PCSI
Room Ballroom South - Session PCSI-2MoM

Atomic Layer Deposition & Etching I

Moderator: Anders Mikkelsen, Lund University, Sweden

9:15am **PCSI-2MoM-10 How Chemistry Drives Microstructure: Probing the Structure of sub-nm ALD Materials using *in-situ* FTIR and Synchrotron Techniques*, Angel Yanguas-Gil,*** Argonne National Laboratory **INVITED**

Atomic layer deposition is a thin film technique that is well known for its ability to coat high surface area materials.[1] However, it is also an ideal model system to understand how surface interactions drive the growth and evolution of microstructure of materials at the nanoscale: processes based on self-limited precursor-surface interactions are ideally suited for multimodal characterization, allowing the design of experiments and reactors that are optimized for specific characterization techniques.

To complement in-situ techniques such as quartz crystal microbalance, FTIR, or XPS, which focus primarily on the surface chemistry and electronic properties of materials, we have developed a modular in-situ reactor at the Advanced Photon Source that gives us access to multiple techniques that can provide detailed microstructural information, including X-ray scattering, XAFS, and PDF. [2]

In this talk I will show how we can apply these techniques to understand the interplay between surface chemistry and microstructure. I will focus on two examples: the synthesis of materials with a controlled distribution of dopants, and the evolution of microstructure from isolated cations to a bulk-like structure. The primary target of our research has been oxide-based materials such as ZnO, In_2O_3, MgO, HfO_2, and nanolaminates.[2-4] However, recently we have expanded to other materials systems, including hybrid organic/inorganic systems and 2D materials such as MoS_2.[5]

Overall, the development of new in-situ characterization tools at synchrotron radiation facilities worldwide is going to be an enabling capability that will help us understand the driving forces behind the emergence of crystallinity and the control of microstructure at low temperatures.

[1] A. Yanguas-Gil, Reactive transport in nanostructured materials, (Springer, New York, 2017).

[2] J. Klug et al, Rev. Sci. Instr. **86**, 113901 (2015)

[3] A. Yanguas-Gil et al, Chem. Mater. **23**, 4295 (2011)

[4] A. Yanguas-Gil et al, Chem. Mater. **25**, 4849 (2013)

[5] S. Letourneau et al, ACS Appl. Nano Mater. **1**, 4028 (2018)

9:45am **PCSI-2MoM-16 Mechanism of Hydrogen Plasma Modified ALD Growth of Metal-enriched Oxides Studied by *In-Situ* Mass Spectrometry*, Thomas Larrabee, S Prokes,*** Naval Research Laboratory

Modifying atomic layer deposition (ALD) growth by inserting argon/hydrogen plasma steps has been shown to alter the stoichiometry of oxides, driving metal-enriched films and lower oxidation states. Altering oxide stoichiometry is useful for changing the electrical conductivity, optical properties, bandgaps, and other device characteristics; often inaccessible from typical ALD growth. It has been unclear what the mechanism of the plasma-surface reactions and modifications to standard chemical (or "thermal") ALD growth has been in these processes, however. To elucidate this mechanism, a quadrupole mass spectrometer has been used to examine both reactant and product gas species during the ALD and plasma-modified ALD reactions of ZnO growth from diethyl zinc (DEZ), water, and H_2/Ar plasmas.

Comparison was made between thermal reactions, inserting H_2/Ar plasma after the metal precursor step, after the oxidant step, between sequential metal precursor steps before the oxidant step, and of argon-only plasma between sequential metal steps. Evidence for a mechanism involving metal-organic ligand desorption and further reaction with the plasma upon H_2/Ar plasma exposure is to be presented. No evidence demonstrating removal of oxygen atoms from the growing film, either by O_2 or H_2O gas evolution was found. Zinc metal enriching in ZnO growth occurs when the H_2/Ar plasma is inserted between sequential DEZ steps before the water steps. When the ethyl-terminated surface (after DEZ reaction) is exposed to plasma, primarily a small amount of methane (M/Z = 16) is produced, with a trace of ethane (M/Z = 28). This is due to ethane desorption and fast reaction with the large excess of hydrogen radicals from the plasma, cracking ethane to methane. After desorption of ethyl ligands, sites open up for additional adsorption of Zn in the second DEZ step. Plasmas containing hydrogen are required, as no ethane nor methane was observed with argon-only plasma.

To verify the generality of this mechanism for plasma-modified ALD using hydrogen plasmas to metal enrich ALD-grown oxides, additional modified oxide materials will also be presented (*i.e.* Nb_2O_5 to NbO_2, etc.).

9:50am **PCSI-2MoM-17 *In Situ* Investigation of Doping of 2D Semiconductors During Atomic Layer Deposition of Dielectrics*, Michael Moody,*** *J Shang, J Chen, A Henning, T Lohr, T Marks, L Lauhon,* Northwestern University

The sensitivity of ultrathin and 2-dimensional (2D) semiconductors to the surrounding environment provides a key opportunity for control of material and device behavior. Especially as substitutional dopants may be difficult to control and lead to increased scattering, adlayers are a promising approach to tuning the Fermi level in 2D semiconductors [1]. Despite the growing body of results using oxide dielectrics to this end, there is a lack of mechanistic investigation and understanding of scope and limitations.

In this talk, we build on results using atomic layer deposition of a tunable oxide to dope MoS_2 [2], and investigate mechanisms of growth and doping via *in situ* electrical measurements. Using a modified atomic layer deposition (ALD) reactor, we can measure field-effect transistors during dielectric growth at temperatures up to 300°C. As well as being more efficient than *ex situ* measurements for some studies (e.g. carrier concentration vs. thickness [3]), it enables otherwise-impossible observation of dynamics and changes with each half-cycle of deposition. We are therefore also positioned to learn about growth and reactivity. The first and to date only other such *in situ* electrical measurements identified that physisorption of ozone promotes dielectric growth on graphene [4]. We further observe reversible adsorption of metal-organics for nucleation of dielectrics on MoS_2. Still, while physisorptive nucleation of ALD is not unique to graphene, neither is it universal to van der Waals materials. Even moderately air-stable transition metal dichalcogenides such as $MoTe_2$ can differ notably in reactivity, growth mechanism, and thus semiconductor-dielectric interface. As such, *in situ* measurements are a powerful tool to understand growth on 2D materials.

[1] X. Zhang, Z. Shao, X. Zhang, Y. He, J. Jie, Adv. Mater. **28**, 10409 (2016).

[2] M. J. Moody, A. Henning, T. Jurca, J. Y. Shang, H. Bergeron, I. Balla, J. N. Olding, E. A. Weiss, M. C. Hersam, T. L. Lohr, T. J. Marks, L. J. Lauhon, Chem. Mater. **30**, 3628 (2018).

[3] W. Luo, M. Zhu, G. Peng, X. Zheng, F. Miao, S. Bai, X.-A. Zhang, S. Qin, Adv. Funct. Mater. **28**, 1704539 (2018).

[4] S. Jandhyala, G. Mordi, B. Lee, G. Lee, C. Floresca, P.-R. Cha, J. Ahn, R. M. Wallace, Y. J. Chabal, M. J. Kim, L. Colombo, K. Cho, J. Kim, ACS Nano. **6**, 2722 (2012)

9:55am **PCSI-2MoM-18 The Impact of the Annealing Temperature of the Seed Layer on the Growth and the Electrical Properties of the Main Layer in Atomic Layer Deposition of $SrTiO_3$ Films*, Sang Hyeon Kim,*** Seoul National University, Republic of Korea*; W Lee,* Northwestern University*; C An, D Kwon, D Kim, S Cha, S Cho, C Hwang,* Seoul National University, Republic of Korea

The atomic layer deposition of $SrTiO_3$ (STO) films was studied with $Sr(^iPr_3Cp)_2$ and $Ti(CpMe_5)(OMe)_3$ (Pr, Cp, and Me are propyl, cyclopentadienyl, and methyl groups, respectively) on Ru and Si substrates at 370 °C. The second STO layer (main layer) was grown on the annealed first 3-5 nm-thick STO layer (seed layer) to induce the in-situ crystallization. The electrical properties and the growth behavior of the main layer were studied with the variations in the seed layer condition, which was varied by varying the annealing temperature of the seed layer in the range of 450-650 °C. The STO films were remained in amorphous by annealing below 500 °C. They were started to be crystallized at 550-575 °C, and well crystallized at 600 °C or above. The growth rate of the main layer on the crystallized seed layer (0.15 nm/cycle) was 50 % higher than that on the amorphous seed layer (0.10 nm/cycle). As a result, the root-mean-square roughness of the main layer increased from 0.5 nm on the amorphous seed layer to 2.1 nm on the mixed phase (amorphous and crystalline) seed layer, where the main layer growth on the crystallized portion was higher than that on remaining amorphous portion. When the seed layer was well crystallized, the main layer roughness decreased again to 1.0 nm by the uniformly high growth rate across the entire surface. The dielectric constants of the main layers increased from 20 to 100 when the annealing temperature of the

seed layer increased from 450 to 650 °C due to the improvement of the film crystallinity.

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