Nanostructure Synthesis and Fabrication
Room Arteveldeforum & Pedro de Gante - Session NS-TuP
Nanostructures Synthesis and Fabrication Poster Session

NS-TuP-7 In situ Thermal Annealing of ALD Fabricated Pt Nanoparticles and Their Stabilization via Al₂O₃ Overcoating, *E Solano,* NCD-SWEET beamline, ALBA Synchrotron Light Source, Spain*; J Dendooven, J Feng,* Ghent University, Belgium*; P Brüner,* IONTOF GmbH, Germany*; **Matthias Minjauw**, R Ramachandran, M Van Daele, K Van de Kerckhove, T Dobbelaere,* Ghent University, Belgium*; A Coati,* Sychrotron SOLEIL, France*; D Hermida-Merino,* ESRF European Synchrotron Radiation Facility, France*; C Detavernier,* Ghent University, Belgium

The activity and selectivity of supported Pt nanoparticles in heterogeneous catalysis depends on the particle size, shape and coverage [1]. Particle coarsening induced by the often required harsh thermal and chemical conditions during catalytic processes is undesirable since it limits the availability of catalytic sites. Large efforts and resources have been invested to prevent particle coarsening, aiming to prolong the performance and lifetime of nanocatalysts. Among the diverse approaches, particle overcoating via ALD has emerged as a promising method for coarsening prevention while enabling catalyst accessibility through pores and cracks in the overcoat [2]. However, there is a delicate balance in terms of film thickness: a thin overcoat may not be enough for particle coarsening prevention while a thick layer could totally block the surface accessibility for the catalytic application.

Here, we report an *in situ* synchrotron Grazing Incidence Small Angle X-ray Scattering (GISAXS) study on the thermal stability of supported Pt nanoparticles when overcoated with an Al_2O_3 layer deposited by means of ALD (Figure 1). As model system, we fabricated two distinct sets of samples with equivalent Pt loading but distinct particle coverage [3]. A series of different Al_2O_3 thicknesses were deposited onto the supported nanocatalysts prior to *in situ* annealing up to 850 ºC in an O_2-rich atmosphere. The real-time GISAXS patterns provided a near-continuous feed of information on the evolution of particle size and spacing during the annealing process [4]. *In situ* data demonstrated that the overcoating methodology requires isolated nanoparticles for an effective stabilization, while stabilization of the closely packed supported nanoparticles turned out to be more challenging, showing the dependence of the minimum overcoat thickness on the initial morphology. Moreover, Pt surface accessibility was evaluated by Low Energy Ion Scattering (LEIS), confirming that the amount of exposed Pt for the coated samples augments during the thermal treatment due to the cracks and pores formation (Figure 2). After a long isothermal annealing, the coated sample with isolated nanoparticles has a larger amount of exposed Pt surface area than an uncoated (and hence coarsened) sample, proving the efficiency of an ALD Al_2O_3 layer as stabilization tool for supported nanocatalysts.

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NS-TuP-10 Surface Functionalization and Atomic Layer Deposition of Metal Oxides on MoS₂ Surfaces, *Theodosia Gougousi, J Kropp, C Ataca,* University of Maryland, Baltimore County

Transition metal dichalcogenides (TMD) have been studied for device applications due to their electronic properties and their possession of a bandgap (1.8eV for single layer MoS_2). The fabrication of electronic devices requires deposition of high-quality dielectrics on the hydrophobic TMD surface and remains a challenge.

In this work we will provide examples of TiO_2 and Al_2O_3 Atomic Layer Deposition (ALD) film growth from tetrakis dimethyl amino titanium (TMDAT), trimethyl aluminum (TMA) and H_2O at 100-200°C on exfoliated and Chemical Vapor Deposition (CVD) MoS_2 flakes. We find that the initial surface condition of exfoliated MoS_2 flakes varies greatly due to residual adhesive contamination resulting in large variation in the film morphology. More controlled growth is obtained for CVD MoS_2 flakes but even in this case the surface coverage is thickness dependent for films as thick as 10 nm.

In order to alter the surface energy, seeding with inorganic and organic species have been investigated. Mercaptoethanol (ME) is a small thiol that contains a -SH functional group at one end and -OH termination at the other end. The -SH termination is expected to react with the MoS_2 surface leaving the surface -OH terminated as desired for the onset of the ALD chemistry. Atomic Force Microscopy (AFM) measurements confirm that ME treatment alone does not promote more uniform film growth. Computational studies of the ME-MoS_2 surface interaction using Density Functional Theory (DFT) reveal that ME interacts with the sulfur vacancies almost exclusively. Vacancy density is less than ~5% for as-deposited CVD MoS_2, and depositions result in non-continuous coverage for typical thermal ALD. Argon ion sputtering was used to remove Sulfur atoms from the surface and increase the vacancy density up to ~20%. AFM confirms the formation of continuous 6 nm TiO_2 films at 100°C for both ME treated and control samples. DFT calculations reveal that TDMAT can interact directly with the vacancy. However, the calculated Density of States for these defect rich surfaces contain gap states that are undesirable for high quality devices. Treatment of defect rich surfaces with ME results in the removal of the gap states which is expected to result in good electrical properties.

$HAuCl_4$ solutions have been also used to seed the surface with -Cl terminal species to initiate film growth. XPS data confirm both the presence of Au on the surface and absence of residual chlorine. AFM shows only partial surface coverage for films as thick as 6 nm. A distinct difference in the film morphology is obtained though as a result of this treatment indicating that the film growth mechanism has been altered.

NS-TuP-11 Comparison of Growth Characteristics and Nanoparticle Formation by O₂ or H₂ Reactant Gas in Pt ALD, *Tatsuya Nakazawa, D Kim, T Nam, J Park, H Kim,* Yonsei University, Republic of Korea

The utilization of platinum nanoparticles has already been commercialized in catalysts, Pharmaceutical applications, and device fabrication. The size control of nanoparticles is significant for obtaining the desired properties of nanoparticles, for example, catalytic ability, interaction with pharmacological agents, quantum effect. Therefore, we focused on an atomic layer deposition (ALD) process that controls particle size by self-limiting growth. Thus, the conformal growth can be caused in each initial particle on the substrate; it is expected that the particle size and the cycle number is in a linear relationship.

Lee *et al.* reported that DDAP (Dimethyl(N,N–Dimethyl-3-Butene-1-Amine–N) Platinum) is a candidate precursor for Pt ALD with O_2 reactant. [1] DDAP is a promising precursor to prepare the Pt film because of its high vapor pressure and low decomposition temperature. Additionally, the high purity of the deposited platinum by DDAP precursor is expected to be applied in the semiconductor industry. However, PtO_x generated in an oxidizing atmosphere has a high diffusion coefficient. It is an advantageous effect forming a uniform thin film having, but it is difficult to control the size and dispersibility of nanoparticles. Several studies of Pt ALD have been reported to prepare Pt nanoparticles using H_2 reactants as well as O_2 reactants. [2][3] O_2 and H_2 reactants have different reaction mechanisms, which may affect growth characteristics and chemical composition of Pt deposition. In this study, we first compared the Pt ALD using DDAP with O_2 and H_2 as reactants for application to the Pt nanoparticle preparation process. The film thickness, surface morphology, and nanoparticle distributions were measured by FE-SEM (Field Emission Scanning Electron Microscopy) and image analysis. Moreover, chemical composition and chemical states were determined by XPS (X-ray Photoelectron Spectroscopy). We will discuss the differences in the reaction mechanism from each growth characteristic and chemical analysis. Based on these results, size-controlled nanoparticle production studies with Pt ALD using DDAP were conducted. Also, we clarified the relationship between particle size and cycle number and growth temperature in the preparation of nanoparticles using DDAP. We have found that the conditions for nanoparticle formation are entirely different depending on the ligand gases. Therefore, we will talk about the mechanism of growth when O_2 or H_2 is used as reactant gases.

Reference

[1] W-J. Lee *et al.*, Chem. Mater. **31**, 5056 (2019).

[2] A. M. Lubers *et al.*, J. Nanopa. Res. **17**, 179 (2015).

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method was approximately 9 times greater than that of the film formed via conventional ALD. These results indicate that our method can be employed for obtaining complete single layers of various materials or developing high-quality monolayer-scale 2D materials using ALD.

Nanostructure Synthesis and Fabrication
Room Auditorium - Session NS-WeM

2D Nanomaterials by ALD I

Moderators: Tae Joo Park, Hanyang University, Virginia Wheeler, U.S. Naval Research Laboratory

10:45am **NS-WeM-1 Exploring ALD 2D Chalcogenides Beyond MoS$_2$**, *Miika Mattinen,* University of Helsinki, Finland **INVITED**

Two-dimensional (2D) materials have rapidly emerged as promising materials for a range of applications from microelectronics to sensing as well as energy storage and production. Deposition of 2D materials as high-quality films of controlled thickness on large, temperature-sensitive, and complexly shaped substrates is one of the main challenges hindering industrial applications. ALD can fulfill these requirements, but unlocking the full potential of ALD of 2D materials requires careful examination of precursor chemistry, nucleation, substrates, film characteristics, and device performance.

Much of the ALD research on 2D transition metal dichalcogenides (TMDCs) has focused on semiconducting MoS$_2$. Lately, some of the efforts have shifted to other 2D semiconductors, which may offer improved charge carrier characteristics (e.g. WS$_2$ and WSe$_2$) and lower processing temperatures (SnS$_2$), for example. So far, little attention has been given to ALD of metallic TMDCs (e.g. NbS$_2$ and TaS$_2$), which may be used to complement 2D semiconductors in devices or by themselves in energy storage and production. Furthermore, ALD of selenide and telluride TMDCs is still in its infancy.

Deposition of these "new" 2D chalcogenides by ALD is no simple feat. This talk focuses on finding precursors for a range of 2D chalcogenides from MoS$_2$ to other semiconductors including HfS$_2$, SnS$_2$, WS$_2$, and ZrS$_2$ as well as my recent efforts towards metallic sulfide TMDCs. Precursor challenges related to reactivity, thermal stability, and etching reactions will be considered. I will cover some challenges and opportunities related to selenide and telluride TMDCs. I am also going to discuss the stability of the deposited films and deposition of protective layers.

The anisotropic, layered crystal structure of 2D materials affects their growth. The morphology of the grown films in turn affects their properties and performance in applications. The effect of the substrate on morphology, continuity, and crystallinity of 2D films will be discussed through the following three examples. First, the growth of crystalline TMDC films often leads to rough morphology. By depositing amorphous films that are crystallized after deposition, smooth crystalline SnS$_2$ and WS$_2$ films can be obtained. Second, deposition of thin and continuous TMDC films is challenging. It will be shown that thinner continuous SnS$_2$ films can be deposited on sapphire compared to silicon. Third, methods to improve the quality of the films deposited at low temperatures are desired. To this end, I will discuss van der Waals epitaxial growth of 2D chalcogenides.

11:30am **NS-WeM-4 Growth of Wafer-Scale Monolayer MoS$_2$ using Adsorbate-Controlled Atomic Layer Deposition**, D Kim, *Jae Chan Park*, W Kim, Hanyang University, Republic of Korea; J Park, B Shong, Hongik University, Republic of Korea; J Ahn, T Park, Hanyang University, Republic of Korea

Monolayer transition-metal dichalcogenide compounds with two-dimensional (2D) layered structures have attracted considerable attention because of their potential applicability as next-generation active materials for versatile electronic and optoelectronic devices. For industrial application of these materials, a reliable method for well-controlled large-area growth of high-quality material at the wafer scale should be developed. Atomic layer deposition (ALD) of 2D materials has been widely studied for realizing atomically flat monolayer films, but it has limitations regarding the implementation of a perfect monolayer owing to its deposition characteristics.

In this work, we propose a novel chemical route for the deposition of a monolayer MoS$_2$ film with large-area uniformity at wafer scale using ALD. First, by modulating the precursor injection step, the amount of adsorbed precursor in one cycle can be precisely controlled in a range exceeding the limitation imposed by "typical" ALD reaction. Utilizing such process, we successfully realized (for the first time) a uniform and complete monolayer MoS$_2$ film using ALD at the wafer scale. The monolayer MoS$_2$ film exhibited excellent uniformity at the wafer scale, and the luminescence quantum efficiency of a monolayer MoS$_2$ film deposited via the newly-proposed ALD

Nanostructure Synthesis and Fabrication
Room Auditorium - Session NS1-WeA

2D Nanomaterials by ALD II

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

1:00pm NS1-WeA-1 Atomistic Simulation of ALD of 2D Transition-Metal Dichalcogenides, *Mahdi Shirazi, E Kessels, A Bol,* Eindhoven University of Technology, Netherlands **INVITED**

Extensive research has been done during the last decade to unravel the remarkable electronic properties [1], [2] of two dimensional transition-metal dichalcogenides (2D-TMDs) in the monolayer regime. In spite of their astounding electrical properties, these material systems are not ready yet for replacing Si based materials for future nanometer-sized electronic devices. One key challenge is the integration of these materials in bottom-up processes at low temperature (usually < 500 °C) into the semiconductor manufacturing flow. Horizontal growth at wafer scale with a large grain size (typically 1x1 μm^2) is required for nano-electronic devices [3]. The cyclic process of atomic layer deposition (ALD) [4] with tight control over the chemical reactions shows promise as such a bottom-up process. The chemical reactions of ALD are self-limiting and are designed to proceed only at the surface. In this contribution, we have employed density functional theory (DFT) to provide fundamental insight into the reaction mechanisms of the MoS_2 growth. We have studied the deposition of MoS_2 that is initiated by the exposure of metal precursor $Mo(NMe_2)_2(NtBu)_2$ ($C_{12}H_{30}N_4Mo$) to the SiO_2 surface and then followed by exposure of H_2S/H_2 as co-reagent in the second pulse [5]. In this so-called hetero-deposition, the involved chemical reactions during ALD lead to the formation of a buffer layer at the surface of SiO_2 [6]. After formation of this buffer layer, ALD enters into the steady-growth regime (also called homo-deposition). In the steady growth regime, vertically or horizontally aligned MoS_2 structures grow in a layer-by-layer fashion. The calculated reaction energies and activation energies indicate that the reaction kinetics in the hetero-deposition are slower than reaction kinetics in homo-deposition. Artificial intelligence is used to generate an efficient interatomic potential using the calculated energies and forces of configurations obtained by DFT. The generated interatomic potential will be used for larger scale simulations to provide further fundamental insight into the deposition of MoS_2 by ALD.

[1] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, H. Zhang, *Nat. Chem.*, **2013**, *5*, 263.

[2] K. F. Mak, C. Lee, J. Hone, T. Shan, T. F. Heinz, *Phys. Rev. Lett.*, **2010**, DOI:10.1103/PhysRevLett.105.136805.

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[6] M. Shirazi, W. M. M. Kessels, A. A. Bol, *APL Mater.*, **2018**, DOI:10.1063/1.5056213.

1:45pm NS1-WeA-4 ALD of MoSe₂ using New Precursors, *Raul Zazpe,* University of Pardubice, Czech Republic*; R Krumpolec,* Brno University of Technology, Czech Republic*; J Charvot, L Hromadko, H Shopa, M Motola, M Krbal, F Bures, J Macak,* University of Pardubice, Czech Republic

2D semiconductor transition metal dichalcogenides (TMDs) have attracted considerable attention due to their layered structure, suitable band gap for visible light absorption, high carrier mobility, electrochemically active unsaturated edges and relatively good stability against photocorrosion [1]. Recently, 2D $MoSe_2$ has been gaining considerable interest due to its higher electrical conductivity as compared to MoS_2, its wider inter-layer distance (~0.65 nm), narrow bandgap (1.33–1.72 eV), high resistance to photo-corrosion, high surface area layer, electrochemically active unsaturated Se-edges and close to zero Gibbs free energy edges for hydrogen adsorption.These properties are promising for different applications of $MoSe_2$ including hydrogen evolution [2], photocatalysis [3] and Li-ion batteries [4]. However, their low light absorption efficiency, recombination issues of the photogenerated electron–hole pairs and slow charge transfer of the intrinsic semiconducting 2H-phase are a handicap. An efficient strategy to surpass those intrinsic limitations are hybrid nanostructures using conducting supporting materials. In this regard, anodic TiO_2 nanotubes (TNTs) are excellent photoactive supporting material providing a high surface area, unique directionality for the charge separation, and highly effective charge collection. [5] Accordingly, we present anodic TiO_2 nanotubes homogenously decorated with $MoSe_2$ nanosheets by atomic layer deposition (ALD). In parallel, we address the current scarcity of convenient ALD Se precursors by the synthesis a set of new selenium precursors - alkysilyl $(R_3Si)_2Se$ and alkytin $(R_3Sn)_2Se$, and cyclic silylselenides compounds. Those Se precursors were extensively characterized and their reliability as ALD Se precursors explored [6,7]. Several compounds exhibited promising results to be convenient ALD Se precursor as will be presented in the presentation. The synthesis of the $MoSe_2$ nanosheets and their composites with TiO_2 NTs, their physical and electrochemical characterization, and encouraging results in electrochemical characterization, hydrogen evolution reaction (HER) and photocatalysis will be presented and discussed.

2:00pm NS1-WeA-5 Low Temperature Creation of Layered-MoS₂ Thin Films on Large Area High Aspect Ratio Substrates, *Anil Mane, D Choudhury, S Letourneau, J Elam,* Argonne National Laboratory

Thin layers of two dimensional (2D) materials mainly transition metal dichalcogenides (TMDs) and more specifically ultra-thin layered-MoS_2 semiconductor possess exceptional properties such as electrical, optical, magnetic, mechanical and chemical properties. This allows the exploration of internal quantum degrees of freedom of electrons and their potential for use in semiconductor microelectronics, optoelectronic, energy, and sensor and detector applications. These exciting results are being achieved mostly by using exfoliation of flecks from bulk MoS_2 crystal. However, the biggest challenge in realizing TMDs full potential has been the lack of scalable material synthesis methods for such films with high uniformity, conformality and interfacing with other materials such as oxides, metals and its process compatibility.

Among the various thin film deposition methods, atomic layer deposition (ALD) offers the best combination of precisely controlled layer-by-layer thin film growth at low temperature with very high conformality on complex substrates. Here we will present the growth of layered-MoS_2 thin films. To grow high quality layered–MoS_2 thin films, we have developed an ALD-based two step processing approach [1]: firstly the growth of well controlled ultra-thin layer of Mo metal using ALD followed by the sulfurization of the ALD Mo layer at various temperatures. This two-steps processing results in high quality layered-MoS_2 thin films on large substrates. For the Mo ALD process we used molybdenum hexafluoride (MoF_6) and Si_2H_6 precursors. We used in-situ QCM measurements to study interfacial and nucleation effects in the formation of continuous ultra-thin metal layer of Mo. The composition of both the ALD Mo and the layered MoS_2 layers was determined by X-ray photoelectron spectroscopy (XPS). Further, cross-sectional transmission electron microscopy (TEM) was performed to confirm the formation of layered MoS_2 on high aspect ratio trenches and Raman analysis to verify the signature of E^1_{2g} blue shift and A_{1g} red shift in the MoS_2 structure. In this presentation we will discuss the details of the two-step thin film growth process for creating layered MoS_2 layers via ALD Mo and subsequent sulfurization as well as the properties of the MoS_2 films.

[1] Anil Mane, Devika Choudhury, Steven Letourneau, Jeffrey Elam, (US patent application submitted 2018)

2:15pm NS1-WeA-6 Gas Sensing Characteristics of MoₓW₁₋ₓS₂ Synthesized by Atomic Layer Deposition, *Inkyu Sohn, Y Kim, M Lee, J Park, H Kim,* Yonsei University, Republic of Korea

Two-dimensional Transition metal dichalcogenide (2D TMDC) have been attracted great attention as gas sensing materials with high sensitivity in room temperature. [1] Because of this characteristic, 2D TMDC gas sensor could overcome the oxide-based semiconductor which need heating for gas sensing. Therefore, various 2D TMDC gas sensor studies have been ongoing. Recently, it has been shown that the gas sensor property could be improved through the changing the composition in $WS_{2x}Se_{2-2x}$ alloy. [2]

Here we report a synthesis method of $Mo_xW_{1-x}S_2$ alloys for gas sensor by atomic layer deposition. Layer controlled 2D MoS_2 and WS_2 were synthesized with $Mo(CO)_6$, $W(CO)_6$ and H_2S as precursors and reactant. For the first time, we systematically modulate the composition of $Mo_xW_{1-x}S_2$ alloys by changing the configuration of low-temperature ALD super-cycles. AFM and Raman spectroscopy results of $Mo_xW_{1-x}S_2$ alloys demonstrate that the thickness of alloy is accurately controlled by ALD. Also XPS results confirmed that composition of alloy is precisely controlled by ALD super-cycles. Furthermore, gas sensors fabricated by $Mo_xW_{1-x}S_2$ alloys were evaluated for NO_2 gas. It showed response time and recovery characteristics of $Mo_xW_{1-x}S_2$ alloy gas sensor is dramatically enhanced.

References [1] ACS Nano 10, 9287-9296 (2016) [2] ACS Appl. Mater. Interfaces 10, 34163-34171 (2018)

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 In₂O₃ 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/PtOx 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 (H₂* and H₂*+O₂*) on Al_2O_3 substrates. Different from the process with only H₂* as coreactant, an additional O₂* 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, O₂* 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 H₂* and O₂* 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 H₂* process vs. isolated particles for the H₂*+O₂* process. Secondly, to further tune the initial nucleation density, trimethylaluminum (TMA) exposures are introduced during the first ALD cycles of the Pd(hfac)₂/H₂* 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.

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