ALD Fundamentals
Room Van Eyck - Session AF2-TuA
Characterization II

Moderators: Bart Macco, Eindhoven University of Technology, Juan Santo-Domingo Peñaranda, Ghent University, Belgium

4:00pm **AF2-TuA-11 Get the Full Picture: Full-Range Time-Resolved In Situ Mass Spectrometry During ALD**, ***Andreas Werbrouck**, J. Dendooven, C. Detavernier,* Ghent University, Belgium **INVITED**

In situ measurements are indispensable for developing, characterizing, and understanding ALD processes. Quadrupole mass spectrometry (QMS) is one technique available to monitor the gas mix in the reactor (or at the exhaust) while surface reactions are ongoing. In QMS, gas from the reactor is sampled, ionized, and fragmented. These fragments have specific mass-to-charge ratios, and their relative intensities provide a way to fingerprint the chemical species present. However, typical tools can only detect a single mass at a time, leading to poor time resolution. Additionally, the generated reaction products may be complex, unexpected, and as they are generated by a self-limiting surface reaction, they are only present in the reactor for a limited amount of time.

Here, we propose a way to exploit the cyclic nature of ALD, collecting QMS data over multiple cycles in order to collect a full-range, time-resolved picture of the gas mix in the reactor during an ALD process. This allows to effectively bypass the limitations of traditional QMS during ALD with only minimal hardware changes to the reactor. Over the past years, we have used this technique to investigate the archetypal TMA-water process and detected a secondary reaction product for water, to study the deposition of lithium-containing films, and to study the deposition of ruthenium dioxide.

In the first part of the presentation, the data collection and post-processing routines will be clarified. The second part of this talk will handle specific use cases, and the tools that can be used to make sense of the large amount of collected data will be discussed. Time-resolved, full-range quadrupole mass spectrometry measurements may be indispensable to get the full picture of your atomic layer process.

4:30pm **AF2-TuA-13 Strategies to Produce Boron-Containing ALD Thin Films Using Trimethyl Borate Precursor: From Thermal to Plasma to Combined-Plasma Approach**, ***Arpan Dhara**, A. Werbrouck, J. Li, J. Dendooven, C. Detavernier,* Ghent University, Belgium

Recent research takes interest in boron-comprising thin layers that are useful in many applications such as dopant for semiconductors, neutron detection and absorption layer in nuclear reactors, ceramic reinforcements, and lithium ion batteries. The most fundamental boron-containing layer, B_2O_3, is highly hygroscopic, and therefore ternary oxides (like $Al_xB_yO_z$) or B-doped oxide (like ZnO:B) are more commonly prepared, using a so-called ALD supercycle approach. Generally, the boron concentration in these films is unequivocally poor (~1-10%) when the metal oxide to boron oxide cycle ratio is 1:1. Stoichiometric films are obtained only from a particular (pyrazolyl) type of precursor, however the high vaporization temperature (~200°C) hampers their practical use. Therefore, there is a need of finding a suitable precursor and convenient process to produce boron-containing thin films.

In this work, we demonstrate different strategies (figure 1) to produce aluminium borate thin films by ALD using trimethyl borate (TMB) as the boron source. Films obtained from *thermal* processes (***TMA-H_2O-TMB** or **TMA-H_2O-TMB-H_2O***) show a moderate growth per cycle (GPC, 0.85 & 1.5 Å respectively), and contain considerable carbon impurities. Also, a constant increase in growth rate is observed with temperature which suggests a low reactivity of the TMB molecule. The reactivity can be improved by using oxygen plasma (***TMA-O_2*-TMB-O_2****) instead of H_2O as O source. The GPC certainly improves a bit (~1.8 Å) along with a reduction in carbon contamination. However, the boron concentration in the films remains very low for the investigated processes (~5-10%).

To improve the growth rate and boron concentration further, we introduce a novel approach where a combination of H_2O and TMB is used in plasma form (**TMA-[TMB+H_2O]***). It is proposed that the TMB molecules ***polymerize in-situ*** in the plasma, as reported before for trimethyl phosphate plasma.[1] However, using TMB alone in plasma form does not yield self-limiting ALD growth, as polymerized species continuously accumulate on the substrate. Interestingly, by adding H_2O to the TMB plasma, saturated growth of aluminium borate films is achieved with a high GPC of ~3.5 Å/cycle. Moreover, the films contain a considerably larger amount of boron (~15-20%). We hypothesize that H_2O in the TMB plasma helps to hydrolyse surface groups, which in turn aids in preventing continuous polymerization. We also performed ***time resolved transient in-situ mass spectroscopy*** (figure 2) and ***in-vacuo XPS*** studies to reveal the mechanism of all three different approaches explained above.

1. T. Dobbelaere et. al., *Chem. Mater.* **26**, 6863–6871 (2014)

4:45pm **AF2-TuA-14 Examining Large Grain Growth and Low Temperature Crystallization Kinetics for TiO_2 Thin Films Prepared by Atomic Layer Deposition (ALD)**, ***Jamie Wooding**, K. Kalaitzidou, M. Losego,* Georgia Institute of Technology

This presentation will describe an atomic layer deposition (ALD) process to prepare large crystal anatase TiO_2 thin films (>1 micron at <100 nm thickness) and provide a roadmap to determine fundamental crystallization kinetics quantities for thin film systems. Films are deposited using tetrakis(dimethylamino)titanium(IV) (TDMAT) and water at 140 °C and 160 °C, followed by an *ex situ* low-temperature post-deposition anneal (PDA) from 140–200 °C. All as-deposited thin films are amorphous by X-ray diffraction (XRD) and Raman spectroscopy. During the post-deposition anneal, the crystallization process is tracked via scanning electron microscopy (SEM). As depicted in Figure 1, these low anneal temperatures achieve large grain growth resulting in crystal sizes of 0.8–1.2 µm in lateral dimension for a film thickness of 50 nm. The time-dependent transformation fraction is fit to the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model (Figure 2a), which reveals a continuous nucleation process and a two-dimensional growth mechanism, consistent with the observed large grains.Crystal nucleation rate is observed for short annealing times to determine the critical free energy for anatase nucleation and then combined with the transformation reaction rate from the JMAK equation to determine the activation energy for grain growth (Figure 2b). The energy required for nucleation of 1.32–1.35 eV K^{-1} $atom^{-1}$ is an order of magnitude greater than the activation energy for grain growth of 0.12–0.24 eV K^{-1} $atom^{-1}$; as such, nucleation has the more significant energy barrier at these lower temperatures. Films deposited at 160 °C have higher nucleation rates than those deposited at 140 °C despite both films having comparable critical free energies for nucleation. These greater nucleation rates originate from an increased nucleation frequency factor (Figure 2b), indicating improved mobility or a higher degree of proto-nuclei. Using this TiO_2 large grain crystal growth study as a prototype, this work demonstrates a method to predict post-deposition crystallization behavior in ALD thin films.

5:00pm **AF2-TuA-15 Deposition and Characterization of Hafnium Dioxide Films Embedding Nickel Nanoparticles**, ***Markus Otsus**, J. Merisalu, T. Viskus, T. Kahro, A. Tarre, K. Kalam, A. Kasikov, P. Ritslaid, J. Kozlova, K. Kukli, A. Tamm,* University of Tartu, Estonia

Controlled defects introduced in nanolaminates designed for use in resistive switching devices can improve the overall performance of memristors. Nanoparticles (NP) can guide the process of conductive filament formation thus lowering voltage and enhancing stability of resistive switching [1]. As overall the density of conductive filaments is low, observations of conductive filaments in or around a NP with scanning transmission electron microscopy (STEM) imaging could be possible. Studying the filaments shape and composition with STEM imaging and energy dispersive X-ray spectroscopy (EDS) analysis may allow us to better understand the process and mechanism of their formation [2].

Resistive switching properties of four different structures were examined. The aim was to produce otherwise similar structures (Figure 1) with and without Ni-NPs, using two different precursor systems at the same substrate temperature (220 °C), $HfCl_4$ +O_3, and tetrakis(ethylmethylamino)hafnium (TEMAH) + O_2 plasma, and two different atomic layer deposition (ALD) reactors – a flow-type in-house built hot-wall reactor and a Picosun R200 Advanced System, respectively. Starting with a Si(100) planar wafer substrate covered with a conductive TiN film, a two-step ALD process was used to embed the nickel NPs in-between a HfO_2 layer. Following the deposition of the dielectric layer, titanium top electrodes were produced using maskless photolithography and electron beam evaporation.

Scanning electron microscopy (SEM) showed the NPs uniformly dispersed across the sample area, apart from a few clusters observed. Current-voltage measurements were carried out, and in the samples with NPs,

lower voltages were needed to switch between high-resistive state (HRS) and low-resistive state (LRS) (Figure 1), compared to the particle-free samples. SEM-focused ion beam was used to produce lamellas from films with and without Ni-NPs, which were then analyzed with STEM and EDS to evaluate the composition and uniformity of the layers (Figures 2 and 3). Nanocrystals were monitored in HfO_2 grown from TEMAH, while the $HfCl_4$ based oxide layer appeared structurally homogenous. Conclusively, electrical and microscopy findings were compared and a possible cause for the results observed was proposed.

[1] W. Banerjee, Q. Liu, and H. Hwang, “Engineering of defects in resistive random access memory devices,” *J. Appl. Phys.*, 127 (2020) 051101, doi: 10.1063/1.5136264.

[2] D.-H. Kwon *et al.*, “Atomic structure of conducting nanofilaments in TiO_2 resistive switching memory,” *Nat. Nanotechnol.*, 5 (2010) 148-153 doi: 10.1038/NNANO.2009.456.

5:15pm **AF2-TuA-16 Biased QCM for Studies of Reductive Surface Chemistry Induced by Plasma Electrons***, **Pentti Niiranen**, H. Nadhom, D. Lundin, H. Pedersen,* Linköping University, IFM, Sweden

Metallic films are an immensely important part of the modern world e.g., in a variety of applications such as sensors, catalysts, optoelectronics and nanoelectronics. For any ALD, or CVD, approach to metal films using a metal precursor with a positive valence, the fundamental surface chemistry is a reduction reaction. However, reduction of electropositive metals in ALD and CVD is especially difficult due to the shortage of precursors with the appropriate reduction power to overcome the thermodynamical disadvantage and complete the reduction. In a recent study, the electrons from a plasma discharge was used for the reduction of first-row transition metals (Co, Fe and Ni) in a CVD process, instead of using a co-reactant as a reduction agent.[1] By applying a positive bias to the surface, the plasma electrons were drawn to the substrate surface and facilitated metal growth. The process is also demonstrated to be inherently area-selective from the electrical resistivity of the substrate, depositing metal only on low-resistivity surfaces, leaving high-resistivity surfaces uncoated.[2] The surface chemical model for this process must be developed to understand and develop the method. As a first step to develop the surface chemical model, we here present a biased QCM system, capable of attracting plasma electrons to the QCM-head. Initial result shows the great potential of the modified QCM for the process where plasma electrons are used as reducing agents.[1] By using the biased QCM in combination with residual gas analysis and quantum chemical modelling we are building a surface chemical model of the process. The biased QCM-method can also aid us in our efforts to develop the method into a time-resolved method. We note from the QCM-curves that they suggest that self-limiting surface chemistry is possible using the new plasma electron based CVD method.

[1] Nadhom, et al. *J. Vac. Sci. Technol. A*, 2020, 38, 033402, 2020.

[2] Nadhom, et al. *J. Phys. Chem. Lett.*, 2021, 12, 4130.

5:30pm **AF2-TuA-17 NHC Monolayer Growth Behaviour and Film Durability Measured by QCM***, **Eden Goodwin,*** Carleton University, Canada*; A. Veinot, I. Singh,* Queens University, Canada*; P. Ragogna,* Western University, Canada*; C. Crudden,* Queens University, Canada*; S. Barry,* Carleton University, Canada

We have previously seen N-heterocyclic carbene (NHCs) containing gold precursors etch gold surfaces during quartz crystal microbalance (QCM) studies (Goodwin, AVS ALD 2021). Although we have proposed an etch mechanism, the role of the surface NHC remains unclear.

NHCs have been shown to reconstruct gold surfaces by dislocation and displacement of individual atoms on the surface and to bind to gold surfaces in several different conformations (upright, flat, in clusters) dependant upon their functionalization (Smith et al., 2019). The di-isopropyl NHC that was previously reported is expected to bind in an upright manner, a binding behaviour that can not be predicted and needs to be determined through scanning tunneling microscopy (STM) imaging on single crystal gold surface. Analyzing NHC binding behaviour this way has several downsides: cost of single crystal gold surfaces, availability of STM imaging facilities, and lengthy processing time. To alleviate these issues, we propose to quantify coverage and corroborate binding geometry by QCM studies. Additionally, we are investigating the effect of gold species ($AlCl_3$, (Me)AuNHC, $(Me)_3AuPMe_3$) on both the carbene monolayer and gold surface.

In this work we deposit a series of simple NHCs in a home-made tube furnace reactor using a 100-cycle pulse sequence (60s pulse, 20s N_2 purge) and subsequently expose these to gold-containing species. Real time high resolution (10 counts per second) surface analysis is done using a 6 MHz in-situ polished gold coated QCM crystal. Time resolved mass gain analysis is used to confirm saturative growth behaviour, determine the number of occupied gold sites, and to test film stability when exposed to a variety of Au species. A low resolution (<300 AMU) in-situ quadrupole mass spectrometer (QMS) is used to confirm the presence of free NHC and determine volatile products formed during surface decomposition or etch processes.

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