ALD Fundamentals
Room Van Eyck - Session AF4-MoA

Surface Science

Moderators: Annelies Delabie, IMEC, Virginia Wheeler, U.S. Naval Research Laboratory

4:15pm **AF4-MoA-12 Thickness Matters: Sintering Inhibition of Pt Nanoparticle Catalysts via Sequential Control of MgO Overcoats***, **Zhiwei Zhang**, M. Filez, M. Minjauw, J. Li, C. Detavernier, J. Dendooven,* Ghent University, Belgium

Overcoating of metal nanoparticles (NPs) to modulate the performance and thermal stability of catalysts has been proven as an effective method.[1] However, most studies focus on the catalytic effects that overcoats bring to the table, while researching their deposition processes is rare, but crucial to tailoring their properties. Here, atomic layer deposition (ALD) of magnesium oxide (MgO) overcoating on platinum (Pt) NPs is developed and investigated. The thickness of the MgO overcoat is precisely controlled by ALD. The prime function of the overcoat is to prevent rapid NP coarsening during the catalyst lifetime, here simulated by high-temperature annealing. During annealing, the NP properties are monitored in real-time by in-situ grazing incidence small angle X-ray scattering (GISAXS)[2,3].

$Mg(EtCp)_2$ and H_2O are used as Mg precursor and reactant of the MgO ALD process, respectively, while both 150 ℃ and 200 ℃ deposition temperatures were compared. The ALD process of MgO is initially more selective to Pt than to SiO_2 when using bare SiO_2 and sputtered Pt reference substrates. Via *ex-situ* XPS after MgO ALD on Pt NP-decorated SiO_2, the evolution of the relative Mg intensity as the function of the number of ALD cycles is shown (Figure 1). It is found that MgO shows a higher growth per cycle at 150 ℃ compared to 200 ℃, consistent with previous work. [4] In addition, during the first cycles, MgO mainly covers the Pt NPs, since the Pt signal decreases while the Si contribution remains constant. During the subsequent cycles, the Si intensity also decreases in XPS, suggesting MgO is now grown on the SiO_2.

In-situ GISAXS during annealing (from 25 ℃ to 800 ℃) is adopted to study the influence of MgO overcoating on the Pt NP coarsening behavior. A clear sintering delay is observed for both 150 ℃ and 200 ℃ sample sets with increasing number of MgO ALD cycles. However, the very first cycles (e.g. 1-3) do not contribute too much to the anti-sintering behavior which suggests that decorating the Pt NPs with MgO alone is insufficient for catalyst protection (Figure 2a). The sintering onset temperature is significantly delayed as the number of MgO cycles increases beyond the first cycles, which indicates the NPs thermal stability is mainly enhanced once MgO coats the SiO_2 substrate. This trend is generally applicable for both deposition temperatures, clearly showing a critical amount of MgO is necessary to prevent catalyst coarsening (Figure 2b).

[1] Brandon. J. O'Neill, et al. ACS Catal. 2015, 5, 1804.

[2] Jolien. D, et al. Nat. Comm. 2017, 8, 1074.

[3] Eduardo. S, et al. Nanoscale 2020, 12, 11684.

[4] Burton. B. B, et al. J. Phys. Chem. C 2009, 113, 1939.

4:30pm **AF4-MoA-13 Route to Low Temperature Area-Selective Atomic Layer Deposition of Ni***, **Himamshu Nallan**, X. Yang, J. Ekerdt,* The University of Texas at Austin

Nickel and nickel oxide are utilized within various device heterostructures for chemical sensing, solar cells, batteries, etc. Recently, the increasing popularity of flexible electronics to enable ubiquitous as well as large-area consumer electronics such as next-generation displays and sensors has driven interest in the development of low temperature fabrication processes for the integration of inorganic devices with polymeric substrates. Given the thermal constraints of the substrate as well as the desire for high-throughput and large-area scalability, ALD is a suitable fabrication method. Here we investigate the low temperature area-selective ALD (AS-ALD) of Ni by reduction of preformed NiO. Area-selective deposition of NiO is performed at 100 °C using bis(N,N'-di-t-butylacetamidinato)nickel(II) and water on SiO_2. NiO grows two dimensionally and without nucleation delay on oxide substrates; pre-patterned sp^3 carbon-rich resists inhibit the nucleation of NiO. In this way, first, carbon-free NiO may be patterned. Subsequent thermal reduction of NiO to Ni was investigated using H_2 (50 mTorr) and thermally-generated H atoms ($2.5x10^{-6}$ Torr chamber pressure). Due to relatively high surface energy, Ni films undergo dewetting at elevated temperatures when solid-state transport is enabled. Reduction of NiO to Ni is demonstrated at 100 °C and below using atomic hydrogen. *In-situ* x-ray photoelectron spectroscopy is used to determine oxidation state and *ex-situ* x-ray reflectivity and atomic force microscopy are used to probe the film thickness and surface morphology, respectively.

4:45pm **AF4-MoA-14 Hydrogen Plasma-Assisted Atomic Layer Deposition of sub-Nanometer AlO_x for Low-Impedance Contacts to GaN***, **Maximilian Christis**, A. Henning,* Walter Schottky Institute and Physics Department, Technical University of Munich, Germany*; J. Bartl,* Walter Schottky Institute, Physics Department, and WACKER-Chair for Macromolecular Chemistry, Department of Chemistry, Technical University of Munich, Germany*; A. Zeidler,* Walter Schottky Institute and Physics Department, Technical University of Munich, Germany*; B. Rieger,* Department of Chemistry, WACKER-Chair for Macromolecular Chemistry, Technical University of Munich, Germany*; M. Stutzmann, I. Sharp,* Walter Schottky Institute and Physics Department, Technical University of Munich, Germany

To achieve low-impedance tunneling contacts, wet-chemical pretreatments are usually required to prepare the semiconductor surface by removing the native oxide layer. Following this step, it is critical to produce continuous sub-nanometer thin coatings, which are challenging to achieve by atomic layer deposition (ALD) due to surface inhomogeneities and precursor steric interactions that result in island growth during film nucleation. Here, we report a novel atomic layer deposition process that alleviates the need for wet chemical etching and achieves full encapsulation of *c*-plane gallium nitride (GaN) with an ultimately thin (~3 Å) AlO_x monolayer, which is enabled by the partial transformation of the GaN surface oxide into AlO_x. This is accomplished using repeated cycles of trimethyl aluminum (TMA) and hydrogen (H_2) plasma exposure in a commercial plasma-enhanced ALD reactor (Ultratech Fiji G2). The introduction of ultra-thin AlO_x significantly modifies the physical and chemical properties of the surface, decreasing the work function and introducing new chemical reactivity [1][2]. Electrochemical cyclic voltammetry (CV) measurements show that the ultra-thin film poses a significantly smaller tunneling barrier to charge carrier transport than the thinnest homogenous AlO_x coatings achievable with the conventional TMA/H_2O ALD process.

Depending on the H_2 plasma parameters, the GaO_x surface oxide on GaN can be fully converted into AlO_x, reducing surface band bending and Schottky barrier height at the n-GaN/metal interface. Titanium-contacted n-doped GaN with an ultra-thin interfacial AlO_x layer shows a low contact resistance value and Ohmic behavior even before annealing. Unlike conventional Ohmic contacts to n-type GaN, this annealing-free contact allows for the integration of GaN with other semiconductors such as Si, for which the thermal budget is relatively low (≤ 400 °C). Given the high reactivity of TMA with surface oxides, the presented monolayer AlO_x deposition scheme likely can be extended to other dielectrics and III-V-based semiconductors, with significant relevance to applications in optoelectronics, chemical sensing, and (photo)electrocatalysis.

[1] A. Henning, J. D. Bartl, A. Zeidler, S. Qian, O. Bienek, C.-M. Jiang, C. Paulus, B. Rieger, M. Stutzmann, I. D. Sharp, *Adv. Funct. Mater.* 2021, 31, (33), 2101441.

[2] J. D. Bartl, C. Thomas, A. Henning, M. F. Ober, G. Savasci, B. Yazdanshenas, P. S. Deimel, E. Magnano, F. Bondino, P. Zeller, L. Gregoratti, M. Amati, C. Paulus, F. Allegretti, A. Cattani-Scholz, J. V. Barth, C. Ochsenfeld, B. Nickel, I. D. Sharp, M. Stutzmann, B. Rieger, *J. Am. Chem. Soc.* 2021, 143, (46), 19505–19516.

5:00pm **AF4-MoA-15 Tunable Ti^{3+}-Mediated Charge Carrier Dynamics of Atomic Layer Deposition Grown Amorphous TiO_2***, **Jesse Saari**, H. Ali-Löytty,* Surface Science Group, Tampere University, Finland*; M. Kauppinen,* Competence Centre for Catalysis and Department of Physics, Chalmers University of Technology, Sweden*; M. Hannula,* Surface Science Group, Tampere University, Finland*; R. Khan,* Photonic Compounds and Nanomaterials group, Tampere University, Finland*; K. Lahtonen,* Faculty of Engineering and Natural Sciences, Tampere University, Finland*; L. Palmolahti,* Surface Science Group, Tampere University, Finland*; A. Tukiainen,* Faculty of Engineering and Natural Sciences, Tampere University, Finland*; H. Grönbeck,* Competence Centre for Catalysis and Department of Physics, Chalmers University of Technology, Sweden*; N. Tkachenko,* Photonic Compounds and Nanomaterials group, Tampere University, Finland*; M. Valden,* Surface Science Group, Tampere University, Finland

Amorphous titania (am.-TiO_2) has gained broad interest in the field of photocatalysis due to its exceptional disorder-mediated optical and electrical properties compared to crystalline TiO_2 [1–3]. For instance, Ti^{3+} defects within am-TiO_2 can enable essential charge carrier transport through a protective am-TiO_2 photoelectrode coating in photoelectrochemical (PEC) cells [1], and Ti^{3+}-mediated visible light active amorphous “black” titania is regarded as a potential material for photocatalytic applications [2]. Atomic layer deposition (ALD) allows for tuning the defect composition and structure of am.-TiO_2 thin films via precursor choices and process parameters. Recent progress in computational analysis of am.-TiO_2 [3] has provided means to accurately correlate experimental insights with theoretical models, which can be utilized to tailor am.-TiO_2 coatings with desired properties.

This work examines how intrinsic titanium and nitrogen defects in am.-TiO_2 can be tailored in a controlled and elegant manner via tuning the ALD growth temperature between 100–200 °C when using tetrakis(dimethylamido)titanium(IV) (TDMAT) and water (H_2O) as the precursors. X-ray photoelectron spectroscopy (XPS) analysis and density functional theory (DFT) calculations allowed us to identify structural disorder-induced penta- and heptacoordinated Ti^{4+} ions ($Ti_{5/7c}^{4+}$), which are interrelated to the formation of Ti^{3+} defects in am.-TiO_2 without releasing oxygen, i.e., simultaneous formation of oxygen vacancies and interstitial peroxo species leading to defective but stoichiometric am.-TiO_2. When changing the ALD growth temperature from 100 °C to 200 °C, increase in Ti^{3+} concentration results in “black” TiO_2 and electrical conductivity via polaron hopping mechanism. Furthermore, transient absorption spectroscopy (TAS) shows that the high concentration of Ti^{3+} defects in “black” TiO_2 increases the carrier lifetime to the nanosecond time domain comparable to crystalline low-defect TiO_2. These insights into the formation of Ti^{3+} defects in am.-TiO_2 and into tuning the charge transport properties of ALD grown am.-TiO_2 are beneficial in wide range of applications, such as protective photoelectrode coatings.

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[2] V.-A. Glezakou, R. Rousseau, *Nat. Mater.* **17** (10), 856–857 (2018).

[3] D. Mora-Fonz, M. Kaviani, A. L. Shluger, *Phys. Rev. B* **102** (5), 054205 (2020).

5:15pm **AF4-MoA-16 Temperature-Time-Thickness (Ttt) Topography Maps: A Parameter Space Visualization Approach for ALD Processes**

***Parag Banerjee**, N. Berriel, U. Kumar, C. Feit,* University of Central Florida*; A. Arunachalam,* University of Texas at Dallas*; K. Basu,* University of Texas at Dallas, USA*; S. Seal,* University of Central Florida

ALD processes are developed and optimized in a limited, 1D process parameter space. The establishment of a steady growth rate within a temperature ‘window’ occurs via a series of experiments, where the independent variable – temperature is varied while holding pulse time constant. Similarly, saturation curves are obtained by varying the independent variable - pulse time (*i.e.,* dose) of the precursors while holding temperature constant. The demonstration of i) a viable temperature window and, ii) saturation curves constitute the establishment of an ALD process. The limitation of these approaches is that process parameter interdependencies cannot be studied. Thus, it is not possible to study the impact of temperature on dose saturation and *vice versa*. We hypothesize that these interdependencies hold a rich source of undiscovered ALD operation regimes and can lead to efficient process development, robust control and optimization outcomes.

In this talk, we present temperature-time-thickness (TTT) topography maps of ALD processes generated using *in situ* spectroscopic ellipsometry. Based on the methodology shown by our group recently[1], we demonstrate TTTof several ALD processes including, Al_2O_3, ZnO, CeO_2 and TiO_2 and plasma enhanced ALD (PEALD) of TiO_2. The visualization of these processes in 3D is through a combination of temperature and dose times for thermal ALD processes and as temperature and plasma power for PEALD processes. Saturation regimes of growth rates are observed as 2D surfaces i.e., plateaus and valleys. Precursor adsorption kinetics and thermodynamic parameters are extracted assuming ideal Langmuir adsorption behavior. We propose that a comprehensive database of TTT topographic maps can be used for deeper understanding of processes and to enable robust process control and optimization outcomes.

References:

[1]U. Kumar *et al.*, "In situ ellipsometry aided rapid ALD process development and parameter space visualization of cerium oxide nanofilms," *J. Vac. Sci. Technol., A,* vol. 39, no. 6, 2021, doi: 10.1116/6.0001329.

5:30pm **AF4-MoA-17 *in situ* TEM Study to Unravel Dynamic Processes during the Synthesis of Ultrathin Crystalline ALD Nanotubes**

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By using Atomic Layer Deposition (ALD), amorphous nanotubes can be successfully made of various metal oxides. However, the creation of **high quality crystalline nanotubes** for example made of sapphire is still a challenging process. To control the crystal structure of ALD based systems, it is indispensable to use microscopy techniques to understand the dynamic processes occurring on atomic scale. In this study, we present a universal approach to create **ultrathin crystalline** ALD nanotubes by using a comprehensive annealing process of specific core-shell nanowires. In combination with correlative *ex situ* observations, ***in situ* TEM** heating experiments unravel diffusion processes going on at small scales and give insights about temperature induced changes of the metal-ALD interface. Heating core-shell nanowires (e.g. Cu/ALD-Al_2O_3) at temperatures below 1000°C lead to the creation of hollowed amorphous ALD nanotubes. While the ALD framework is stable, the **diffusion of the metallic core material** is activated. The conformal ALD shell acts as barrier for the material diffusion and forces the core to continuous diffusion towards the cracked end of the nanowire (Figure 1a). As a first heat-induced phenomenon we observe the creation of voids, which is caused by vacancy agglomeration. Vacancies are induced during the growth process of the metal nanowires at elevated temperatures. However, heating for longer time, the voids and therefore the vacancies get compensated. The thermal activation for the material diffusion can be observed *in situ* with **high resolution** imaging (figure 1b). The energy barrier to release an atom from the bonded state can be overcome by heat treatment and the released atoms diffuse within the inner cavity of the ALD tube. The time for releasing atoms scales directly with the temperature (figure 1c). By holding the temperature, no core material is left within the ALD framework and an amorphous nanotube is created. The nanotubes have a **high aspect- ratio** with lengths up to 40 µm and a wall thickness of 4 nm. At temperatures above 1000°C, a **phase transition** is induced and a crystalline dense microstructure (κ-Al_2O_3) is achieved (figure 1d).
This type of ultrathin nanotubes shows promising optical and mechanical properties and are the ideal candidate for further functionalization processes.

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