ALD Fundamentals
Room Hall 3A - Session AF2-WeA

Growth and Characterization: *In-situ* and *in-vacuo* Analysis, Surface Science of ALD II

Moderators: **Markku Leskelä**, University of Helsinki, Finland, **Mikko Ritala**, University of Helsinki

4:00pm AF2-WeA-11 In vacuo XPS Growth Studies During ALD of ErNiO₃, *Matthias Minjauw,* Ghent University, Belgium*; A. Illiberi, M. Givens,* ASM, Belgium*; A. Leonhardt, I. Issah, L. Bottiglieri,* ASM, Finland*; J. Dendooven, C. Detavernier,* Ghent University, Belgium

Rare-earth nickelates ($RNiO_3$, with R = rare earth element) have a broad range of unique and tunable physical properties, making them relevant for future applications in electronics, electrocatalysis, solid oxide fuel cells, electrochromic windows and microelectromechanical systems. As a result, several $RNiO_3$ ALD processes (R = La, Nd) have been reported, and the general approach is to combine two binary ALD processes for R_xO_y and NiO in supercycles.[1-3] As two distinct ALD processes are combined into one ALD process, several non-idealities may occur, such as a larger impurity content than for the binary processes, nucleation effects leading to irreproducibility issues, and unexpected high/low growth leading to deviating compositions.[4]

In this work, we combined the ALD $NiCp_2/O_3$ and $Er(MeCp)_3/O_3$ processes at 300°C using the supercycle approach, leading to $Er_xNi_yO_z$ films with low impurity content. Figure 1a shows the growth per cycle (GPC) of the ALD process as a function of the NiO cycle ratio. Ideally, a linear curve should be obtained between the GPC values for the binary processes, but this is clearly not the case. In Figure 1b, it is seen that the Ni atomic concentration as found by *in vacuo* XPS is also much lower than expected based on the rule of mixtures.[4]

To investigate the origin of these non-idealities, *in vacuo* ALD-XPS nucleation studies were conducted, and a selection of XPS data is shown in Figure 2. Although an Er signal is visible from the first $Er(MeCp)_3$-pulse on an ALD NiO substrate, it takes ~ 4 cycles of the NiO process to get a clear Ni signal on an ALD Er_2O_3 surface. In Figure 3, a plot is shown of the Ni and Er atomic percentage as a function of ALD cycles, obtained by quantifying the XPS data. The fact that there is a nucleation delay for NiO growth on Er_2O_3, but not for Er_2O_3 on NiO, explains the non-idealities described above. The present XPS data hint that incomplete surface reactions of the $NiCp_2/O_3$ process on the carbon-rich ALD Er_2O_3-surface are at the basis of this nucleation delay, with more research currently ongoing to elucidate this.

References:

[1] H. Seim et al. *J. Mater. Chem.* **7**, 449–454 (1997).

[2] H. H. Sønsteby *et al. Nat. Commun.* **11**, 2872 (2020).

[3] Y. Sun et al. *ACS Appl. Electron. Mater.* **3**, 1719–1731 (2021).

[4] A. J. M. Mackus et al. *Chem. Mater.* **31**, 1142–1183 (2019).

4:15pm AF2-WeA-12 Surface Chemistry of Aluminum Nitride ALD, *Pamburayi Mpofu, H. Hafdi, H. Pedersen,* Linkoping University, Sweden

The properties of aluminum nitride (AlN), including a wide bandgap (6.2 eV), high dielectric constant ($k \sim 9$), high electrical resistivity ($\rho \sim 10^{11}$–10^{13} Ω cm), and high thermal conductivity (2.85 W/K cm)[1] make it one of the commonly used materials in microelectronics and optoelectronics. AlN is also used in microelectromechanical systems (MEMS devices) due to its piezoelectric properties. It also presents good miscibility with other nitrides and can be used in ternary materials when combined with Ga, In, Ti and Hf, which increases the range of its potential applications.

Although ALD of AlN from $AlMe_3$ (TMA) has been widely reported to date, the surface chemistry of AlN ALD from other precursors, particularly $Al(NMe_2)_3$ (TDMAA) have not yet been reported. We compared AlN ALD with TMA and TDMAA as Al precursors and NH_3 with and without plasma activation as the N precursor in the temperature range from 100 to 400 °C. Using mass spectrometry, we find that the surface chemistry of the TMA-process involves reductive elimination and ligand exchange from the gaseous CH_4 detected both during the TMA- and NH_3 pulses. The TDMAA-process also involves transamination mechanisms from the $N(Me)_2$ and $HN(Me)_2$, and CH_4 detected during the NH_3 pulses.

By comparing our experimental results to modeling results[2] drawn from density functional theory methods, we can deduce a detailed, atomistic surface chemical mechanism of TMA on an NH_2-terminated AlN surface. No literature is available for theoretical studies of AlN ALD from TDMAA, making our surface chemical mechanism for the TDMAA-process less detailed.

Refs.:

1. Kot, M. *et al.* Comparison of plasma-enhanced atomic layer deposition AlN films prepared with different plasma sources. *J. Vac. Sci. Technol. A* **37**, 020913 (2019).

2. Rönnby, K. *et al*. Surface chemical mechanisms of trimethyl aluminum in atomic layer deposition of AlN. *J. Mater. Chem. C*, **11**, 13935-13945 (2023).

4:30pm AF2-WeA-13 Investigating Hf Oxide Growth with Ambient Pressure XPS and Ozone as Co-Reactant, *Esko Kokkonen,* Max IV Laboratory, Sweden*; R. Jones,* Lund University, Sweden*; V. Miikkulainen,* Aalto University, Finland*; C. Eads, A. Klyushin,* Max IV Laboratory, Sweden*; J. Schnadt,* Lund University, Sweden

Hafnium oxide is a promising material to be used in many applications such as high-k dielectrics or in advanced metal-oxide-semiconductor devices. The accurate knowledge of the deposition is crucial for creating pure, defect free, interfaces as well as optimising the reaction process timing and decreasing material consumption. In the past few years, ambient pressure X-ray photoelectron spectroscopy (APXPS) [1] has been used to study the ALD of HfOx on various surfaces [2,3]. These studies have focused on revealing intricate details within the first few half-cycles and have discovered new surface species, inter- and intramolecular reactions, and bimolecular reaction pathways.

The previous APXPS studies have used water as the co-reactant, but in this work, we turn our focus to ozone. We show how the experimental APXPS setup was modified to incorporate an ozone generator, and the results from the XPS analysis. The measurements were conducted in such a way that we were able to separate the contributions from oxygen and ozone to the growth in the co-reactant half-cycle.

The data indicates that oxygen alone creates very strong changes on the surface and contributes to the growth of the layers removing some ligands from the Hf precursor. Each co-reactant pulse was initiated in pure oxygen and the ozone was only started after a short delay. Deposition temperature was varied in a large range which shows strong affects on the reaction mechanism of the first few half-cycles. The study shows the importance of in situ experiments and separating the process into its constituent components in order to understand them better.

[1.] E. Kokkonen, M. Kaipio, H.-E. Nieminen, F. Rehman, V. Miikkulainen, M. Putkonen, M. Ritala, S. Huotari, J. Schnadt, and S. Urpelainen, *Ambient Pressure X-Ray Photoelectron Spectroscopy Setup for Synchrotron-Based* in Situ *and* Operando *Atomic Layer Deposition Research*, Review of Scientific Instruments **93**, 013905 (2022).

[2.] G. D'Acunto et al., *Bimolecular Reaction Mechanism in the Amido Complex-Based Atomic Layer Deposition of HfO ₂*, Chem. Mater. **35**, 529 (2023).

[3.] R. Timm et al., *Self-Cleaning and Surface Chemical Reactions during Hafnium Dioxide Atomic Layer Deposition on Indium Arsenide*, Nat Commun **9**, 1412 (2018).

4:45pm AF2-WeA-14 ALD/ALE 2024 Closing Remarks, *Mikko Ritala,* M. *Leskelä,* University of Helsinki, Finland*; F. Roozeboom,* University of Twente and Carbyon B.V., The Netherlands*; D. Suyatin,* AlixLabs A.B., Sweden

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