## ALD Fundamentals
## Room Van Eyck - Session AF3-MoA

### Plasma Enhanced ALD

**Moderators:** Sumit Agarwal, Colorado School of Mines, Andreas Werbrouck, Ghent University, Belgium

1:30pm **AF3-MoA-1 Revisited Thermal and Plasma Enhanced Atomic Layer Deposition Processes of Metal Nitrides**, ***Elisabeth Blanquet***, SIMaP, CNRS , University Grenoble Alpes, France; *A. Mantoux,* SIMaP, University Grenoble Alpes, France; *F. Mercier,* SIMaP, CNRS, University Grenoble Alpes, France; *R. Boichot,* SIMAP, Grenoble-INP, University Grenoble Alpes, France; *I. Nuta,* SIMAP, CNRS, University Grenoble Alpes, France; *C. Jimenez,* LMGP, CNRS, University Grenoble Alpes, France **INVITED**

Metal nitrides films stand out as candidates for many strategic industrial applications as they exhibit superior functional properties such as mechanical, electrical and thermal properties. Complementary chemical vapor deposition techniques from High Temperature Chemical Vapor Deposition (HTCVD) to Thermal and Plasma Enhanced Atomic Layer Deposition (T-ALD and PEALD) have been investigated to fabricate metal nitrides thin films. Coupling or combining these techniques might open new opportunities. In each case, one of the major challenges is the synthesis of high quality, pure (with no oxygen contamination) material. Among ALD developments, efforts have been focused on the exploration of thermal stabilities of different precursor molecules, chemical reactions as well as growth processes sequences and conditions.

In this presentation, the examples of various metal nitride deposition process development with special focus on Aluminum nitride will be presented. AlN is a multifunctional material, which has been widely investigated for many potential applications in recent years, due to its high melting point, excellent thermal conductivity and good chemical stability and behavior towards oxidization and abrasion with respect to other nitrides. It is a semiconductor material with a wide bandgap, offering transparency even in the UV region. Moreover, its oxidation rate is low at temperatures below 1100°C. AlN films are attractive for applications in energy, aeronautics, electronic or optoelectronic devices. For instance, thin films are investigated in piezoelectric based applications, as passivating and protective coatings for metallic architectures, as AlN substrate in high power applications.

We report on the optimizing routes and strategies via coupling deposition processes to obtain the best film properties on various systems.

2:00pm **AF3-MoA-3 Plasma-Enhanced Low-Temperature ALD Process for Molybdenum Oxide Thin Films and Its Evaluation as Hydrogen Gas Sensors**, ***Jan-Lucas Wree***, *J. Klimars,* Ruhr University Bochum, Germany; *N. Saliha,* Heinrich-Heine University Düsseldorf, Germany; *D. Rogalla,* Ruhr University Bochum, Germany; *K. Schierbaum,* Heinrich-Heine University Düsseldorf, Germany; *A. Devi,* Ruhr University Bochum, Germany

The versatile properties of molybdenum oxide strongly depend on the structural features and in particular on its crystallinity, composition and morphology. This makes it an interesting material class for a variety of applications, i.e., (opto)electronics, (photo)catalysis and gas sensors. Moreover, the performance of these applications is significantly enhanced by the implementation of the active material in thin film form. Therefore, the development of atomic layer deposition (ALD) processes for the fabrication of nanostructured molybdenum oxide thin films has grown steadily in the recent years. As a consequence, the demand for suitable molybdenum precursors with improved physico-chemical properties is rising as the library for appropriate molybdenum precursors is rather small.

In this study, molybdenum oxide thin films were deposited using a new plasma-enhanced ALD (PEALD) process employing the molybdenum precursor $Mo[(N^tBu)_2(^tBu_2DAD)]$, recently developed in our group, and oxygen plasma. The process yielded a growth rate of 0.75 Å/cycle on Si(100), which is in the range of other PEALD processes reported for molybdenum oxide. Furthermore, the linear dependence of the thickness on the number of cycles was confirmed within a temperature window between 100°C and 240°C. X-ray diffraction (XRD) patterns show that on the lower end of the temperature window the films appear to be amorphous while crystallization starts at the higher end (240°C), yielding nanocrystalline β-$MoO_3$ thin films. Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA) and X-ray photoelectron spectroscopy (XPS) analyses revealed the formation of pure films, while SEM analysis showed the smooth morphology of the films with crystallite formation at higher deposition temperatures. Furthermore, sensor substrates were coated with molybdenum oxide to investigate the resistive hydrogen sensitivity of the thin films with respect to their morphology. This study demonstrates that the recently developed molybdenum precursor is suitable for the utilization in ALD applications. The resistive response of the deposited $MoO_x$ thin films towards hydrogen gas reveals the potential of this material for thin film hydrogen gas sensors. Moreover, the overall quality of the films makes it also promising for implementation in other applications such as catalysis and optoelectronics.

2:15pm **AF3-MoA-4 Low-Temperature Plasma-Enhanced Atomic Layer Deposition of Crystalline Tin Disulfide Thin Films**, ***Femi Mathew***, *N. Poonkottil, R. Karuparambil Ramachandran, B. Zhao, Z. Hens, C. Detavernier, J. Dendooven,* Ghent University, Belgium

Among the layered metal dichalcogenide materials, semiconducting tin disulfide ($SnS_2$) is a potent candidate for photocatalysis, field-effect transistors, lithium-ion batteries, and gas sensing applications. Hence, there is a demand for a scalable technique to uniformly and conformally deposit $SnS_2$ thin films, preferably at low temperatures. Here, we present a plasma-enhanced atomic layer deposition (PE-ALD) technique to deposit crystalline $SnS_2$ using tetrakis(dimethylamino)tin (TDMASn) precursor and $H_2S$/Ar plasma at temperatures as low as 80°C.

TDMASn precursor was previously combined with $H_2S$ to deposit tin sulfides via thermal ALD.[1] We employed $H_2S$ plasma as the reactant inspired by previous reports demonstrating a significant effect of using plasma on the ALD growth characteristics and material properties.[2] The new PE-ALD process is self-limiting with a growth per cycle of 0.45-0.15 Å/cycle in a temperature range of 80 –180 °C. (**Fig. 1)** In contrast to the thermal ALD process which deposits amorphous $SnS_2$ thin films at 80°C and a mixture of SnS and $SnS_2$ phases at 180°C, crystalline $SnS_2$ thin films are deposited with the PE-ALD process in the temperature range of 80-180°C.**(Fig. 2)** Moreover, scanning electron microscopy analysis shows an evolution in thin-film morphology from grain-like structures with size in the range of 30-50 nm to out-of-plane oriented structures for $SnS_2$ deposited by the PE-ALD process at 80°C and 180°C, respectively. **(Fig. 3)** Optical transmission measurements detected an indirect bandgap in the range of 2.1-2.3eV in all the as-deposited $SnS_2$ thin films. **(Fig. 4)**

$SnS_2$ nanostructures with different morphologies have been previously investigated as anode materials in lithium-ion batteries to counter the problems of poor capacity retention associated with significant volume changes during cycling. Thus, we compared the electrochemical performance of $SnS_2$ thin films with three different morphologies as anode material in Lithium-ion batteries. The $SnS_2$ thin films with out-of-plane orientation structures exhibit better cycling stability with a capacity retention of 77% in contrast to the amorphous films which show 34% capacity retention after 100 cycles. **(Fig. 5)** We assume these out-of-plane orientation sites facilitate the diffusion of $Li^+$ ions thus limiting the pulverization and retaining the capacity.

1. Ham, G.; Shin, S.; Park, J.; Choi, H.; Kim, J.; Lee, Y.-A.; Seo, H.; Jeon, H., *ACS Applied Materials & Interfaces* **2013,***5* (18), 8889-8896.

1. Kuhs, J.; Dobbelaere, T.; Hens, Z.; Detavernier, C., *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2017,***35* (1), 01B111.

2:30pm **AF3-MoA-5 Leveraging Non-Saturated Oxidation Conditions in Plasma-Enhanced Atomic Layer Deposition for Tuning Functional Properties of $CoO_x$ Catalyst Layers**, ***Matthias Kuhl***, *A. Henning, L. Haller, L. Wagner, C. Jiang, V. Streibel, I. Sharp, J. Eichhorn,* Technical University Munich, Germany

Electrocatalysts often suffer from poor stability under operating conditions due to (electro)chemical susceptibilities and/or poor adhesion to the support structure. For the realization of highly active and stable catalytic layers, catalyst-support integration and interface engineering play important roles. Interface engineering is also decisive for the integration of electrocatalysts with semiconductor light absorbers for solar-to-chemical energy conversion. For designing surfaces and interface layers of energy conversion devices, plasma-enhanced atomic layer deposition (PE-ALD) has emerged as a powerful method. These processes are typically developed with the aim of ensuring saturated surface oxidation reactions. However,

exploring less aggressive process parameters opens new opportunities to precisely tailor the functional properties of active catalysts.

Here, we elucidated non-saturated oxidation of cobaltocene precursor by varying the plasma exposure time and plasma power to precisely control structural, mechanical, and optical properties of biphasic $CoO_x$ thin films, thereby tailoring their catalytic activities and chemical stabilities.[1] Short pulses and low plasma power facilitate the formation of porous, unstable $Co(OH)_2$ layers with high electrochemical activity, while long pulses and high power yield stable, inactive $Co_3O_4$ layers. The best combination of stability and activity is observed for intermediate plasma exposure times leading to the formation of biphasic films consisting of a $Co(OH)_2$ surface and $Co_3O_4$ interface layer. The underlying reason for the formation of a porous $Co(OH)_2$ surface layers is the incomplete decomposition of the precursor at either short pulse durations or low plasma power, which also leads the incorporation of carbon impurities. The corresponding change in the chemical composition is reflected in the respective growth chemistry, which is characterized by reduced precursor adsorption and changes in the growth per cycle. The gained mechanistic insights were applied in a two-step growth process to intentionally engineer bilayer films consisting of a stable $Co_3O_4$ interface layer with a catalytic $Co(OH)_2$ surface exhibiting improved electrochemical performance without sacrificing chemical stability. This work highlights that unsaturated oxidation allows access to different material phases with tailored properties for engineering active catalysts and their interfaces.

[1]. Kuhl, M. *et al.* Designing multifunctional $CoO_x$ layers for efficient and stable electrochemical energy conversion, *chemrxiv,* DOI:10.26434/chemrxiv-2022-23ck4 (2022).

2:45pm **AF3-MoA-6 Low-temperature $HfO_2/SiO_2$ Gate Stacked Film Grown by Neutral Beam Enhanced Atomic Layer Deposition***, Daisuke Ohori,* Tohoku University, Japan*; B. Ge,* Tohoku University, China*; Y. Chen,* National Yang Ming Chiao Tung University, Taiwan*; T. Ozaki,* Tohoku University, Japan*; K. Endo,* National Institute of Advanced Industrial Science and Technology, Japan*; Y. Li, J. Tarng,* National Yang Ming Chiao Tung University, Taiwan*; S. Samukawa,* Tohoku University, Japan

Fabrication of the high-quality insulating film with reduction of the thermal budget in a process is required for the metal-oxide-semiconductor (MOS) transistor fabrication with next-generation semiconductor material such as Ge and SiGe. Hafnium dioxide ($HfO_2$) is one of the promising candidate materials due to its high dielectric constant (high-k-value), thermal stability, and a high-quality interface between $HfO_2$ and $SiO_2$ for reduction of the gate leakage current with miniaturization of fabrication scale. To deposit a high-quality gate dielectric film on a high aspect ratio channel, the atomic layer deposition (ALD) method has been adopted with high coverage and thickness control. We have already successfully deposited high-quality $SiO_2$ films using defect-free neutral beam enhanced ALD (NBEALD) at low substrate temperature (30 ºC).In this study, we demonstrated a high-quality amorphous $HfO_2/SiO_2$/Si structure using low-temperature NBEALD.

The NBEALD was carried out in a large chamber for an 8-inch diameter. A precursor and carrier gases were Tetrakis(ethylmethylamino)hafnium (TEMAH) and Ar, respectively. The Si(100) substrate was cleaned with sulfuric acid hydrolysis (4 sulfuric acid:1 hydrogen peroxide) and 1% hydrofluoric acid, and then high-quality $SiO_2$ with a thickness of 1.6 nm could be initially formed after oxygen NB irradiation. After that, samples were grown under the following ALD growth conditions: gas supply (5 sec), purge (5 sec), oxygen NB irradiation (20 sec), oxygen gas purge (5 sec). Oxygen plasma for oxygen neutral beam was discharged at 1300 W, while the bias was not applied, and the stage temperature was at the room temperature, 30 ºC. Different thicknesses of $HfO_2$ films were deposited by using 50, 100, 150, and 200 cycles to evaluate the film characteristics. The surface roughness and crystalline state of deposited $HfO_2$ films were evaluated by atomic force microscopy (AFM) X-ray diffraction (XRD) measurements. The surface roughness increased from 0.3 to 1.1 nm with increasing growth cycle. XRD results were measured by the θ-2θ scan. Any typical diffraction peaks were not observed for all the samples. Therefore, we could successfully form high uniformity amorphous $HfO_2/SiO_2$ thin films even at low temperatures in an in-situ environment. It is suggested that this technique can contribute to the development of the MOS transistor fabrication process with a small heat budget in the future. Finally, we can discuss the electrical characteristics of nano-devices.

3:00pm **AF3-MoA-7 Effect of $O_2$ Plasma Exposure Time During Atomic Layer Deposition of Amorphous Gallium Oxide***, Florian Maudet,* Helmholtz Zentrum Berlin, Germany*; H. Kröncke, S. Banerjee, K. Nair, C. Van Dijck,* Helmholtz-Zentrum Berlin, Germany*; S. Wiesner, J. Albert, V. Deshpande,* Helmholtz Zentrum Berlin, Germany*; C. Dubourdieu,* Helmholtz-Zentrum Berlin, Germany

Crystalline gallium oxide is an attractive ultrawide bandgapsemiconductor, which can be intentionally donor-doped with a large range of accessible electron carrier densities. Amorphous gallium oxide, on the other hand, has been comparatively less studied although it can demonstrate benefit for applications in photovoltaics and electronics. We have investigated the ability to self-doped amorphous gallium oxide thin films grown by atomic layer deposition (ALD) to tune their electrical properties from insulating to semiconducting.

Amorphous gallium oxide (GaOx) thin films were grown at 200 °C by plasma-enhanced ALD on (100) silicon substrates from trimethylgallium $Ga(CH_3)_3$ precursor and $O_2$ plasma. The effect of $O_2$ plasma exposure time during ALD cycles on the optical and electrical properties was investigated with the help of *in situ* and *ex situ* spectroscopic ellipsometry and electrical characterization. The $O_2$ plasma exposure time was varied from 1s up to 30 s. We will first discuss the regrowth of the interfacial $SiO_x$ during the plasma-enhanced ALD. We will then present the effect of the $O_2$ plasma exposure time on the optical index, extinction coefficient, dielectric constant and leakage currents. An increase in the $O_2$ plasma exposure time during each ALD cycle up to 30 s - well beyond the time needed to reach a constant growth per cycle - leads to a drastic decrease in the leakage current density by more than five orders of magnitude (for 30 nm films). Interestingly, a concomitant increase in the dielectric constant is observed, reaching a value of $\varepsilon_r \sim 14.2$, larger than that of the single crystalline β-$Ga_2O_3$. At $O_2$ plasma exposure times below 8 s, the presence of oxygen vacancies is evidenced with an increasing amount as the exposure time decreases. Finally, we will discuss the information gained from the analyses of *in situ* spectroscopic ellipsometry in the very first stages of the growth (first 10 cycles). A method was developed to unambiguously determine the thickness and optical properties of the growing oxide. We will discuss the change in thickness as a function of time for each of the four steps of the ALD cycles. The change in optical properties, determined after each step within one cycle and for all cycles, give information on the evolution of the film until a "bulk-like" gallium oxide film is reached.

Our study highlights the crucial role of $O_2$ plasma exposure time during PEALD of amorphous gallium oxide films in the control and tuning of their electrical properties. The ability to self-doped this material can be used to design e.g. semiconducting a-$GaO_x$ channel field-effect device.

# Author Index

## Bold page numbers indicate presenter