Nanostructure Synthesis and Fabrication
Room Auditorium - Session NS2-WeA

Nanomaterials by ALD - Nanoparticles and ALD on Polymers

Moderators: Jeffrey W. Elam, Argonne National Laboratory, Hyungjun Kim, Yonsei University, Korea

3:00pm **NS2-WeA-9 Visualizing the Nucleation of ALD on Polymers***, Laura* ***Astoreca****,* Ghent University - IMEC, Belgium*; P Esbah Tabaei,* Ghent University, Belgium*; D Schaubroeck, M Oop de Beeck,* Ghent University - IMEC, Belgium*; R Morent,* Ghent University, Belgium*; H De Smet,* Ghent University - IMEC, Belgium*; N De Geyter,* Ghent University, Belgium

Polyimides are vastly used in the microelectronics industry as they can withstand the conditions of many processes due to their mechanical robustness, and thermal and chemical stability. A specific polyimide (PI 2611) has been used as packaging material for flexible implantable medical devices and electrodes due to its relatively good water barrier properties and biocompatibility. Yet, it cannot provide the necessary hermeticity for long term implantation. Therefore, this PI can be combined with metal oxide ALD layers (SiOx, AlOx, TiOx or HfOx) to develop ultra-hermetic barriers (WVTR = 10^{-6} g/cm²day). To characterize the interaction between the PI and the ALD layers it is fundamental to understand the nucleation of the ALD layer on the polymer. These are commonly studied by quartz microbalance, ellipsometry, FTIR, or XPS, all of which provide valuable information but do not allow visualizing the nucleation behavior during the initial stages of ALD growth until full closure of a layer on polymers. In this contribution, a new qualitative method to study this is proposed and applied to the Al_2O_3 and HfO_2 ALD deposition on PI. The deposited metal oxide acts as a hard mask during PI reactive ion etching (RIE). This results in local features of the deposited ALD being visible in FEG SEM images. The samples were also analyzed by XPS to verify the Al or Hf content present on the surface. The proposed method produces repeatable results, and by increasing the exposure time of the RIE it was confirmed that the deposited Al_2O_3 or HfO_2 was not damaged by the etching step. As expected, the images taken and the XPS results showed a faster nucleation and growth of a fully closed layer of the AlOx compared to HfOx. In both cases an island-coalescence type of nucleation and growth was observed. First, islands were formed on the surface of PI, growing into filamentous structures that progressively coalesced into meshes, which became denser until eventually a closed layer was formed. The Al or Hf content measured by XPS presented an equivalent increase behavior. The content of Al or Hf was low and constant at the beginning, corresponding to the island stage. It progressively increased as the mesh structures were formed and became denser until it stabilized at a constant value. Herein, a qualitative method to visualize the nucleation and growth of a full ALD layer on polymers was introduced. It is not presented as an alternative to the available techniques but rather as a complementary tool.

3:30pm **NS2-WeA-11 Pt-Doped In_2O_3 Thin Films: Control of the Chemical State and Structure via ALD***,* ***Ranjith K. Ramachandran****, M Filez,* Ghent University, Belgium*; E Solano,* Ghent University, Belgium, Spain*; H Poelman, M Minjauw, M Van Daele, J Feng,* Ghent University, Belgium*; A La Porta, T Altantzis,* University of Antwerp, Belgium*; E Fonda,* Synchrotron SOLEIL, SAMBA Beamline, France*; A Coati, Y Garreau,* Sychrotron SOLEIL, France*; S Bals,* University of Antwerp, Belgium*; G Marin, C Detavernier, J Dendooven,* Ghent University, Belgium

It is well known that noble metal addition to metal oxides improves the electronic properties of the oxides. Depending on the targeted application of the resulting material, another mode of addition is demanded. While noble-metal doped semiconducting metal oxides show improved catalytic and gas sensing properties, metallic nanoparticles (NPs) embedded in metal oxides are used as charge storage materials in single-electron memory devices. In any case, accurate tuning of the dopant level/NP's size is crucial to achieve an optimal performance.

Here, a novel atomic layer deposition (ALD)-based method for doping Pt into In_2O_3 is demonstrated.[1] We combine alternating exposures of Pt and In_2O_3 ALD processes in a single "supercycle" followed by supercycle repetition leading to multilayered nanocomposites (**Figure 1**). The resulting samples of Pt embedded in an In_2O_3 matrix are characterized chemically and structurally using a variety of X-ray-based techniques, such as X-ray fluorescence (XRF), X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), grazing-incidence small-angle X-ray scattering (GISAXS), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), combined with energy dispersive X-ray spectroscopy (EDXS).

The proposed method enables controlled doping of Pt/PtO_x species inside the In_2O_3 matrix with the ability to fine-tune their chemical and structural properties. For example **Figure 2** shows the results from a series of samples (samples B1 – B6) where the number of Pt ALD cycles was varied from 1 to 30 while keeping the number of In_2O_3 cycles at 30. XAS and XRD shows that a few Pt ALD cycles lead to the formation of oxidized Pt species due to their highly dispersed nature. GISAXS and HAAD-STEM, combined with EDXS, show that Pt is evenly distributed in the In_2O_3 matrix without the formation of clusters. For a larger number of Pt ALD cycles, the oxidation state gradually evolves toward fully metallic, and metallic Pt clusters are obtained within the In_2O_3 matrix.

In addition to giving valuable information on the dopant distribution and its chemical state, which provides strategies for fine-tuning the properties of doped metal oxides, this approach allows characterization of the nucleation stages of metal ALD processes by freezing those states through embedding and stacking them multiple times. This allows the use of XAS and other techniques to study even a single-metal ALD cycle, without the need for the use of high-surface-area supports.

References

1. Ramachandran, R. K. *et al. Chem. Mater.* **31**, 9673–9683 (2019).

3:45pm **NS2-WeA-12 Study of Tuning Size, Coverage and Shape of Pd Nanoparticles Using Atomic Layer Deposition Through X-ray Based In-situ Characterization***,* ***Ji-Yu Feng****,* Ghent University, Belgium*; E Solano,* NCD-SWEET beamline, ALBA Synchrotron Light Source, Spain*; R Ramachandran, M Minjauw, M Van Daele,* Ghent University, Belgium*; D Hermida-Merino,* ESRF European Synchrotron Radiation Facility, France*; A Coati,* Synchrotron SOLEIL, France*; C Detavernier, J Dendooven,* Ghent University, Belgium

Atomic-level control of the morphology of supported nanoparticles (NPs) is of great importance in heterogeneous catalysis, because the catalytic performance is closely related to the size, interparticle distance and shape of the NPs. On this aspect of uniformity and precise control, ALD has proven to be a promising synthetic method for catalytic applications, where several studies have focused on the relationship between processes and NPs morphology evolution. Synchrotron-based in situ X-ray fluorescence (XRF) and grazing incident small-angle scattering (GISAXS) experiments can offer insights in the NP morphology evolution during the nucleation stages of ALD processes.[1]

In this work, we study the evolution in Palladium (Pd) NP morphology during plasma-enhanced ALD using in situ XRF and GISAXS. Firstly, the role of the co-reactant choice is investigated by comparing Pd NP growth by ALD processes using $Pd(hfac)_2$ as precursor and different plasma sequences as co-reactants (H_2* and H_2*+O_2*) on Al_2O_3 substrates. Different from the process with only H_2* as coreactant, an additional O_2* step leads to an increase in initial nucleation density, which is explained by a cleaning effect of O radicals towards poisoning surface species from the reaction between the hfac ligands and the surface. Moreover, O_2* induces enhanced mobility of Pd atoms and/or particles, thus resulting in a more dynamic coalescence during further growth, as observed from the continuous increase in center-to-center distance. The 2D GISAXS patterns also reveal that the H_2* and O_2* exposures have a different impact on the particles' shape and wetting behavior. As a result, a clear difference in Pd particles morphology for both studied processes is observed at higher loadings: worm-like structure for the H_2* process vs. isolated particles for the H_2*+O_2* process. Secondly, to further tune the initial nucleation density, trimethylaluminum (TMA) exposures are introduced during the first ALD cycles of the $Pd(hfac)_2$/H_2* process to clear the surface blocking species.[2] XRF-GISAXS shows TMA exposures in the early ALD cycles lead to an increase in initial nucleation sites, thus making smaller Pd NPs with a larger coverage when comparing samples with the same Pd loading. When gradually increasing the applied number of TMA pulses from 1 to 10, the NP dimensions (coverage) can be tuned from high (low) to low (high). Based on this knowledge, an ALD based strategy is developed for the synthesis of well-designed Pd NPs, e.g. by adjusting the number of TMA pulses and applied ALD cycles.

1. J. Dendooven et al. *NAT COMMUN* , 2017, 8, 1074.

2. D. N. Goldstein et al. *APPL PHYS LETT*, 2009, 95, 13121.

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