ALD Fundamentals
Room Grand Ballroom A-C - Session AF1-TuM
In-Situ Characterization of ALD Processes

Moderators: Christophe Vallée, LTM/CNRS-UJF, France, Erwin Kessels, Eindhoven University of Technology, the Netherlands

8:00am **AF1-TuM-1 Surface Chemistry during ALD of Nickel Sulfide***, **Xinwei Wang**,* Peking University, China

ALD of metal sulfides has recently aroused great interest, and many new sulfide ALD processes have emerged during the past several years. Surface chemistry plays a key role in ALD, but it remains yet to be investigated for many recently developed sulfide ALD processes. In this representation, I will report our study on the surface chemistry of the ALD of nickel sulfide (NiS) from a Ni amidinate precursor ($Ni(amd)_2$) and H_2S, using the in situ characterization techniques of X-ray photoelectron spectroscopy (XPS), low-energy ion scattering (LEIS), quartz crystal microbalance (QCM), and quadrupole mass spectrometry (QMS). The surface chemistry is found to deviate from the conventional ligand-exchange ALD scheme, and a formation of a nonvolatile acid-base complex from acidic surface sulfhydryl and basic amidine is suggested during the H_2S half-cycle [1]. We further investigate the initial ALD growth of NiS on a SiO_x surface, and the initial growth mechanism is found to be rather different from that in the later steady film growth. In the initial ALD cycles, the XPS results show a drastic cyclic variation of the signals for the Ni−O bonds, with prominently observable Ni−O signals after each $Ni(amd)_2$ dose but almost negligible after the subsequent H_2S dose. These results suggest that the Ni−O bonds are first formed on the surface in the $Ni(amd)_2$ half-cycles and then mostly converted to NiS in the following H_2S half-cycles. To describe this initial ALD growth process, a reaction-agglomeration mechanistic scheme is proposed [2].

References

[1] R. Zhao, Z. Guo, X. Wang, *J. Phys. Chem. C* (2018) 122, 21514.

[2] R. Zhao, X. Wang, *Chem. Mater.* (2019) 31, 445.

8:15am **AF1-TuM-2 In situ and In vacuo Studies on Plasma Enhanced Atomic Layer Deposited Cobalt Films***, **Johanna Reif**, M Knaut, S Killge, N Hampel, M Albert, J Bartha,* Technische Universität Dresden, Germany

Outstanding properties like high thermal and electrical conductivity as well as an unique magnetic behavior make cobalt thin films suitable for demanding applications in modern microelectronic devices. With physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques, it is already possible to deposit such films with high quality. However, cobalt metal film growth by atomic layer deposition (ALD) is required to satisfy conformality and thickness requirements in nanoscale devices.

In this report we will present experiments and results on the deposition of cobalt films with various plasma enhanced ALD (PEALD) processes using different standard cobalt precursors (e.g., cyclopentadienylcobalt dicarbonyl ($CpCo(CO)_2$), cobaltocene ($CoCp_2$) and tricarbonylnitrosylcobalt ($Co(CO)_3NO$)) combined with hydrogen, nitrogen, ammonia and argon based plasma gases. All our experiments were performed in a cross-flow ALD reactor, which is equipped with a capacitively coupled hallow-cathode plasma source, specially designed for the deposition of conductive films. In situ and in real-time highly sensitive quartz crystal microbalances (QCM) measurements allowed a rapid and low-cost process development. The utilized ALD reactor was clustered to an ultra-high vacuum analytic system for direct surface analysis like X-ray photoelectron spectroscopy (XPS) and scanning probe microscopy (SPM). The combination with a non-destructive analytic system enabled a sample transfer without vacuum break and thereby a direct qualification and quantification of the chemical surface composition under quasi in situ conditions. The high sensitivity of these measurements allowed investigations of interface reactions for a single PEALD pulse as well as initial film growth mechanism on different substrate materials. Furthermore we studied the impact of various cobalt precursors combined with different plasma gas compositions on the resulting film properties. The influence of process parameters (e.g., pulse times, plasma power, pressure and substrate temperature) on the film composition and film properties was also investigated. Cobalt films grown using the precursor $CpCo(CO)_2$ and H_2/N_2 plasma as coreactant showed a stable film composition of 75 at.% cobalt, 4 at.% carbon and 21 at.% nitrogen. Using scanning electron microscopy and four point probe measurements a moderate electrical resistivity of about 80 µΩcm is calculated for a 14 nm thick film.

Beyond those results in our publication we will discuss the suitability of the precursors for the deposition of high-quality cobalt films as well as the occurrence of sputtering and temperature effects due to high plasma powers.

8:30am **AF1-TuM-3 Investigation of PEALD Grown HfO_2 Thin Films via Near Ambient Pressure XPS: Precursor Tuning, Process Design and a New In-situ Examination Approach for Studying Film Surfaces Exposed to Reactive Gases***, **David Zanders**,* Ruhr University Bochum, Germany*; E Ciftyurek,* Heinrich Heine University Düsseldorf, Germany*; C Bock, A Devi,* Ruhr University Bochum, Germany*; K Schierbaum,* Heinrich Heine University Düsseldorf, Germany

Hafnium (IV) oxide (HfO_2) is a high-k dielectric whose thin films have become a fundamental part of electronics since their commercial usage in CMOSFETs in 2008.[1] Furthermore, interest in orthorhombic HfO_2 is arising owing to the discovery of its ferroelectric nature in 2011,[2] which may lead to electronics beyond present limits.[3] Atomic layer deposition (ALD) and plasma enhanced (PE)ALD are favorable for such applications due to the low processing temperatures, precise control of thickness as well as dense and conformal coverage over complex device geometries. Furthermore, it must be ensured that films exhibit the desired stoichiometries with only low surface defect densities as the presence of surface defects, allows interactions with reactive gases and moisture that can initiate surface degradation of the dielectric, having a negative effect on its electrical properties.[4]

We report on the development of a promising PEALD process employing a precursor originating from the novel mono-guanidinato tris-alkylamido class. Four variants were subjected to thermal and chemical analysis proving their tunable volatility and thermal stability (Fig. 1). Typical ALD growth characteristics in terms of saturation, ALD window and linearity were confirmed and the growth behaviour upon variation of plasma pulse lengths was studied (Fig. 2). The obtained HfO_2 layers exhibited high quality evidenced by XRR, AFM, RBS/NRA and XPS investigations. Selected films were exposed to reactive gases such as H_2, O_2 and H_2O vapor at different temperatures and *in-situ* characterized by near ambient pressure (NAP)-XPS. Surface compositional changes and responses were monitored in a new methodical approach that has not been reported so far for thin films to the best of our knowledge. Finally, metal-insulator-semiconductor (MIS) capacitors were fabricated using HfO_2 as dielectric layer to assess its performance in device structures. This is a first report on a highly promising PEALD process for HfO_2 in a broad temperature range (60 – 240) °C developed from a new Hf precursor exhibiting optimal properties for ALD. Employing NAP-XPS is shown to be a promising development as investigations of surfaces during exposure to defined reactive gas atmospheres leads to new in-sights into stability or triggered changes of composition and states indicating either presence, absence or formation of surface defects which strongly influence the functional properties of the layers.

[1] Ahvenniemi, E.;*et al.*; *JVST A:***2017**, *35*, 10801.

[2] Park, M. H.; et al.;*MRC***2018**, *8*, 795–808.

[3] Hoffmann, M.; et al.;*Nature***2019**, *565*, 464–467.

[4] Wen, L.; Doctoral dissertation. Hdl.handle.net/1969.1/3225.

8:45am **AF1-TuM-4 Surface Science Studies of GaN Substrates Subjected to Plasma-Assisted Atomic Layer Processes***, **Samantha G. Rosenberg**,* ASEE*; D Pennachio,* University of California, Santa Barbara*; E Young, Y Chang, H Inbar,* University of California Santa Barbara*; J Woodward,* U.S. Naval Research Laboratory*; Z Robinson,* SUNY College at Brockport*; J Grzeskowiak,* University at Albany-SUNY*; C Ventrice, Jr.,* SUNY Polytechnic Institute*; C Palmstrøm,* University of California Santa Barbara*; C Eddy, Jr.,* U.S. Naval Research Laboratory

III-N semiconductors are well suited for applications in several important technological areas, including high current, normally-off power switches.[1,2] Such devices require heterostructures not readily achievable by conventional growth methods. Therefore, we have developed a technique adapted from ALD, called plasma-assisted atomic layer epitaxy (ALEp).[2] Using surface science techniques, we strive to develop not only a fundamental understanding of the ALEp growth process but also complimentary atomic level processes (ALPs) that will result in the best preparation method for a pristine GaN starting surface for ALEp.

Here we employ *in-situ* and *in-vacuo* surface studies of GaN substrate preparation to advance fundamental understanding of the ALEp process.

Having optimized our GaN surface preparation process (gallium flash off ALP),[3] we conduct *in-vacuo* X-ray photoelectron spectroscopy (XPS), reflection high-energy electron diffraction (RHEED), and scanning tunneling microscopy (STM) studies conducted at the Palmstrøm Lab at UCSB to further refine both our process and our understanding. Preliminary XPS results show that a GFO ALP conducted at 250°C for 12 cycles reduces the oxygen content by 5% but shows no reduction in the carbon content, while a GFO ALP conducted at 400°C for 30 cycles reduces the carbon content by 60% but shows no reduction in the oxygen content. In addition, we conducted comparable temperature program desorption (TPD) and low energy electron diffraction (LEED) experiments at SUNY Polytechnic Institute to correlate structural and chemical changes that occur on the GaN surface during our GFO ALP. TPD shows that NH_3 is released from GaN surfaces not subjected to GFO ALP as it is heated past 150°C, while GFO ALP GaN surfaces show no NH_3 release upon subsequent TPD experiments. Both GaN surfaces show an unreconstructed 1x1diffraction pattern in LEED.

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

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

3. S. Rosenberg, et. al., J. Vac. Sci. Technol. A 37, 020908 (2019)

9:00am **AF1-TuM-5 Infrared and Optical Emission Spectroscopy on Atmospheric-Pressure Plasma-Enhanced Spatial ALD of Al_2O_3,** ***Maria Antonietta Mione****, R Engeln, E Kessels,* Eindhoven University of Technology, Netherlands*; F Roozeboom,* Eindhoven University of Technology and TNO, Netherlands

In the past decade, atmospheric pressure spatial atomic layer deposition (AP-SALD) has gained momentum as a fast deposition technology for functional thin layers. The unparalleled merits of conventional ALD, such as superior control of layer thickness, conformality and homogeneity, joined with the high throughput offered by the spatially separated half-reactions and the cost-effectiveness of vacuum technology free systems, make AP-SALD well-suited for industrial large-area applications. Additionally, the use of atmospheric pressure plasmas as co-reactants enables to rapidly deposit high-quality, dense films at relatively low temperatures. [1]

Despite its industrial relevance, the chemistry at the base of the atmospheric pressure plasma-enhanced spatial ALD processes largely remains unaddressed. Effective ALD metrology techniques are of great importance to gain detailed insight into the nature of the process as well as to improve its perfomance thus opening the way to its wide industrial implementation. However, due to the dynamic nature of the spatial concept, monitoring AP-SALD processes can be rather challenging, especially in the case of close-proximity systems where the substrate is at ~100 micrometer distances from the gas injection head.

In this work, we employed optical emission spectroscopy (OES) and infrared spectroscopy on effluent plasma gasses as diagnostic tools to study the underlying chemistry of the AP-SALD process of Al_2O_3 films prepared using $Al(CH_3)_3$ and Ar-O_2 plasma. We identified the main reaction products and studied their trend as a function of the exposure time to the precursor to verify the ALD layer-by-layer growth characteristic. Findings show that the spatial separation of the ALD half-reactions and the use of an atmospheric pressure plasma as the reactant give rise to a complex underlying chemistry. Infrared absorbance spectra show CO, CO_2, H_2O and CH_4 as the main ALD reaction byproducts originating from 1) combustion-like reactions of the methylated surface with oxygen plasma radicals and ozone, and 2) a concurrent latent thermal component due to surrounding substrate. In addition, CH_2O and CH_3OH are identified as ALD reaction byproducts either formed at the surface or in the plasma by electron-induced dissociation. Furthermore, the investigated trends in CO_2, CO and CH_4 formed as a function of the exposure time confirmed self-limiting ALD behavior. Finally, OES results corroborated that, as soon as the plasma-enhanced SALD process takes place, emission from OH and CH arises while excited oxygen species are consumed.

[1] Mione *et al.*, ECS J. Solid State Sci. Technol. **6**, N243 (2017), and references therein.

9:15am **AF1-TuM-6 Fingerprinting of ALD Reaction Products with Time-Resolved In situ Mass Spectrometry*, Andreas Werbrouck*,** *F Mattelaer, J Dendooven, C Detavernier,* Ghent University, Belgium

The importance of in-situ process monitoring during atomic layer deposition has been highlighted extensively by, among others, the review of Knapas and Ritala [1]. However, the examination of ALD processes via quadrupole mass spectrometry (QMS) is especially hard (compared to other fields where it is employed) since there is only a limited amount of reaction products, which are present in the chamber for only a fleeting moment. This shows the need for time-resolved measurements. However, most commonly available equipment is limited to a real-time resolution of only a few ion/radical masses. In QMS measurements, incoming molecules are cracked and ionized into a composite 'fingerprint' spectrum of several mass-to-charge (m/z) ratios. Thus, it is very likely that information is lost if only a few individual masses are tracked, in particular because the decision on which mass-over-charge ratios have to be measured usually depends on preliminary assumptions, knowledge of the precursor ligands and gut feeling. This limits the practical use of QMS to the detection of simple reaction products and may introduce a bias towards certain reaction chemistries. A novel data acquisition method is described which allows for time-resolved measurements of full m/z-spectra. This allows for 'fingerprinting' molecules present at a certain time instead of using a priori assumptions to decide which m/z ratios have to be monitored.

ALD processes have the exploitable advantage that they are of cyclic nature. Hence after the first cycles where initial growth effects could be of importance, the chemistry of each cycle should be identical and can be repeated as often as necessary to obtain data with good signal-to-noise ratio. In this work, we combine data from several ALD cycles to construct a time-resolved m/z spectrum of one cycle, over the full relevant range of the process, measured with a standard quadrupole mass spectrometer (Hiden HPR-30). As such, complete time-resolved mass spectrum analyses of ALD reaction chemistries is enabled.

A proof of concept is delivered with the standard TMA-H_2O chemistry, before we move on to the reaction mechanism of a more complex process. Lithium hexamethyl disilyl azide (LiHMDS) and trimethyl phosphate (TMP) can be combined to grow a crystalline lithium phosphate. As is shown in the accompanying figure, time-resolved measurements offer a unique and unbiased insight in the growth mechanism of this process.

[1] Kjell Knapas & Mikko Ritala (2013) In Situ Studies on Reaction Mechanisms in Atomic Layer Deposition,

Critical Reviews in Solid State and Materials Sciences, 38:3, 167-202, DOI: 10.1080/10408436.2012.693460

9:30am **AF1-TuM-7 Studying Pt and Pd Nanoparticle ALD through X-ray based In situ Characterization*, Jolien Dendooven*,** *J Feng,* Ghent University, Belgium*; E Solano,* ALBA Synchrotron Light Source, Spain*; R Ramachandran, M Minjauw, M Van Daele,* Ghent University, Belgium*; D Hermida-Merino,* ESRF European Synchrotron, France*; A Coati,* Synchrotron SOLEIL, France*; C Detavernier,* Ghent University, Belgium **INVITED**

The performance of supported nanoparticles (NPs) in heterogeneous catalysis is closely related to their size, shape and interparticle distance. Tailoring the structural properties of noble metal NPs is attractive to elucidate performance-structure relationships and tune the catalytic activity, selectivity and stability. In this regard, there is an increasing interest in ALD to conformally deposit noble metal NPs with atomic-scale control over the metal loading (atoms per cm^2) and NP size. Here, we aim to demonstrate that in situ X-ray fluorescence (XRF) and grazing incidence small angle X-ray scattering (GISAXS) can offer unique insights in the ALD growth and thermal stability of metal NPs, offering approaches towards superior size and coverage control, and improved stability.

In a first study, the Me_3(MeCp)Pt precursor is combined with either O_2 gas or N_2 plasma to grow Pt NPs on planar SiO_2 surfaces, and in situ XRF and GISAXS measurements provide the evolution of Pt loading, NP dimensions and spacing. It is found that O_2 induces atom and cluster surface diffusion and promotes the ripening of the Pt NPs, while diffusion phenomena seem to be suppressed during N_2 plasma-based ALD. This insight inspired a tuning strategy that combines both processes and offers independent control over NP size and coverage [Nat. Comm. 8, 1074 (2017)]. Next, in situ GISAXS is used to investigate the coarsening behavior of the Pt NPs [Nanoscale 9, 13159 (2017)] and probe the influence of stabilizing Al_2O_3 overcoats. The overcoat thickness required to stabilize the NPs is investigated for different Pt NP coverages and sizes, revealing that one single ALD cycle is sufficient to stabilize widely spaced NPs, while it is challenging to avoid NP coarsening for closely packed Pt NPs.

A second case study concerns plasma-enhanced ALD of Pd NPs on planar Al_2O_3 surfaces with the $Pd(hfac)_2$ precursor at 150°C, comparing a purely reducing chemistry (H_2 plasma as reactant) with three-step processes that include an oxidizing agent (sequential dosing of H_2 plasma and O_2 plasma or vice versa). The choice of reactant and reactant sequence has a clear impact on the initial nucleation density. The highest areal density is obtained for the three-step process that uses H_2 plasma followed by O_2 plasma, explained by the cleaning role of O radicals towards poisoning hfac ligands on the Al_2O_3 surface. Finally, the use of TMA to clear the surface from site-blocking species [APL 95, 143106 (2009)] is systematically investigated on planar SiO_2 using in situ GISAXS, providing a way to control the Pd NP coverage.

Author Index

Bold page numbers indicate presenter