Thin Films Division
Room: 20 - Session TF+SE-ThM

Control, Characterization, and Modeling of Thin Films I
Moderators: Hilal Cansizoglu, University of California, Davis, Tansel Karabacak, University of Arkansas at Little Rock

8:00am **TF+SE-ThM1 *In Situ* Synchrotron Characterization Techniques Enabled Nanostructured Materials using ALD**, ***Yu Lei***, University of Alabama in Huntsville

To achieve the goal of rational design of next generation of advanced materials, we have been working on developing atomic layer deposition (ALD) as a promising method to tailor size and composition of nanostructured materials for a wide range of applications. Benefiting from self-limiting surface reactions, ALD enables conformal coatings of materials on three-dimensional substrates. The atomic level control of depositions makes it attractive to precisely synthesize the size and composition of nanomaterials. The size and composition of nanomaterials play important roles in achieving high performance in many applications. In this talk, we will discuss nanomaterials synthesized using Pd ALD and their applications in catalysis and energy storage. We will also illustrate that *in situ* characterization techniques such as synchrotron X-ray based X-ray absorption spectroscopy (XAS), X-ray pair distribution function (PDF), and FT-IR significantly advance our understandings of ALD in terms of surface chemistry and surface dynamics.

8:20am **TF+SE-ThM2 Probing the Atomic Scale Structure of Polar Oxide Interfaces**, ***Sanaaz Koohfar***, *D.P. Kumah*, North Carolina State University

Complex oxide heterostructures possess a wide range of functional electronic and magnetic properties including metal-insulator transitions, superconductivity, ferroelectricity and colossal magnetoresistance effects. At epitaxial interfaces formed between atomically thin complex oxide films, electronic, chemical and structural interactions can be used to effectively tune the physical properties of these materials. Using a combination of atomic-scale controlled thin film synthesis and high resolution synchrotron diffraction based imaging, we show that structural distortions at the interfaces between polar $La_{1-x}Sr_xMnO_3$ films and non-polar substrates can be effectively tuned by chemical modifications at these interfaces to control ferromagnetism in [001]-oriented $La_{1-x}Sr_xMnO_3$ films with thickness less than 1 nm. We show that atomic-scale chemical control at polar/non polar oxide interfaces provides a powerful route to engineer novel electronic and magnetic phenomena at complex oxide interfaces.

8:40am **TF+SE-ThM3 CVD Chemistry of Trimethylboron - Gas Phase Reactions and Surface Poisoning Effects**, ***Henrik Pedersen***, *L. Souqui, M. Imam,* Linköping University, Sweden, *R. Tonner,* Philipps Universität Marburg, *H. Högberg,* Linköping University, Sweden

Organoborons with short alkyl groups; trimethylboron (TMB), $B(CH_3)_3$, triethylboron (TEB), $B(C_2H_5)_3$, and tributylboron (TBB), $B(C_4H_9)_3$, were suggested as alternative, highly reactive, less-poisonous, non-explosive B-precursors in the mid 1990's[1].TEB was found to exhibit the best properties for CVD of boron-carbon films, making it a popular CVD precursor[2]. TMB and TBB were deemed not suitable as CVD precursors as no boron was found in the films deposited from these molecules. Consequently, these molecules are less investigated in CVD.

We study the gas phase chemistry of TMB in a thermal CVD process, using a combination of B-C film deposition experiments at several temperatures in both hydrogen and argon atmosphere and quantum chemical calculations for a wide range of possible gas phase reactions. We suggest that without assistance from the carrier gas, i.e. in argon ambient, TMB most likely decomposes by α-H elimination of CH_4 to form H_2CBCH_3. Methane is not highly reactive in CVD at deposition temperatures below 1000 °C, meaning that the H_2CBCH_3 species is the major film forming species. This correlates well with the B/C ratio of about 0.5 observed for films deposited in Ar at 700-900 °C. At higher temperatures, the B/C ratio of films increases as attributed to further decomposition to H_2BCH_3.

With assistance from the hydrogen carrier gas, TMB can also decompose to $HB(CH_3)_2$ that can further decompose to H_2BCH_3 and finally to BH_3, all with negative Gibbs free energies, albeit with some high energy barriers. This in combination with the unimolecular α-H elimination with a somewhat lower energy barrier, can explain the higher B/C ratios of films deposited in H_2.

Furthermore, we note that the onset of film deposition from TMB is 700 °C and at then at a very low deposition rate. Interestingly the film thickness does not increase with longer deposition time at 700 °C, indicating a surface poisoning effect. As this is seen both in Ar and H_2, we speculate that this is caused by CH_4 or H_2CBCH_3, which is currently the subject of our further investigations.

[1] J. S. Lewis et al. Chemical vapor deposition of boron-carbon films using organometallic reagents. *Mater. Lett.* **1996**, *27*, 327.

[2] M. Imam et al. Gas phase chemical vapor deposition chemistry of triethylboron probed by boron–carbon thin film deposition and quantum chemical calculations. *J. Mater. Chem. C* **2015**, *3*, 10898.

9:20am **TF+SE-ThM5 *In Situ* Synchrotron-based Characterization of Noble Metal ALD Processes**, *J. Dendooven,* ***Eduardo Solano****, R.K. Ramachandran, M.M. Minjauw,* Ghent University, Belgium, *A. Coati,* Synchrotron SOLEIL, France, *D. Hermida-Merino,* ESRF, France, *C. Detavernier*, Ghent University, Belgium **INVITED**

Supported noble metal nanoparticles (NPs) are widely used in heterogeneous catalysis because of their high resistance against chemical poisoning. Atomic Layer Deposition (ALD) can be used to synthesize noble metal NPs on different high surface area supports, and offers sub-monolayer control over the metal loading (atoms per cm^2 of support) [1]. However, an improved understanding of how the deposition parameters influence the formation and growth of noble metal NPs is required to fully exploit the tuning potential of ALD.

We developed a synchrotron-compatible high-vacuum setup that enables in-situ monitoring during ALD [2]. Using this setup and focusing on ALD of Pt with the $MeCpPtMe_3$ precursor at 300 °C [3], we present an in-situ investigation of Pt NP growth on planar SiO_2 substrates by means of X-ray fluorescence (XRF) and grazing incidence small-angle X-ray scattering (GISAXS). The surface density of Pt atoms was determined by XRF. Analysis of the GISAXS patterns [4] yielded dynamic information on average real space parameters such as Pt cluster shape, size and spacing. The results indicate a diffusion-mediated particle growth regime for the standard O_2-based Pt ALD process, marked by a decreasing average areal density and formation of laterally elongated Pt clusters. Growth of the Pt NPs is thus not only governed by the adsorption of Pt precursor molecules from the gas-phase and subsequent combustion of the ligands, but is largely determined by adsorption of migrating Pt species on the surface and diffusion-driven particle coalescence [5].

Next, we have studied the influence of the reactant type (O_2 gas, O_2 plasma, N_2 plasma, NH_3 plasma [6]) on the Pt NP growth. Surprisingly, a clear difference in island growth behavior was found for the oxygen- vs. nitrogen-based processes. The latter processes were marked by a constant average particle distance during the growth process. Particle dimension analysis furthermore revealed vertically elongated NPs for the N_2 and NH_3 plasma-based Pt ALD processes. Therefore, it is concluded that atom and cluster surface diffusion phenomena are suppressed during the nitrogen-based processes. Finally, this insight provided the ground for the development of a tuning strategy that is based on combining the O_2-based and N_2 plasma-based ALD processes and offers independent control over NP size and coverage.

[1] Lu et al., Surf. Sci. Rep. 71 (2016) 410. [2] Dendooven et al., Rev. Sci. Instrum. 87 (2016) 113905. [3] Aaltonen et al., Chem. Mater. 15 (2003) 1924. [4] Schwartzkopf et al., Nanoscale 5 (2013) 5053. [5] Mackus et al., Chem. Mater. 25 (2013) 1905. [6] Longrie et al., ECS J. Solid State Sci. Technol. 1 (2012) Q123.

11:00am **TF+SE-ThM10 *In-situ* FTIR Study of the Atomic Layer Deposition of Scandium Oxide Films using Bis(methylcyclopentadienyl)3,5-dimethylpyrazolatoscandium with Ozone and with Water**, ***Rezwanur Rahman****, J.P. Klesko, A. Dangerfield,* University of Texas at Dallas, *J.-S. Lehn, C.L. Dezelah, R. Kanjolia,* EMD Performance Materials, *Y.J. Chabal*, University of Texas at Dallas

Scandium oxide (Sc_2O_3) thin films have been thoroughly studied for their use in microelectronic devices.[1–2] However, processes for the atomic layer deposition (ALD) of Sc_2O_3 films are scarce, and have mostly involved $Sc(thd)_3$,[1] $ScCp_3$,[1] $Sc(MeCp)_3$,[2] and $Sc(amd)_3$[3] precursors. To date, the only mechanistic investigation has focused on the $Sc(MeCp)_3/H_2O$ process using *in-situ* time-resolved quadrupole mass spectrometry to probe the Sc_2O_3 ALD chemistry.[2]

Herein, we have explored the Sc_2O_3 ALD using bis(methylcyclopentadienyl)3,5-dimethyl pyrazolatoscandium ($Sc(MeCp)_2(Me_2pz)$) with ozone and with D_2O. This precursor reacts with hydroxyl-terminated silicon, Si(111)– SiO_2–OH, at 150 °C and appears to remain thermally stable to 450 °C. Between 225 and 275 °C, there is a clear ligand exchange with ozone observed in the differential IR absorption spectra involving the formation of intermediate formate and carbonate species (1400–1600 cm^{-1}) after each ozone pulse. A short incubation period (≤ 5 ALD cycles) is observed at 225 °C prior to the onset of steady-state ligand exchange. The signature for the formation of Si–O–Sc bonds (1240 cm^{-1}) is clearly present after cycles 1–2 for the ozone process at 275 °C. The Sc_2O_3 growth is quantified by X-ray photoelectron spectroscopy (XPS) and by spectroscopic ellipsometry (SE), from which a growth rate of ~0.3–0.9 Å/cycle is extracted over the 225–275 °C temperature range.

In contrast, there is no ligand exchange observed for the D_2O process within the same temperature range, although some deposition occurs. The deposition rate for the D_2O process calculated by XPS and SE, is ~1.3 Å/cycle within the 225–275 °C window, which is higher than the non-uniform growth rate measured for the ozone process within that temperature range. The higher growth rate and lack of ligand exchange observed with D_2O is tentatively attributed to a CVD component that dominates the film growth process.

1. Putkonen, M.; Nieminen, M.; Niinist ö, J.; Niinist ö, L.; Sajavaara,T. *Chem. Mater.* **2001**, *13*, 4701−4707.

2. Han, J. H.; Nyns, L.; Delabie, A.; Franquet, A.; Van Elshocht, S.; Adelmann, C. *Chem. Mater*. **2014**, *26*, 1404−1412.

3. de Rouffignac, P.; Yousef, A. P.; Kim, K. H.; Gordon, R. G. *Electrochem. Solid-State Lett*. 2006, *9*, F45–F48.

11:20am **TF+SE-ThM11 Ultra Fast Compositional Depth Profile Analysis for Microelectronics Applications**,

Agnès Tempez, Horiba France S.a.s., France, *Y. Mazel, J.-P. Barnes, E. Nolot,* CEA/LETI-University Grenoble Alpes, France, *S. Legendre*, Horiba France S.a.s., France, *M. Chausseau*, HORIBA Instruments Incorporated

Wouldn’t it be a considerable gain of time to be able to check the stoichiometry of just deposited thin films in a few minutes? A recently commercially available sputter-based technique called plasma profiling time-of-flight mass spectrometry (PP-TOFMS) is capable to produce, in a few minutes, nm-scale depth resolved profiles of all elements (including light elements) of the periodic table, over a wide dynamic range (from 100% down to ppm)[1]. A simple ratio of the amount of ions detected from a given layer provides a calibration free semi-quantification.

For such fast feedback purposes a PP-TOFMS instrument (Horiba Scientific, Horiba FRANCE SAS, France) has been installed in the clean room of the CEA-LETI in close proximity to process tools.

In this paper we will present data obtained from microelectronics and nanotechnology thin films to demonstrate the performance of the technique. It will be shown that PP-TOFMS can be used for determining composition, detecting contamination, measuring doping level, and characterizing diffusion mechanisms.

For example we will show the ease of detecting, identifying, and locating in depth the presence of unexpected contamination in magnetic Iron Cobalt Boron multi-layers. Another example will show the depth profile of a Germanium Antimony Tellurium alloy deposited on silicon oxide used for phase change memories, a type of non-volatile random access memory. PP-TOFMS depth profiles agree with TOF-SIMS and STEM-EDX analyses for both the first nanometers and the in-depth composition.

[1] A. Tempez et al., J. Vac. Sci. Technol. B (2016) 34

11:40am **TF+SE-ThM12 Surface Termination of Fe_3O_4(111) Films Studied by CO Adsorption**,

Francesca Mirabella, *E. Zaki, F. Ivars, S. Shaikhutdinov, H.-J. Freund,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *X. Li, J. Paier, J. Sauer*, Humboldt Universität zu Berlin, Germany

Although the (111) surface of Fe3O4 (magnetite) has been investigated for more than twenty years, substantial controversy remains in the literature regarding the surface termination [1, 2]. To shed more light on this issue, we performed CO adsorption studies on (111) and (001) oriented thin films, using in-situ infrared reflection absorption spectroscopy, temperature programmed desorption, and scanning tunneling microscopy. The experimental results were rationalized on the basis of theoretical calculations, thus leading to a unified picture in which the Fe_3O_4(111) surface is terminated by 1/4 monolayer of tetrahedrally coordinated Fe^{3+} ions on top of a close-packed oxygen layer as previously determined by low energy electron diffraction. However, surface defects play a crucial role in adsorption properties and most likely dominate chemical reactions on Fe_3O_4(111) when exposed to the ambient.

[1] Weiss, W. and W. Ranke, Surface chemistry and catalysis on well-defined epitaxial iron-oxide layers. Progress in Surface Science, 2002. 70(1-3): p. 1-151.

[2]Parkinson, G.S., Iron oxide surfaces. Surface Science Reports, 2016. 71(1): p. 272-365.

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