ALD Fundamentals
Room Van Eyck - Session AF1-TuA

Characterization I

Moderators: Jan-Willem Clerix, Imec , Aile Tamm, University of Tartu

1:30pm **AF1-TuA-1 Reaction Mechanisms of ALD of Transition Metal Oxides from Metal Amido Complexes and Water*, Giulio D'Acunto,*** *R. Timm, J. Schnadt,* Lund University, Sweden

Atomic layer deposition (ALD) is an outstanding deposition technique to deposit highly uniform thin films with atomic precision. In particular, ALD of transition metal oxide layers from metal amido complexes and water finds its way in several technological fields, including green energy devices and the semiconductor industry. These ALD reactions are believed to follow a reaction scheme based on the ligand exchange mechanism. The first half cycle of ALD of HfO_2, via tetrakis-dimethylamido hafnium and water, is expressed, according to the ligand exchange scheme, by the following equation: HfL_4 + nS-(OH) -> S-O_n-HfL_{4-n} + nLH, where S stands for surface and L for the amido ligand of the metal precursor.

Here, the surface S is supposed to play a largely passive role, and it is that it is hydroxylated. L remains chemically unchanged during the reaction. To address whether the model is correct or not, we employed time-resolved *in situ* and *operando* ambient pressure X-ray photoelectron spectroscopy (APXPS) during the ALD of HfO_2 on InAs covered by a thermal or native oxide, TiO_2, and SiO_2.

We find that the classic ligand exchange reaction mechanism does not describe the reaction path in any of the investigated sample systems. In particular, we find that ALD of HfO_2 on SiO_2 follows a bimolecular reaction mechanism based on the insertion of a β-hydride of one of the ligands in an amido complex dimer into the bond between another ligand and of the Hf ions in the dimer. As a result of its bimolecular nature, this reaction can take place only at sufficiently high coverage of physisorbed complexes on the SIO_2 surface. On TiO_2 we find that the early stage of the reaction is based on dissociative adsorption, followed by mono- or bi-molecular reaction paths, leading to the formation of new sets of surface species never identified in ALD reactions.

Moreover, for an easily reducible surface we find evidence of HfO_x formation already during the first ALD half-cycle due to the transfer of O atoms from the surface to the metal complex. Clearly, this contradicts the passive role of the surface in standard ALD models. Interesting, in the case of InAs covered by a thermal or native oxide, this phenomenon, which lies behind the so-called self-cleaning effect, guarantees a sharp interface between the III-V material and HfO_2, a prerequisite for next-generation MOSFETs.

Our results open new doors for improving devices based on ALD. Time-resolved *in situ* and *operando* APXPS allows us to follow the kinetics and mechanisms involved in ALD, in real time at second time resolution with significant benefit for the further improvement of our general understanding of ALD reactions.

1:45pm **AF1-TuA-2 An *in-Vacuo* X-Ray Photoelectron Spectroscopy Study of the Reaction of Trimethylaluminum With Water, Oxygen and Argon Plasma for Low Temperature Atomic Layer Deposition***, L. Cao,* ***Jin Li,*** *M. Minjauw, J. Dendooven, C. Detavernier,* Department of Solid State Sciences, Ghent University, Belgium

Low temperature atomic layer deposition (ALD) has been drawing great research interest because of its capability to coat on heat-sensitive substrates, such as flexible devices, polymers and biological materials. As a process with widespread applications, the surface chemistry of Al_2O_3 ALD at low temperature is still under extensive investigation.[1,2] In this work, the growth of Al_2O_3 using trimethylaluminum (TMA)/water and TMA/O_2 plasma have been investigated with *in vacuo* X-ray photoelectron spectroscopy (XPS) in the temperature range from 60 to 300 °C. Samples are transferred back and forth between the ALD chamber and the XPS analytical chamber without vacuum break to analyze the surface chemical state after each reactant exposure, providing insight into the evolution of surface species.

Our results confirm that the low temperature TMA/water process undergoes an incomplete surface reaction during the water exposure (Figure S1), resulting in a low growth per cycle of 0.66 Å/cycle at 60 °C. Persistent -CH_3 groups are present on the growth surface after the water exposure and its concentration increases with reducing temperature, in accordance with previous reports.[1,2] In spite of the continuous presence of surface -CH_3 groups during the whole process, the C impurity concentration in the film is found to be surprisingly low. XPS depth profiling showed that C only exists at the very surface region, and is not incorporated into the film (Figure S2). According to *in situ*spectroscopic ellipsometry data, the growth at low temperature still displays a linear growth behavior (Figure S3). Our results indicate that, although the reaction during one water half cycle is incomplete at lower temperature, the next few water half cycles tend to finish the job and no carbon is built into the film. In contrast, oxygen plasma can combust all carbon ligands regardless of the surface temperature (Figure S1), boosting the growth rate to 2 Å/cycle at 60°C. To further explore the power of plasma for low temperature ALD, a three-step TMA/Ar plasma/H_2O process is also investigated. The Ar plasma is found to change the Al–CH_3 surface groups into an intermediate product that can react more easily with H_2O to allow a more complete reaction, increasing the growth rate from 0.66 Å/cycle to 1.1 Å/cycle at 60°C while avoiding potentially damaging effects on sensitive substrates caused by the chemically active O_2 plasma.

[1] V. Vandalon and W.M.M. Kessels, Appl. Phys. Lett. **108**, 1 (2016).

[2] Z. Jin, S. Lee, S. Shin, D.S. Shin, H. Choi, and Y.S. Min, J. Phys. Chem. C **125**, 21434 (2021).

2:00pm **AF1-TuA-3 *In Vacuo* Cluster Tool for Studying Reaction Mechanisms in ALD and ALE Processes*, Heta-Elisa Nieminen,*** *M. Chundak, M. Putkonen, M. Ritala,* University of Helsinki, Finland

Film growth during an ALD process is solely dependent on the chemical reactions on the substrate surface. Well-behaving surface chemistry enables the key qualities which make ALD a superior thin film deposition method. In addition, surface reactions define the outcome of each process and can set critical challenges on the process development and integration. For these reasons, studying the chemical reactions in the film growth is of utmost importance to fully understand the growth process and exploit the advantages ALD has to offer. Exactly the same applies to atomic layer etching (ALE) processes.

A new cluster tool in HelsinkiALD laboratory allows reaction mechanism studies on a wide variety of process chemistries without exposing the sample to ambient atmosphere. In this tool a commercial flow-type ALD reactor is connected directly to a set of ultra-high vacuum analysis techniques so that after interrupting the process at a selected point the substrate can be transferred *in vacuo* straight from the ALD reactor to surface analysis. The chemical composition of the surface including reaction intermediates can be precisely investigated after each precursor pulse individually. The resulting information will be beneficial for resolving the overall ALD and ALE mechanisms.

The cluster tool contains currently x-ray photoelectron spectroscopy (XPS), hard x-ray photoelectron spectroscopy (HAXPES), ion scattering spectroscopy (ISS), Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), low-energy electron diffraction (LEED), ultraviolet photoelectron spectroscopy (UPS), and temperature programmed desorption (TPD). The film growth can also be monitored *in situ* by a quartz crystal microbalance (QCM) and ellipsometer which are connected directly to the ALD chamber. As the system contains a flow-type ALD reactor, the mechanisms can be solved without compromising true ALD conditions. The system has been tested and the operation procedures optimized with TMA and H_2O for depositing Al_2O_3 at temperatures of 150 – 300 ˚C. The state of the surface was investigated by TPD and XPS after each precursor pulse. After the initial testing with this well-known process, new ALD and ALE chemistries will be studied in detail.

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2:15pm **AF1-TuA-4 Watching the ALD of Pt Films in Real-Time*, Esko Kokkonen,*** Max IV Laboratory, Sweden*; M. Kaipio, H. Nieminen,* University of Helsinki, Finland*; F. Rehman,* Lund University, Sweden*; V. Miikkulainen,* Aalto University, Finland*; M. Putkonen, M. Ritala, S. Huotari,* University of Helsinki, Finland*; J. Schnadt,* Lund University, Sweden*; S. Urpelainen,* University of Oulu, Finland

We have used in situ and operando techniques to study the growth of Pt films on different substrates in real-time. In this study, we have focused on investigating the growth of metallic Pt on Si, Ir, and Ir oxide substrates. The precursors for this reaction were chosen as trimethyl(methylcyclopentadienyl)platinum(IV), or $MeCpPtMe_3$ and O_2 gas.

The experiments were done using the so-called ALD cell, which is an synchrotron-based ambient pressure X-ray photoelectron spectroscopy (APXPS) sample environment specifically dedicated for studies of ALD processes. The system is located on the SPECIES beamline [1] at the MAX IV Laboratory in Lund, Sweden. With a wide energy range of 30-1500 eV, the beamline offers wide measurement capabilities for both core-level XPS as well as valence band (ultraviolet photoelectron spectroscopy) UPS using surface sensitive photon energies. This setup has been recently used in several studies to gain deeper insight into different ALD processes [2, 3].

We have followed various core-levels on the surface using XPS as it was exposed to the first half-cycle with the $MeCpPtMe_3$ precursor. Interesting effects are seen on the three different substrates. Firstly, the Pt 4f core-level shows a clear intensity increase, naturally following from the addition of Pt containing precursor onto the surface. However, an interesting finding is that for all substrates, the Pt 4f binding energy shifts during the deposition. Moreover, the shifting of the Pt 4f peaks occur at a different timescale than the saturation of the surface based on the XPS intensity. A tentative explanation could be that the Pt precursor initially attaches to the surface with a higher oxidation state, perhaps still partially attached to some of the methyl groups, which rather quickly dissociate (or combust) and are released into the gas phase. This mechanism then could be on-going while the surface is only partly covered by the Pt since saturation is not yet reached.

[1] E. Kokkonen, et al. "Upgrade of the SPECIES beamline at the MAX IV Laboratory." *Journal of Synchrotron Radiation*28, 2, 588-601 **(2021)**, DOI: 10.1107/S1600577521000564
[2] G. D'Acunto, et al. "Oxygen relocation during HfO_2 ALD on InAs." *Faraday Discussions* Accepted Manuscript (2022). DOI: 10.1039/D1FD00116G
[3] E. Kokkonen, et al. "Ambient pressure x-ray photoelectron spectroscopy setup for synchrotron-based in situ and operando atomic layer deposition research." *Review of Scientific Instruments* 93.1, 013905 (2022). DOI: 10.1063/5.0076993

2:30pm **AF1-TuA-5 In Situ X-Ray Studies of Lamellar Dichalcogenides Prepared by Molecular Layer Deposition and Thermal Annealing*, Petros Abi Younes,*** CEA/LETI-University Grenoble Alpes, France*; E. Skopin,* LTM - MINATEC - CEA/LETI, France*; M. Zhukush, C. Camp,* Univ. Lyon, CNRS-UCB Lyon 1, France*; N. Aubert , G. Ciatto,* Synchrotron SOLEIL Beamline SIRIUS, France*; N. Schneider,* UMR-IPVF, CNRS, France*; M. Richard,* ESRF, France*; N. Gauthier,* CEA/LETI-University Grenoble Alpes, France*; E. Quadrelli,* Univ. Lyon, CNRS, France*; D. Rouchon,* CEA/LETI-University Grenoble Alpes, France*; H. Renevier,* Laboratoire des Matériaux et du Génie Physique, France

Metal Dichalcogenides **(MDs)** have recently emerged as a class of exceptional materials with many potential applications and are receiving great attention. Among them, lamellar Titanium disulfide (**TiS_2**) is the lightest and cheapest member of the Transition MDs(**TMDs)** family,[1]with a 1T-TiS_2 crystallographic structure. Its electrical properties allow it to use in many fields of applications (optics, thermoelectric, and batteries).[2–5]

However, the lack of scalable fabrication methods of continuous ultra-thin films on developed surfaces, at moderate temperature, stems a sizeable bottleneck for the full deployment of these materials. Besides the conventional Atomic Layer Deposition (ALD) process, which suffers from limitations, an innovative **2-step process** comprising Molecular Layer Deposition (**MLD**) and **thermal annealing** has been developed to achieve an atomically-thin synthesis of 2D TMDs MoS_2 and WS_2.[6,7] Interestingly, the process does not use the highly toxic H_2S molecule. By using this approach we have succeeded to synthesize continuous and textured TiS_2 thin films on thermal SiO_2[8]. An intermediate amorphous polymer (Ti-thiolate) is deposited by MLD at low temperature (T_{sub} = 50°C) upon a reaction between the metal precursor (TDMAT = $Ti(NMe_2)_4$) and organic sulfide molecule (1,2-ethanedithiol). Then, the amorphous thin film undergoes a thermal annealing under hydrogenated argon flow.

Both the MLD and thermal annealing were monitored by *in situ* synchrotron radiation techniques, including x-ray fluorescence (XRF), x-ray reflectivity (XRR), and x-ray absorption fine structure (XAFS), at SIRIUS beamline (SOLEIL, St Aubin), and *in situ* ellipsometry. The main results will be presented. Importantly, both the sulfur K and Ti K fluorescence line intensities could be recorded simultaneously, allowing us to monitor simultaneously the S and Ti contents throughout the whole process and from the very early stage of the Ti-thiolate deposition. The repetitive self-limiting growth behavior during the MLD step could be demonstrated. Upon thermal annealing, the Ti-thiolate thin film transforms into lamellar TiS_2 monolayers parallel to the substrate surfaces observed by Raman spectroscopy, transmission electron microscopy (TEM) and x-ray linear dichroism at the Ti K-edge. Angle-Resolved X-ray Photoelectron Spectroscopy (ARXPS) and lab-scale Hard XPS (HAXPES) show stoichiometric TiS_2 in the presence of carbon.

References

[1]*Nano Today***2014**,*9*,604; [2]*Nano Lett.***2018**,*18*,4506; [3]*Phys. Rev. B***2019**,*99*,165122; [4]*Photonics Res.***2018***6*,C44; [5]*Phys.Chem.Chem.Phys.* **2012**,*14*,15641; [6]*Nanoscale***2017**,*9*,538; [7]*JVST A.***2017**,*35*,061502. **[8]Chem Mater 2022 (submitted)**

2:45pm **AF1-TuA-6 *In Situ* Spectroscopic Ellipsometry of 3D Patterned Nanostructures for Real Time Profile Evolution During ALD*, S. Novia Berriel,*** University of Central Florida*; N. Keller,* Onto Innovation*; P. Banerjee,* University of Central Florida

In situ techniques are used to gain understanding of ALD processes in real time. In nearly all cases, planar substrates are used to monitor surface reactions and film growth. However, since ALD is used for conformal deposition in high-aspect ratio structures, the use of in situ techniques on planar substrates present a challenge in interpreting deposition characteristics on non-planar substrates and optimizing processes which can lead to conformal growth of ALD films inside high-aspect ratio structures.

In this talk, we will describe an optical-based metrology technique to monitor real time growth of ALD ZnO on patterned SiO_2 nano trenches. The primary advantage of this technique is that our hardware remains a spectroscopic ellipsometer (SE), whereas back-end data analysis and modeling is conducted using a rigorous coupled-wave analysis (RCWA) technique.

Patterned SiO_2 trenches with a width of 80 nm and a depth of 325 nm were used as substrates. Real-time polarization data (Ψ and Δ) were obtained across two runs – one, in which the trenches were parallel; and two, in which the trenches were perpendicular to the beam path. The profile evolution of ALD ZnO was monitored for 300 cycles, corresponding to a thickness of 55 nm on planar substrates. RCWA of the polarization data was used to generate 3D cross-section profiles of the SiO_2 trenches filling with ZnO from the beginning to the end of deposition.

The film thicknesses at various points along the trench and the resulting conformality were confirmed using cross-section SEM analyses. We find that RCWA is successfully able to predict thickness to within 7.8% and conformality to within 8.1% of true experimental data. Furthermore, the RCWA predicts the merging of growth fronts at the bottom of the trench in accordance with geometrical modeling and experimental observations. These promising results highlight the potential for real-time monitoring of in-trench conformality via a combination of SE and RWCA techniques

3:00pm **AF1-TuA-7 Pyroelectric Calorimetry: Measuring the Time-Resolved Heat of ALD Half Reactions*, Ashley R. Bielinski,*** *A. Martinson,* Argonne National Laboratory **INVITED**

In Situ characterization methods provide insight into ALD reactions as they occur.We've implemented pyroelectric calorimetry as an *in situ* technique to measure the heat evolved in ALD half reactions with unrivaled thermal and temporal resolution.On high surface area substrates like nanoparticles or metal organic frameworks, ALD has been observed to cause temperature increases greater than 10°C.The small temperature changes (<0.1 °C) predicted for planar substrates are more challenging to accurately measure.We designed custom pyroelectric calorimeters for implementation in an ALD tool with thermal and temporal resolution down to 0.1 $\mu J/cm^2$ and 50 ns.To put this in perspective, this corresponds to a temperature increase of about 10^{-5}°C, which is less than 0.1% of the heat evolved in the reaction between trimethylaluminum (TMA) and water.The calorimeter response time is more than 10^4 times faster than our measurement of the reaction time of TMA on a hydroxylated alumina surface.

Analysis of time resolved heat generation in ALD reactions provides information on thermodynamics and kinetics as well as how real reactions deviate from simplified textbook examples.Experimental reaction heats can be compared with theoretical and computational predictions of the interaction between specific precursors and surface sites, showing which of the hypothetical pathways best represent reality.Additionally, pyroelectric calorimetry is orders of magnitude faster than many complementary *in situ* analysis techniques, providing more granular insight and subdivision of individual half reactions.

We've combined pyroelectric heat generation analysis with *in situ* spectroscopic ellipsometry in a saturation study of the prototypical reaction between TMA and water.This represents the most accurate measurement to-date of ALD reaction heats.Comparison between these parallel *in situ* measurements provides insight into the reaction energy as the surface saturates within a single half reaction and the time-resolved data highlights the limitations of slow water reaction kinetics.In addition to fundamental studies of ALD surface reactions, careful analysis of heat transfer due to precursor flow can provide information on precursor delivery and flow dynamics within the ALD reactor.

The development of pyroelectric calorimetry for ALD provides many opportunities for future investigations.Of particular interest are applications requiring sub monolayer detection such as precursor reactions with specific surfaces sites in area or defect selective ALD as well as time-resolved kinetics studies.

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