Tuesday Afternoon Poster Sessions, June 30, 2020

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 Al_2O_3 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.

[1] Nesselberger, M. et al. Nat. Mater. 12 (2013) 919–924

[2] J. Lu et al. Science, 335(9), (2009) 105–1208

[3] J. Dendooven et al., Nat. Commun. 8 (2017) 1074

[4] E. Solano, J. Dendooven, et al., Nanoscale 9 (2017) 13159–13170

NS-TuP-10 Surface Functionalization and Atomic Layer Deposition of Metal Oxides on MoS_2 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 O_2 or H_2 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).

[3] T. D. Gould *et al.*, ACS Cataly. **5**, 1344 (2015).

Author Index

Bold page numbers indicate presenter