×6, we found that the faulted surface As atoms were removed and lines of Ga-O-Y bonds stabilized the interface.[4] The interfacial Ga_2O (Ga^+)-like state explains the low D_{it}.

In this work, we have improved the electrical characteristics in ALD-Y_2O_3/GaAs by *in-situ* UHV annealing the initial 1-nm Y_2O_3. The idea is motivated by removing the freed As atoms and hydrocarbons remained in the ALD layer. Note that, an amount of hydrocarbons at such critical interface can degrade the device performances. ALD-Y_2O_3 was grown by thermal ALD with sequential $Y(EtCp)_3$ and H_2O pulses, and *in-situ* UHV annealing up to 600 °C was conducted in another chamber in our system right after the ALD growth. MBE-Y_2O_3 is relatively pure and employed as a reference.

Fig. 1 shows the capacitance-voltage (CV) and quasi-static CV (QSCV) curves for MOSCAPs. The UHV-annealed ALD-Y_2O_3/GaAs was improved with a reduced frequency dispersion (F.D.) in the accumulation/depletion region, and a lowered trap-induced hump in the inversion region. Fig. 2 presents the D_{it} spectra extracted from QSCVs. The UHV-annealed ALD-Y_2O_3/GaAs shows a reduced D_{it}, also hinted by the sharp transition of QSCVs and the narrow gap between QSCVs and CVs. Fig. 3 shows the O 1s core-level spectra, where O-Y is from the stoichiometric Y_2O_3 and O* is from the interfacial Ga-O-Y and the surface Y-O-H.[4] Note that the ratios of O-Y of our 1-nm Y_2O_3 films are significantly higher than the one reported.[5] Upon UHV annealing, the residue O* may be attributed to the interfacial Ga-O-Y with the surface Y-O-H mostly removed. This UHV annealing approach is significant in perfecting ALD-Y_2O_3/GaAs and is applicable to many other material systems.

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ALD Applications
Room Grand Ballroom A-C - Session AA1-WeA
Emerging Applications II

Moderators: Arrelaine Dameron, Forge Nano, Se-Hun Kwon, Pusan National University

1:30pm **AA1-WeA-1 Atomic Layer Deposited Nano-Coatings to Protect $SrAl_2O_4$ Based Long-Life Phosphors from Environmental Degradation***, **Erkul Karacaoglu**,* Georgia Institute of Technology*; E Ozturk,* Karamanoglu Mehmetbey University, Turkey*; M Uyaner,* Necmettin Erbakan University, Turkey*; M Losego,* Georgia Institute of Technology

Strontium aluminate ($SrAl_2O_4$) phosphors activated with Eu^{2+} and co-doped with RE^{3+} elements (RE: Nd, Dy, etc) are long-life phosphors (>12 hrs of persistent luminescence) of significant commercial relevance. These phosphors have been widely used as luminescent additives in many commercial products including plastics and textiles. Today, these phosphors are of interest for zero-energy safety lighting both in residential markets and on roadways. However, these phosphors are prone to degradation in moist or humid conditions. This talk will discuss our work to use ALD to protect these phosphors from degradation in aggressive aqueous environments. We specifically study degradation of $SrAl_2O_4$ powders co-doped with Eu_2O_3 and Dy_2O_3 and then coated with Al_2O_3 or TiO_2 by atomic layer deposition (ALD). ALD coatings of about 10 to 250 nm in thickness are investigated. Uncoated phosphor powders dispersed directly in water show rapid hydroxylation as tracked with increasing water basicity from pH 7 to 13. XRD analysis, FT-IR spectroscopy, and optical microscopy all confirm post-mortem that these uncoated powders readily decompose to SrO, $Al(OH)_3$, and Al_2O_3 within 3 hours of water exposure and fully degrade to $Sr_3Al_2O_6$ and $Al_2O_3{\cdot}H_2O$ after 48 hrs of water exposure. This degradation results in a severe loss of phosphorescence. Powders that are ALD coated with even 5 nm of Al_2O_3 or TiO_2 show minimal change in aqueous pH and no change in morphological appearance after 48 hours of direct water exposure. 10 nm coatings are found to protect the phosphor powders for up to 2 weeks in direct water exposure. XRD confirms no emergence of secondary phases and photoluminescence properties are retained. Achieving good conformality over all powder surfaces appears to be an important requirement. Interestingly, the photoluminescence intensity of the raw powders also appears to increase with Al_2O_3 ALD coating thickness. This photoemission increase continues even up to a 250 nm coating thickness which shows a 1.5x increase in phosphorescence. This enhancement of emission intensities for ALD coated samples could be attributed to increased radiation absorption caused by surface defects or surface strain introduced by the coatings. Prior work on other luminescent materials has shown similar effects, and our current understanding of these photophysics phenomena will be discussed.

1:45pm **AA1-WeA-2 Enhanced Interfacial Fracture Toughness of Polymer-Epoxy Interfaces using ALD Surface Treatments***, **Yuxin Chen**, N Ginga, W LePage, E Kazyak, A Gayle, J Wang, M Thouless, N Dasgupta,* University of Michigan

Polymer interfaces play a critical role in a variety of applications, including consumer products, structural components, biomedical devices, and flexible electronics. In many cases, polymers need to be bonded with adhesives to create structural joints or multi-layer structures. For adhesives to efficiently wet and bond to a substrate, the surface free energy of the substrate must be equal to or higher than the surface free energy of the adhesive. However, the surface energy of most polymers is low, which makes adhesion difficult. Thus, there often is a need to increase the surface energy of a polymer without changing the bulk mechanical and chemical properties.

In this work, we demonstrate that atomic layer deposition (ALD) can be applied on poly(methyl methacrylate) (PMMA) and fluorinated ethylene propylene (FEP) to increase their surface energies and, hence, to increase the interfacial fracture toughness when bonded to an epoxy adhesive.

ALD alumina films were deposited on each type of polymer to modify the surfaces towards high energy surfaces of metal oxide. Transmission-electron microscopy (TEM) and atomic-force microscopy (AFM) were used to study the film morphology on the polymers. These indicated that the ALD treatment increased the surface roughness and changed the sub-surface chemistry by vapor-phase infiltration (VPI). The increase in surface energy after ALD was measured by the sessile-drop test with water, ethylene glycol and glycerol.

The interfacial fracture toughness of each polymer-epoxy interface was measured using a customized motor-controlled wedge tester. After ALD film growth, the interfacial fracture toughness of the PMMA-epoxy and FEP-epoxy interfaces increased by factors of up to 7 and 60, respectively. The two ALD samples and two control samples were tested at the same level of humidity. Furthermore, we observed stress-corrosion cracking of the ALD-polymer interfaces. By conducting wedge tests in different levels of humidity, we found that although ALD increased equilibrium interfacial fracture toughness at all humidity, the effect decreased as humidity increased. Scanning-electron microscopy (SEM) of samples after testing provided additional evidence for stress-corrosion cracking of the ALD-polymer interface. These results suggest a new application of ALD for engineering the mechanical properties of chemically inert surfaces.

2:00pm **AA1-WeA-3 Atomic Layer Deposition of Pd on ZnO Nanorods for High Performance Photocatalysts***, **Jong Seon Park**, B Kim, G Han, K Park, E Kang, H Park, J Shim,* Korea University, Republic of Korea

The metal oxide-metal heterostructure is reported to be effective for improving the performance of photocatalysts. Zinc oxide (ZnO) is widely used as a photocatalyst due to its proper band gap (3.3 eV) that enables outstanding semiconducting characteristics. Also, ZnO has been fabricated in variety of forms including thin film, particles or nanowires, that are useful for catalysis with high surface area. Palladium (Pd) is considered as a well-matching metal with ZnO to synergistically improve photocatalytic performance with an appropriate Fermi level. Recombination of generated charges are prohibited since Pd catches excited charges from ZnO leading to highly improved photocatalytic efficiency.

In this study, ZnO nanorods coated with Pd nanoparticles is evaluated as photocatalysts. The ZnO nanorods are prepared by hydrothermal growth on silicon wafers. The Pd nanoparticles are fabricated by atomic layer deposition (ALD). ALD Pd is conducted using Pd(II) hexafluoroacetylacetonate ($Pd(hfac)\text{-}_2$) precursor with formalin in a customized ALD chamber (ICOT Inc.). The growth temperature is 90ºC. To evaluate the photocatalytic performance, the degradation rate of methylene blue is measured under the ultraviolet radiating condition. As a result, it is confirmed that the degradation rates are accelerated with the ZnO-ALD Pd catalysts compared to bare ZnO nanorods. This result will be discussed in more details at the presentation.

2:15pm **AA1-WeA-4 Accelerating Light Beam (ALB) Generation through Dielectric Optical Device Fabricated by Low Temperature Atomic Layer Deposition (ALD)***, W Zhu, C Zhang, A Agrawal, H Lezec,* National Institute of Standards and Technology*; **Huazhi Li**,* Arradiance LLC

Accelerating light beam (ALB) or bended light along an arbitrary curvature enables many intriguing applications such as particle manipulation, optical illusion and cloaking[1]. To date, one common method to generate ALBs is based on spatial light modulators (SLMs)[2], which are large and lack spatial resolution due to the large pixel size of the SLMs. Acceleration control of Airy beams (one representative form of ALB) in a photorefractive crystal by applying ultrahigh voltages have been recently reported[3]. However, the scheme usually only operates at a specific wavelength, or imposes a stringent requirement on the ALB generation process. Furthermore, the ALB is generated inside the crystal, not in free-space.

In this presentation we successfully demonstrated a novel scheme to generate ALBs through an ultrathin all- dielectric optical metasurface consisting of nano-posts with cylindrical cross-sections. By properly configuring the lateral dimensions of the nano-post (major axis length and short axis length), as well as its orientation angle, arbitrary phase modulations of an incident beam can be created, thus providing an efficient approach to generate ALBs. The dielectric metasurfaces are fabricated by first creating the reverse patterns in an electron beam (E-beam) resist, followed by low-temperature atomic layer deposition (ALD) of TiO_2, which fills the openings in the exposure E-beam resist in a conformal manner without causing any degradation of the resist (enabled by low temperature ALD).

The proof-of-concept devices demonstrated include: 1) Generation and switch between two arbitrary ALBs that follow different caustic trajectories in free-space (schematically represented in the following figure); 2) simultaneously achieving efficient and broadband generation and dynamic control of ALBs across the visible region. Our study opens up the possibility of creating ultra-compact, fine-spatial-resolution, and flat-profile nanophotonic platforms for efficient generation and dynamical control of structured light beams.

Literature:

1. Cai, W.; Chettiar, U. K.; Kildishev, A. V.; Shalaev, V. M. *Nat. Photonics* 2007, 1, 224−227; Valentine, J.; Li, J.; Zentgraf, T.; Bartal, G.; Zhang, X. *Nat. Mater*. 2009, 8, 568−571.

2. Siviloglou, G. A.; Broky, J.; Dogariu, A.; Christodoulides, D. N. *Phys. Rev. Lett.* 2007, 99, 213901.

3. Ye, Z.; Liu, S.; Lou, C.; Zhang, P.; Hu, Y.; Song, D.; Zhao, J.; Chen, Z. *Opt. Lett.* 2011, 36, 3230−3232.

2:30pm **AA1-WeA-5 Tunable Plasmonic Colours Preserved and Modified by Atomic Layer Deposition of Alumina***, J Guay, A Lesina, G Killaire,* University of Ottawa, Canada*; **Peter Gordon,*** Carleton University, Canada*; C Hahn,* University of Ottawa, Canada*; S Barry,* Carleton University, Canada*; L Ramunno, P Berini, A Weck,* University of Ottawa, Canada

Decorative colouring of pure silver and gold surfaces is an important application for jewelry and coinage, particularly collector's coins. In order to preserve the purity of these substrates, colours created by adding materials like inks or patinas should be avoided. A novel colouring method that uses careful laser treatment to create a surface with nanoscale, plasmonic features has been developed but the bare surface features undergo dynamic coalescence that dulls and shifts the available colour palette. This work demonstrates that colours generated by nanostructured plasmonic silver surfaces can be preserved and tuned by overcoating with alumina films by ALD. These colours were observed to shift with increasing alumina film thickness.

Two types of laser treatment were used to create surface features on silver that gave rise to colours in the visible spectrum: burst and nonburst. For burst surfaces, the colours first degrade with increasing alumina film thickness but recover at larger thicknesses with an expanded colour range. For nonburst surfaces the colours degraded with increasing thickness without any recovery. Underlying periodic structures specific to the burst method are responsible for this behavior. FDTD modeling of representative surfaces, including the conformal alumina layer, helps explain these colour changes. For alumina thicknesses smaller than the nanoparticle gaps, the changes in the perceived colours are due to the perturbation of plasmonic resonances. For alumina thicknesses larger than the nanoparticle gap, the change in colours originates primarily from the complex reflectance response of the alumina coated structures and modification of the refractive index of the resulting complex surface.

The coloured surfaces were evaluated for applications in colourimetric and radiometric sensing showing large sensitivities of up to 3.06/nm and 3.19 nm/nm, respectively. The colourimetric and radiometric sensitivities are observed to be colour dependent.

2:45pm **AA1-WeA-6 TFE of OLED Displays by Time-Space-Divided (TSD) PE-ALD and PE-CVD Hybrid System***, **Bongsik Kim,*** JUSUNG Engineering, Republic of Korea

In this paper we introduce a time space divided (TSD) plasma assisted deposition equipment available to in-situ atomic layer deposition (ALD) and chemical vapor deposition (CVD) process and a thin film encapsulation (TFE) of organic light emitting diodes (OLEDs) deposited by the above mentioned equipment, TSD hybrid system. Figure 1 represents a structure of the TSD hybrid system. The 1st electrode, included protruding rod-like metal bars, is composed of two types of gas injection systems and the protruded parts are inserted into holes of the 2nd electrode. Each electrode is rigorously designed considering the hollow cathode effect (HCE), the plasma sheaths and the surface area for optimizing RF power efficiency. The remote plasma source cleaning (RPSC) system enables an in-situ cleaning to etch away the film residue in the chamber.

Figure 2 show cross-sectional views of two kinds of TFEs in particle environments. Figure 2-1 represents seam defect of general SiO film, deposited by using the hexamethyldisiloxane (HMDSO), and figure 2-2 represents the cross-sectional view of the coated particle by flowable SiO, named pp-HMDSO. Because deposited films generally growth to the direction from which the gas is flowing, almost films which are deposited by the general CVD process cannot avoid to growth of the defect from the blind spot. So, we, by controlling process conditions, fabricated the TFE which includes flowable SiO film in order to fill the blind spot and hardened the film to reinforce the adhesion to neighbored layers.

Figure 3 show measured characteristics of the TFE structure of the figure 2-2, deposited by the TSD hybrid system at low substrate temperature (<100℃). In order to suppress film defects, induced by particles, first, we coated particles with the pp-HMDSO and then, the ALD SiO layer is deposited as a second barrier and a buffer layer between the SiO and the SiN. Even if the film coats conformally without any defect, the permeation of water and oxygen through the film bulk direction would be occurred. So, finally, we coated with the CVD SiN layer for an ultra-low water vapor transmission rate (WVTR). As shown in figure 3, the WVTR of <5x10^{-5}g/m^{2}day at 40 ℃ /100%RH conditions is measured by MOCON Aquatran2 and also we get the optical transmittance (>95%) and the low film stress (<100MPa) data.

The TSD hybrid system can make various kinds of thin films, such as CVD SiN, SiON, SiO, ALD SiO, SiN, etc, by in-situ ALD or CVD process and also can control characteristics of thin films widely by changing the process conditions. By TSD hybrid system, manufactured by JUSUNG engineering, we expecting to contribute the OLED industry development.

3:00pm **AA1-WeA-7 Tailoring the Ferroelectricity of ZrO_2 Thin Films using Ultrathin Interfacial Layers Prepared by Plasma-Enhanced Atomic Layer Deposition***, **Sheng-Han Yi**, B Lin, T Hsu, J Shieh, M Chen,* National Taiwan University, Republic of China

In recent years, HfO_2/ZrO_2-based ferroelectric thin films have been recognized as promising candidates for memory devices and negative-capacitance field-effect-transistors to achieve a further improvement of device performance. The ferroelectric(FE) and antiferroelectric(AFE) properties of these CMOS-compatible oxides have been confirmed to originate from the polar orthorhombic phase and non-polar tetragonal phase, respectively. In this work, we report the significant impact of ALD-deposited interfacial layers on the microstructures and FE/AFE properties of ZrO_2 thin films. Sub-nanometer interfacial layers deposited by plasma-enhanced atomic layer deposition are intentionally introduced between the ZrO_2 thin film and the electrodes of metal-insulator-metal structures to tailor the crystalline phase and ferroelectricity of the ZrO_2. The interfacial layers boost the formation of orthorhombic ZrO_2, leading to significant enhancement of the ferroelectricity with a significant increment of the remanent polarization. On the other hand, another interfacial layers contribute to the formation of tetragonal ZrO_2, giving rise to the dramatic transformation of ZrO_2 from ferroelectricity to antiferroelectricity. The findings indicate that interface engineering by ALD is an effective and advantageous approach to tailor the FE/AFE characteristics of materials.

3:15pm **AA1-WeA-8 Spin-Hall-Active Platinum Thin Films Grown Via Atomic Layer Deposition***, **Michaela Lammel,*** IFW Dresden, Germany*; R Schlitz,* Technische Universität Dresden, Germany*; A Amusan,* IFW Dresden, Germany*; S Schlicht,* FAU Erlangen, Germany*; T Tynell,* IFW Dresden, Germany*; J Bachmann,* FAU Erlangen, Germany*; G Woltersdorf,* Martin-Luther-Universität Halle-Wittenberg, Germany*; K Nielsch,* IFW Dresden, Germany*; S Goennenwein,* Technische Universität Dresden, Germany*; A Thomas,* IFW Dresden, Germany

Due to its strong spin orbit coupling platinum (Pt) is often used as a spin injector/detector in spintronics. We used atomic layer deposition (ALD) to fabricate platinum thin films on a substrate consisting of liquid phase epitaxy grown yttrium iron garnet ($Y_3Fe_5O_{12}$, YIG) on gadolinium gallium garnet ($Gd_3Ga_5O_{12}$). Magnetotransport experiments were performed on the YIG/Pt heterostructures in three mutually orthogonal rotation planes, revealing the fingerprint of spin Hall magnetoresistance. Samples with different platinum thicknesses were used to estimate the spin transport parameters of the Pt thin films. Comparing the values for the spin Hall angle as well as the spin diffusion length with literature we found the spin diffusion length in the ALD Pt thin films agrees well with results reported for high-quality sputtered platinum. The spin Hall magnetoresistance however is smaller by approximatley a factor of 20. Clearly, further experiments will be required to optimize the interface quality in such ALD-based heterostructures. Nevertheless, our results show that spin Hall active Pt thin films can be fabricated by ALD featuring an appropriate quality for spin transport. The reported results build the framework for establishing conformal coatings for non-planar surface geometries with spin Hall active metals via ALD which in the future can provide the basis for developing 3D spintronic devices [1].

[1] Schlitz et al., Appl. Phys. Lett. **112**, 242403 (2018)

ALD Applications
Room Grand Ballroom H-K - Session AA2-WeA
ALD for ULSI Applications II

Moderators: Iian Buchanan, Versum Materials, UK, Robert Clark, TEL Technology Center, America, LLC

1:30pm **AA2-WeA-1 Silicon-Based Low k Dielectric Materials with Remote Plasma ALD***, **Hyeongtag Jeon**,* Hanyang University, Republic of Korea **INVITED**

As the devices continue to shrink in size, resistive-capacitive (RC) time delay due to parasitic capacitance of devices is becoming a major problem. Low dielectric films with having high thermal stability and excellent step coverage is needed for applications such as barriers and gate sidewall spacers. Silicon oxycarbide (SiOC), silicon oxycarbonitride (SiOCN), silicon carbon nitride (SiCN) are possible candidates for these requirements because the carbon content and bonding state in the low dielectric materials can control the dielectric constant.

Atomic layer deposition (ALD) can be an ideal method for the high conformality with its self-limited reaction. The introduction of the plasma is necessary to decompose the ligands in the precursor for the ALD reaction by the plasma power. We used remote plasma ALD (RPALD) to prevent films from substrate damages caused ion bombardment.

In this work, we will discuss the trend of low k dielectric ALD studies and report the results of SiOC, SiOCN, and SiCN ALD. We used remote plasma ALD system. Octamethylcyclotetrasiloxane (OMCTS) and O_2, Ar, H_2, N_2 and CH_4+Ar plasmas were respectively used as a precursor and reactants for SiOC and SiOCN thin film deposition. Bis[(diethylaminohigh)dimethylsilyl](trimethylsilyl)-amine (DTDN-2) and N_2 plasma were used as a precursor and reactant for SiCN thin film deposition. X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), transmission electron microscopy (TEM), I-V measurement, C-V measurement, and wet etch rate (WER) test were performed for investigating the characteristics of low k dielectric films.

2:00pm **AA2-WeA-3 SiOC Films by PEALD with Excellent Conformality and Wet Etch Resistance***, **Young Chol Byun**, E Shero,* ASM

As memory devices shrink, electrical and integration constraints have become tighter. As an example, digit line spacer stacks need to demonstrate a low dielectric constant (k<4.5), excellent wet etch rate resistance (an order of magnitude lower than thermal SiO2) and excellent conformality and growth over composite structures comprising a metal, hardmask and poly-Si. Conventional furnace-deposited ALD nitrides (SiN) tend to demonstrate good wet etch rate resistance but suffer high k (>7.0). PEALD oxides (SiO2) have a low-k but poor wet etch resistance and sub-optimal conformality on the composite stack due to the directional nature of the capactively-coupled plasma. But CCP plasma reactors typically offer higher throughput. This motivates the search for SiOC class of films to leverage Si-O bonding for low-k and Si-C bonding for step coverage, preferably deposited by PEALD.

Here, we demonstrate SiOC films with a low-k value (<4.5) with excellent step coverage and wet etch rate resistance due to Si-C backbonding (80X lower than furnace nitride and 500X lower than thermal oxide in hydrofluoric acid). The films also show good step coverage of 100% in upto 10:1 aspect ratio structures. In summary, these PEALD films show a pathway to aggressively scale k and wet etch resistance for front end memory applications.

2:15pm **AA2-WeA-4 ALD TiN for Superconducting Through-Silicon Vias***, **Kestutis Grigoras**, S Simbierowicz, L Grönberg, J Govenius, V Vesterinen, M Prunnila, J Hassel,* VTT Technical Research Centre of Finland Ltd, Finland

Through-silicon vias (TSVs) are a widely used interconnect technique, allowing the creation of non-planar integrated circuits. Recently, the use of TSVs in multichip packages was proposed as a way of improving the addressability and integration of superconducting qubits – the core elements of superconducting quantum processors [1, 2]. In this approach, the primary quantum-coherent elements of a quantum integrated circuit can be separated from the readout and control elements by fabricating them on separate chips, which are then combined with flip-chip bonding. Here, routing signals through TSVs enables the addressability of a large number of qubits. The main requirements for TSV films are superconductivity, small dimensions, and conformality. To satisfy these challenging requirements, we use atomic layer deposition (ALD).

In this work, we investigate the performance of TiN TSV interconnects. We etch arrays of 60 µm diameter TSVs in 495 µm thick 6-inch silicon wafers by deep reactive ion etching using the Bosch process (Omega i2L, Aviza Technology). We use 2 µm thick oxide layers both as a mask (top side) as well as an etch stop layer (back side). We coat the TSVs with a TiN layer by ALD (SUNALE R-150B, Picosun), performing 2,500 cycles at 450ºC, using $TiCl_4$ and ammonia as precursors and nitrogen as a carrier gas. The superconducting behaviour of thin TiN layers has been previously investigated for layers deposited by plasma-ALD [3], but this technique is not applicable for coating high-aspect-ratio trenches (the aspect ratio of our TSVs is about 8:1). Therefore, we use thermal ALD in this work.

Initially, the deposited layers did not become superconducting even at 0.1 K. Optimization of the ALD process by tuning precursor pulse/purge times finally led to superconducting TiN layers with a T_c of approximately 0.85 K. The room temperature sheet resistance for a 47 nm thick layer is approximately 60 Ω/sq, as measured on the flat area of the samples. We confirm the conformality of the TiN inside vias using scanning electron microscopy. Future plans include increasing the T_c as well as integrating TSVs on chips with other structures (resonators, qubits).

[1] Rosenberg et al., npj Quantum Information 42 (2017) 1-5.

[2] Vahidpour et al., arXiv:1708.02226 [https://arxiv.org/abs/1708.02226] [physics.app-ph].

[3] Shearrow et al., arXiv:1808.06009v1 [cond-mat.mtrl-sci]

2:30pm **AA2-WeA-5 Physical and Electronic Properties of Annealed ALD-deposited Ru from Ru(DMBD)(CO)$_3$ and Oxygen***, **Michael H. Hayes**,* Oregon State University*; C Dezelah, J Woodruff,* EMD Performance Materials*; J Conley, Jr.,* Oregon State University

Ru metal is promising for MOS gate electrode and interconnect applications due to its relatively low bulk resistivity, high work-function, conductive oxide (RuO_2), and ease of etching. Because it is insoluble in and adheres well to Cu, Ru also has potential as a liner for metal interconnects. The earliest precursors used for ALD of Ru were often characterized by long nucleation delays (~200 cycles) and island-like growth, both unfavorable for producing uniform thin (< 10 nm) films. Recently, Austin et. al.[1] demonstrated a thermal ALD process using dimethylbutadiene Ru tricarbonyl [Ru(DMBD)(CO)$_3$] and O_2 that results in zero nucleation delay, low resistivity (14 µΩ-cm), and low RMS roughness (0.6 nm). While the resistivity is among the lowest reported, it is still higher than bulk crystalline Ru. In this work, we examine the impact of inert and forming gas anneals on the resistivity (ρ_{Ru}), effective workfunction ($\Phi_{Ru\text{-}eff}$) on ALD Al_2O_3 and HfO_2, crystal structure, and composition of ALD Ru films deposited using Ru(DMBD)(CO)$_3$ and O_2.

ALD Ru films of at least 30 nm in thickness are annealed at 400, 450, and 500 °C in either N_2 or 3% H_2/N_2 ambient in 20 minute increments up to a total of 60 min (Fig. 1). Whereas annealing in pure N_2 reduces ρ_{Ru} from an average of 16 µΩ-cm to 13 µΩ-cm, H_2/N_2 annealing results in a greater reduction in resistivity with the lowest ρ_{Ru} of 9.1 µΩ-cm obtained after 60 min at 500 °C, approaching the bulk value of 7.1 µΩ-cm. ρ_{Ru} vs. Ru film thickness will be discussed at the meeting.

X-ray diffraction (Fig. 2) of the as-deposited films indicates hexagonal Ru with slight (001) preferred orientation and average crystallite size of 6.3 nm. After H_2/N_2 annealing, the relative intensity of the (001) peak is reduced and the crystallite size increased to 12.4 nm. Atomic force microscopy confirmed a slightly rougher film post anneal (2.1 nm RMS). XPS shows low impurity content.

Capacitance-voltage measurements are used to determine the flat-band voltage (V_{FB}) of a series of Ru/Al_2O_3/p-Si and Ru/HfO_2/p-Si MOS capacitors with various thickness ALD dielectrics for both as-deposited and 500 °C 60 min H_2/N_2 annealed samples. The extrapolated zero-oxide-thickness V_{FB} was then used to determine $\Phi_{Ru\text{-}eff}$ for each dielectric (Fig. 3). Annealing increases $\Phi_{Ru\text{-}eff}$ to 4.9 eV and 5.3 eV for the Ru/Al_2O_3/p-Si and Ru/HfO_2/p-Si devices, respectively. Fast nucleation, low ρ_{Ru} comparable to bulk, and large $\Phi_{Ru\text{-}eff}$ comparable to sputtered films indicate ALD Ru using Ru(DMBD) and O_2 may offer advantages compared to previous reports.

[1] D. Z. Austin *et al.*, "ALD of Ru and RuO_2 Using a Zero-Oxidation State Precursor," *Chem. Mater.* 29(3), 1107 (2017).

2:45pm **AA2-WeA-6 Fluorine Free Boron-Containing Composite Layers for Shallow Dopant Source Applications***, **Anil Mane**, D Choudhury, K Pupek, R Langeslay, M Delferro, J Elam,* Argonne National Laboratory

Conformal and uniform coatings of boron-containing thin films via atomic layer deposition (ALD) could be used as a shallow dopant source for advanced 3D-transistor structures in VLSI manufacturing. Targeting this application, we evaluated three non-halogenated boron compounds for their suitability as ALD precursors: boric acid ($B(OH)_3$), trimethyl borate ($B(OCH_3)_3$), and hafnium borohydride $Hf(BH_4)_4$. The $B(OH)_3$ and $B(OCH_3)_3$ were used in combination with trimethyl aluminum to deposit $B_xAl_{2-x}O_3$ ALD films, and the $Hf(BH_4)_4$ was used with H_2O to deposit HfB_xO_y films. We evaluated the ALD surface chemistries for these processes using in-situ quartz crystal microbalance (QCM) and Fourier transform infrared spectroscopy (FTIR) studies. The QCM measurements also confirmed self-limiting behavior and helped to optimize the ALD timing. The resultant boron containing nanocomposite films were analyzed using X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), ellipsometry, and electrical capacitance measurements. The boron content in the $B_xAl_{2-x}O_3$ and HfB_xO_y composite films was controllable by tuning the ALD cycle ratio and the precursor sequence. We performed rapid thermal annealing of composite films as a function of time and temperature and determined the B-diffusion in silicon as well as changes in the optical properties of the $B_xAl_{2-x}O_3$ and HfB_xO_y layers. Here we will present a detailed investigation of ALD methods for creating B-containing layer for shallow dopant application.

3:00pm **AA2-WeA-7 Impact of Medium Energy Ions on the Microstructure and Physical Properties of TiN Thin Layers Grown by Plasma Enhanced Atomic Layer Deposition (PE-ALD).**, *S Belahcen, C Vallée, A Bsiesy,* ***Marceline Bonvalot,*** LTM-UGA, France

Titanium nitride TiN has been extensively used in common microelectronic devices as an electrode material, where it serves as an interfacial connecting material between a device and the metallic contacts used to drive it, while simultaneously preventing any diffusion of the metal into silicon. TiN is also involved in biological Micro-Electro-Mechanical Systems (bioMEMS) as an electrode material, for instance in cardiac pacemakers or neural stimulation applications, thanks to its unequalled conducting properties at reduced dimensions, as compared to traditional noble metals, and also thanks to its high corrosion resistance to human body fluids. For such applications, a deep knowledge of the microstructural properties of TiN are of utmost importance.

In this work, the impact of processing parameters on the physical properties of TiN has been investigated in details. TiN thin layers (20 nm) have been prepared on SiO_2 (100 nm)/Si substrates by Plasma Enhanced ALD (PE-ALD), using TDMAT as a precursor and N_2 as a plasma gaz. The PE-ALD setup used for this purpose has been equipped with an original Atomic Layer Etching (ALE) kit positionned at the back-face of the substrate holder, which allows medium energy ions to be extracted from the plasma during the ALD growth. Several bias values ranging from 0 W to 90 W have thus been tested during the plasma step to investigate the impact of ions with varying kinetic energies on the morphological properties of TiN.

The rugosity of as deposited TiN layers has been obtained from AFM measurements. XRD and XRR analyses have been systematically carried out in order to evaluate the texturation, cristallinity and mechanical stress in the layer. The impact of medium energy ions during TiN growth has been correlated to the rugosity, density and residual stress. These results will be discussed in view of potential applications of TiN as an electrode material in microelectronic devices.

3:15pm **AA2-WeA-8 ALD Process Monitoring for 3D Device Structures***,* ***Jiangtao Hu,*** Lam Research Corp.

Semiconductor device structures have become increasingly complex, requiring new measurement techniques to support manufacturing. Measurement of high aspect ratio (HAR) structures requires a response signal to depth and profile, and the bottom may be invisible to top-down optical signals. Likewise, certain thick films are opaque to optical thickness measurement. Lateral processing steps occur too deeply in a structure to be visible, and thin conformal deposition films need to be characterized inside the feature.

For ALD applications, a critical requirement is to have complete and uniform coverage from the top to the bottom of a 3D device. A thinner or incomplete deposition at the bottom of a device can often lead to high leakage and high failure rates. Conventional optical thickness measurements of ALD films can identify thickness variations at the top of a high aspect ratio (HAR) device but may not identify process deviations at the bottom of this type of device.

Monitoring ALD using mass metrology is a potential solution to this issue. The direct measurement of mass change due to process enables detection of process excursions. Measurement of the wafer mass before and after a process is a simple and direct means of monitoring and control. This is particularly true for ultra- opaque films and complex stacks, film density monitoring, and conformal and ALD/sidewall deposition, where traditional optical metrology techniques may not be effective.

Conformal deposition typically involves an area much greater than a blanket deposition layer, and even more so on severe/strong/high device topologies. Mass sensitivity to film on a patterned wafer can be as much as 10 times greater than on a blanket wafer (Fig 1).

More importantly, mass metrology directly monitors the amount of material change in a device across the entire HAR structure while conventional optical film metrology typically measures these changes on a test pad or blanket test wafer. Mass metrology instrumentation can detect low coverage of ALD films at the bottom of a HAR device which otherwise would be missed using optical measurement. For example, we can compare mass change induced by flow rate reduction on blanket or patterned wafers (Fig 2). Significant mass change occurs on patterned wafers after a 3% of flow rate reduction, while on patterned wafers this deviation is pronounced after a 1% reduction.

In this discussion, we will discuss how Mass Metrology can be used to monitor ALD process variations in 3D semiconductor devices, along with the applications and benefits of this technology in ALD.

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