

ALD Fundamentals

Room Grand Ballroom E-G - Session AF1-WeM

In Situ Measurement

Moderator: Prof. Mikko Ritala, University of Helsinki

8:00am **AF1-WeM-1 Measuring the Time-Resolved Heat of ALD Surface Reactions, Ashley Bielinski, E. Kamphaus, L. Cheng, A. Martinson**, Argonne National Laboratory

INVITED

Our understanding of ALD reactions is often limited to simplified and idealized models. Developing a mechanistic understanding of ALD surface reactions is beneficial in a wide range of applications such as optimizing film properties, interface engineering, and area- or site-selective ALD. *In situ* measurement techniques such as ellipsometry and IR spectroscopy are increasingly used to investigate ALD processes, but they primarily probe the ALD film between surface reaction steps. Pyroelectric calorimetry provides new insight into ALD processes by enabling quantitative and time-resolved measurement of the heat evolved in ALD surface reactions.

We report the total heat generation and heat generation rates for the ALD reactions between trimethylaluminum (TMA) and water to form Al_2O_3 as well as the ALD reactions between tetrakis(dimethylamino)zirconium (TDMAZr) and water to form ZrO_2 at different temperatures. The calorimetric data was combined with *in situ* spectroscopic ellipsometry and Rutherford backscattering spectrometry analysis of optical growth rates and composition. The total heat generation of each reaction was compared with the theoretical reaction enthalpy and first-principles computational models to investigate the reaction mechanisms and thermodynamics. While the calorimetric measurements of ALD reaction heat agree well with the calculated standard reaction enthalpies, there is significant spread in how the first-principles computational results compare to the experimental values. This enables evaluation of proposed models and mechanisms while providing a benchmark for future models. Additionally, the heat generation rate provides information on reaction kinetics. For example, the water reaction for ZrO_2 was found to proceed approximately 100x faster than the water reaction for Al_2O_3 and the TDMAZr heat generation rate suggests a kinetically resolved two-step reaction.

Pyroelectric calorimetry provides unprecedented measurements of ALD reaction heat with resolution down to 50ns and $0.1 \mu\text{J}/\text{cm}^2$. This provides a unique opportunity to investigate how ALD surface reactions proceed to deepen our understanding of what drives and limits these processes.

8:30am **AF1-WeM-3 HfO_2 ALD on Si(111) - A Mechanistic in-Situ Study through Time-resolved APXPS, Rosemary Jones**, Lund University, Sweden; G. D'Acunto, Stanford University; P. Shayesteh, Lund University, Sweden; J. Gallet, F. Bournel, F. Rochet, Sorbonne Universite, France; I. Pinsard, Lund University, Sweden; A. Head, Brookhaven National Laboratory; J. Schnadt, Lund University, Sweden

The introduction of atomic layer deposition, ALD, to the microelectronics industry has introduced a large number of new possible materials, able to be deposited in layers with atomic thickness control. One such material is the high- κ oxide HfO_2 ; thermally stable and ultrathin HfO_2 films deposited by ALD are a significant contender to replace SiO_2 as the gate oxide in capacitor applications. In such a device the typical support remains Si, and thus the HfO_2 gate oxide/Si interface is an integral part of the device. The characteristics of this interface can dramatically affect the overall performance of the device itself. We present a mechanistic study of the first deposition cycle of HfO_2 on the Si(111) surface using tetrakis(dimethylamido) hafnium (TDMA-Hf) and water as precursors using operando ambient pressure x-ray photoelectron spectroscopy (APXPS). This methodology allows us to observe the chemical reactions in a time-resolved manner, giving details of mechanism and kinetics of the reaction. It is found that even low levels of moisture contamination at the 1×10^{-7} mbar level can dramatically affect the substrate and therefore the initial ALD cycle. Here, we show that the hydroxylation of the clean Si(111) surface by residual water vapour, resulting in a 0.3 monolayer coverage of hydroxyls, leads to instantaneous full surface coverage of TDMA-Hf. The change in the atomic ratio of Hf to C/N found during the first deposition half-cycle, however, does not match the assumed immediate ligand loss through reaction with surface hydroxyls. One would expect an immediate loss of ligands, indicated by a Hf:N ratio of approx. 1:3 as TDMA-Hf deposits onto the surface. However, a Hf:N ratio of 1:4 is seen until 2 minutes after exposure. In addition, there is no evidence that any removed ligands remain on the surface, skewing the Hf:N ratio. The ligand exchange

mechanism proceeds a lot slower than expected with a possible initial physisorption step – in the order of minutes rather than seconds. The slower reaction kinetics have many implications in terms of the quality of the interface when conditions are compared to industrial ALD reactors. Industrial reactors work on much faster timescales and at higher pressures than observed in this study which could result with intact precursor left physisorbed to the substrate unreacted. In addition, the moisture contamination observed in this study would be unavoidable at more standard ALD reactor pressures, which implies that residual water needs to be an important consideration for the ALD performance and eventual interface quality.

8:45am **AF1-WeM-4 In Situ Reflection High Energy Electron Diffraction Investigations of Epitaxial Growth and Crystallization of Gallium Oxide Thin Films, Alexandra Howzen, N. Strandwitz**, Lehigh University

The precursor decomposition temperature sets the maximum growth temperature of the “ALD window” which often limits the structural perfection and crystallinity of the resulting films. Intermittent annealing in between precursor chemical exposures during ALD film growth has been explored previously and shown to increase density and improve the electrical properties of ALD films¹. However, without direct monitoring of one or more of the physical properties of the films, it can be difficult to determine the nuances of film transformation, such as crystallization temperature, crystallographic texture, surface roughening, and dependence on gas ambient.

In this work we utilize a home-built thermal ALD system with integrated reflection high energy electron diffraction (RHEED) for *in-situ* monitoring of both the deposition of direct epitaxial films and the transformation of amorphous ultrathin films during *in-situ* post-deposition annealing. RHEED is a surface sensitive diffraction technique that utilizes high energy (> 10 keV) electrons at a glancing angle, and is most commonly utilized in molecular beam epitaxy and pulsed laser deposition systems. Gallium oxide thin films were grown at several temperatures using trimethyl gallium/Ozone precursors and monitored with RHEED during deposition and post-deposition annealing. Films grown at low temperature were amorphous and films grown at higher temperatures resulted in epitaxial growth of β - Ga_2O_3 on sapphire. The initial phases of a direct epitaxial β - Ga_2O_3 film on sapphire revealed RHEED streaks that were coincident with spots in the zero order Laue zone of the sapphire substrate's diffraction pattern within as few as 5 ALD cycles. Conversely, the blurring-out of the sapphire substrate's diffraction pattern is seen in RHEED during the growth of an amorphous Ga_2O_3 film. *In-situ* RHEED is then used to monitor the structural evolution of the films during an immediate post-deposition, high temperature anneal. Our unique setup allows us to closely monitor the structural evolution of the direct epitaxial and thermally transformed films. It also allows us to determine the conditions in which the metastable polymorphs of Ga_2O_3 form in epitaxial systems. The integration of RHEED with ALD offers a slow-motion picture of traditional epitaxial growth techniques by decoupling the deposition and crystallization steps with simultaneous monitoring of the surface structure.

¹ J.F. Conley, Y. Ono, and D.J. Tweet, Appl. Phys. Lett. **84**, 1913 (2004).

9:00am **AF1-WeM-5 Surface and Film Stress during ALD of Al_2O_3 and ZnO: In Situ Measurements Using Wafer Curvature Techniques, Ryan B. Vanfleet, E. Sorinto, A. Cavanagh, V. Bright, S. George**, University of Colorado at Boulder

In situ surface and film stress were measured during atomic layer deposition (ALD) using wafer curvature techniques in a new custom reactor. Aluminum oxide (Al_2O_3) ALD using trimethylaluminum (TMA) and H_2O as the reactants was used as a model system to test this new apparatus. Al_2O_3 ALD was explored at different deposition temperatures ranging from 130 to 285°C. The *in situ* measured film stress during Al_2O_3 ALD is a tensile stress of 450 MPa at 130°C (Figure 1). The tensile stress decreases with increasing deposition temperature. These *in situ* temperature-dependent Al_2O_3 ALD film stresses are in good agreement with *ex situ* film stress measurements for Al_2O_3 ALD films reported in the literature [1].

High sensitivity wafer curvature measurements are also able to measure the surface stress from individual surface reactions (Figure 2). These *in situ* measurements revealed that the TMA exposure results in a compressive surface stress. This compressive stress is attributed to repulsion between surface methyl species. In addition, the H_2O exposure removes surface methyl species and releases the compressive stress. The compressive surface stress resulting from the TMA exposure grows from 0.4 N/m at 150°C to 0.75 N/m at 285°C. This increase in the compressive surface stress

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from the TMA exposure can be attributed to the greater relative change in methyl coverage at higher deposition temperatures.

Additional *in situ* measurements explored the surface and film stresses during zinc oxide (ZnO) ALD using diethyl zinc (DEZ) and H₂O as the reactants. ZnO ALD showed interesting stress evolution with an initial compressive stress that evolves to tensile stress, then returns to compressive stress (Figure 1). The initial compressive and tensile stress is attributed to the nucleation and coalescence of islands during ZnO film growth. The largest steady-state compressive film stress measured during ZnO ALD was -150 MPa. ZnO ALD shows opposite surface stress behavior compared with Al₂O₃ ALD. The H₂O exposure results in a compressive stress, while the DEZ exposure yields a tensile stress. The magnitude of surface stresses from the DEZ and H₂O surface reactions range between 0.2 N/m to 0.4 N/m and may depend on the dominant crystal orientation at the film surface.

[1]O.M.E. Ylivaara et al., *Thin Solids Films* **552**, 124 (2014)

9:15am **AF1-WeM-6 Chemisorption Mechanisms of Aminosilane Precursors during ALD of SiO₂: *in situ* Characterization and ab initio Study, *Khabib Khumaini, H. Son, H. Roh, O. Kim, R. Hidayat, H. Kim, W. Lee*, Sejong University, Republic of Korea**

The ALD of SiO₂ thin films using aminosilane-type precursors, such as DIPAS (SiH₃(NⁱPr₂)), BDEAS (SiH₂(NEt₂)₂), or TDMAS (SiH(NMe₂)₃), is being used in dielectric deposition and multiple patterning processes. The chemisorption of silicon precursors during the ALD of SiO₂ can be studied by density functional theory (DFT) calculation and *in situ* characterization techniques [1]. DFT studies assumed that dialkylamino ligands of silicon precursors combine with H atoms of surface hydroxyl groups to form amine molecules as the byproduct. However, there was a lack of reports considering the type and distance of the hydroxyl groups on the surface. In addition, *in situ* characterization for comparative studies of precursors with different numbers of dialkylamino ligands is also lacking. Therefore, in this study, we compared the chemisorption of aminosilane-type precursors on different OH-terminated SiO₂ surfaces modeled with different hydroxyl types and distances by DFT simulation. We also compared the chemisorption reactions of DIPAS and BDEAS, the precursors having different numbers of dialkylamino ligands. Reaction energies were calculated for all possible reaction pathways, and then the activation energies were obtained for exothermic pathways. Finally, we compared the number of released ligands (*n*) from the DFT simulation result with the experimental results from *in-situ* quartz crystal microbalance (QCM). For DIPAS, the DFT predicted that the chemisorbed species would be -SiH₃*, which agrees with QCM and FTIR observation. DFT predicted that chemisorbed species of BDEAS would be -SiH₂(NEt)^{*} and -SiH₂* depending on the type of hydroxyl group, which is consistent *n* ~ 1.5 ligands calculated from QCM. Therefore, the surface species predicted by DFT simulation well explains the experimental results from *in-situ* quartz crystal microbalance (QCM) and Fourier-transform infrared (FTIR) spectroscopy.

9:30am **AF1-WeM-7 Seeing It Happen: Insights Into the Surface Chemistry of HfO₂ and TiO₂ ALD from *Operando* Ambient Pressure X-ray Photoelectron Spectroscopy, *Joachim Schnadt*, Lund University, Sweden**

INVITED

The development of ALD processes is based on a number of different considerations and factors. One consideration is the envisaged ALD surface chemistry, which has to match not only the desired process outcome and processing conditions, but also the reaction properties of both the precursor and the surface. For many precursors, their surface chemistry is assumed to follow general reaction schemes. For example, the thermal ALD of transition metal oxides from amido complex and water precursors is typically assumed to follow a ligand exchange mechanism. The wide spread of such general reaction schemes results from that they often provide a sufficiently successful prediction of the ALD process outcome, but also because experimental tools are lacking that allow direct insight into reaction mechanisms. Indeed, it has been noted that surface chemistries can be both more complex and varied than general reaction schemes make believe [1,2].

Methods that allow the time-resolved monitoring of ALD processes, such as quartz crystal microbalance measurements, quadrupole mass spectrometry, pyroelectric calorimetry and ellipsometry provide deepened insight into ALD surface reaction mechanisms. More recently, these methods have been joined by two chemically sensitive techniques for the time-resolved characterisation of ALD processes, namely infrared spectroscopy [3] and ambient pressure x-ray photoelectron spectroscopy (APXPS) (cf., e.g., [4,5]). These two methods are capable of following the

ALD surface chemistry in real time and at processing pressures equal or similar to those in an ALD reactor.

Using the metal amido complex- and water-based ALD of HfO₂ and TiO₂ on different surfaces as examples, I would like to demonstrate the usefulness of time-resolved APXPS for the elucidation of surface species and their evolution as well as for the observation of substrate processes such as oxygen transport. Such information allows to formulate ALD reaction mechanisms. In specific cases, we observe reaction pathways that deviate from the standard models of ALD surface chemistry, we find that surface hydroxylation is not always a prerequisite for oxide ALD, and for reducible supports we find that oxygen ion transport may play a major role in the initial ALD. Hence, APXPS provides us with entirely new information on ALD reaction mechanisms, which is important input for the future optimisation of ALD processes.

1. F. Zaera, *Coord. Chem. Rev.* **257**, 3177 (2013)
2. N. E. Richey et al., *J. Chem. Phys.* **152**, 1 (2020)
3. B. A. Sperling et al., *J. Vac. Sci. Technol. A* **32**, 031513 (2014)
4. R. Timm et al., *Nat. Commun.* **9**, 1412 (2018)
5. G. D'Acunto et al., *Chem. Mater.* **35**, 529 (2023)

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