Thin Films Division

Room 316 - Session TF+AS-ThA

In-Situ Characterization of Thin Films and Interfaces

Moderators: James Fitz-Gerald, University of Virginia, **Robert Grubbs**, IMEC Belgium

2:20pm **TF+AS-ThA-1 *In situ* IRRAS and XPS for the Characterization of Gas Interactions with MOF Nanofilms*, Tianhao Hu,*** Stony Brook University/Brookhaven National Laboratory*; C. Eads,* Max IV Laboratory, Sweden*; D. Stacchiola, A. Head,* Brookhaven National Laboratory

The need for novel solid catalysts for use in industry has demanded the development and the application of new techniques of *in situ* spectroscopy which enables the study of catalysts in conditions close to industry. Infrared spectroscopy and X-ray photoelectron spectroscopy (XPS) are complementary techniques that provide chemical and electronic structure information and have been widely used under *in situ* conditions. However, applying these techniques to insulating powders, such as metal-organic frameworks (MOFs), in controlled environments can be challenging. Here we grow films of archetypical MOFs, UiO-66 and UiO-66(NH_2), via a vapor-assisted conversion method and incorporate Pt catalytic sites (Pt@UiO-66(NH_2)) through solution impregnation. Using ambient pressure XPS, the electronic structure of the MOF and the oxidation state changes of the Pt are followed under various gas dosing conditions. Using infrared reflection absorption spectroscopy (IRRAS) and the adsorption of probe molecules N_2, CO, CO_2, and ethylene, under-coordinated metal sites and the acid strength of hydroxyl groups are characterized. IRRAS was also used to follow the oxidation of CO catalyzed by Pt@UiO-66(NH_2). Signature IR bands for gas phase CO_2 product and CO interacting with Pt^0 sites at 2024 cm^{-1} and 2098 cm^{-1} are found. This study highlights the information to be gained by applying traditional surface science techniques to nanoscale films for chemical, electronic, and reactivity characterization.

2:40pm **TF+AS-ThA-2 AVS Nellie Yeoh Whetten Awardee Talk: Characterizing Early-Stage Morphology and Defect Dynamics in Block Copolymer Thin Films with Environmentally Controlled High-Speed Atomic Force Microscopy*, Julia Murphy*[1]*,*** University of Chicago*; J. Raybin,* University of California at Berkeley*; S. Sibener,* University of Chicago

The spontaneous self-assembly of block copolymers into a variety of nanoscale morphologies makes these systems ideal candidates for next-generation lithography applications. However, industrial application requires long-range control over the domain order and orientation. Extensive work has been done to achieve linearity in nanopatterns on wafer size scales, but there is also a need to control the formation of point defects to generate, for example, T-junctions, jogs, and bends for semiconductor templating applications. As such, a fundamental understanding of block copolymer nanopattern formation and how structural defects contribute to instability in the films is crucial to achieve the perfection required to utilize these thin films as lithographic templates for nanotechnologies. Here, I present recent work on poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) thin films with environmentally controlled high-speed atomic force microscopy (AFM). By imaging films with minor variations in thickness above the glass transition temperature, we capture the early formation of hole, island, and continuous relief structures during thermal annealing. Additionally, we see how the striped nanoscale pattern develops in tandem with the changing mesoscale features. Confining the PS-*b*-PMMA in lithographic templates that are tapered in width, or wedge-shaped, generates dislocations at precise intervals locations in otherwise linearly aligned polymer domains. Examining polymer confined in these films reveals the pathways by which dislocations evolve and annihilate during thermal annealing, and how point defects in nanopatterns influence interfacial fluctuations in the surrounding polymer domains. Together, these studies contribute to the fundamental understanding of the dynamics and ordering of block copolymer thin films and reveal how topography - both native and imposed by lithography – impacts the nanoscale structure.

3:00pm **TF+AS-ThA-3 *In Situ* X-Ray Scattering Studies of the Influence of Plasma Properties on Epitaxial InN Growth by PEALD*, Jeffrey Woodward,*** *S. Rosenberg, D. Boris,* U.S. Naval Research Laboratory*; M. Johnson,* Syntek Technologies*; S. Walton, S. Johnson,* U.S. Naval Research Laboratory*; Z. Robinson,* SUNY Brockport*; N. Nepal,* U.S. Naval Research Laboratory*; K. Ludwig,* Boston University*; J. Hite, C. Eddy,* U.S. Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) enables the epitaxial growth of ultrathin indium nitride (InN) films at significantly reduced temperatures and with atomic-level control of layer thickness. These advantages are challenged by the inherent complexity of the growth process due to the reliance on plasma surface interactions [1], which necessitates a detailed understanding of the relationship between the plasma and the growth kinetics. To this end, synchrotron hard x-ray scattering techniques are well-suited to the *in situ* study of PEALD processes, as they are capable of operating in harsh environments during chemical reactions and can provide real-time information about the structural properties of the film. One such technique, grazing incidence small-angle x-ray scattering (GISAXS), probes nanoscale fluctuations in electron density averaged across the sample, which can provide an in-depth description of surface topography [2]. Initial studies of epitaxial InN growth under fixed plasma conditions demonstrated the utility of GISAXS for understanding the kinetics of PEALD processes, and showed that the growth proceeded in a Stranski-Krastanov mode where the critical thickness for island formation and the coarsening behavior were strongly influenced by temperature [3].

In this work, we utilize *in situ* GISAXS to investigate the early-stage PEALD growth kinetics of epitaxial InN within three different plasma regimes. The GISAXS data are supported by diagnostic studies of the plasma species generation in the inductively coupled plasma source as a function of the relative concentrations of the nitrogen/argon gas mixture used in the growth process. The growth mode is found to be correlated to the production of nitrogen species in the plasma, with high concentrations of atomic N species promoting Volmer-Weber growth and low concentrations promoting Stranski-Krastanov growth. Under conditions of high atomic N production, both the island radius and critical thickness for island formation are found to increase with ion flux. Furthermore, the InN island distance and areal density are found to change only during plasma exposure, and to continue changing with exposure even after the methylindium adlayer is believed to have fully reacted with the plasma. Our results demonstrate the potential to control the growth kinetics during PEALD of epitaxial films by intentionally accessing specific regimes of plasma species generation.

References

[1] D.R. Boris *et al.*, J. Vac. Sci. Technol. A **38**, 040801 (2020)
[2] G. Renaud, R. Lazzari, and F. Leroy, Surf. Sci. Rep. **64**, 255 (2009)
[3] J.M. Woodward *et al.*, J. Vac. Sci. Technol. A **37**, 030901 (2019)

3:20pm **TF+AS-ThA-4 Optical Monitoring of $MoCl_5$ and H_2S Delivery During Atomic Layer Deposition of MoS_2*, Berc Kalanyan,*** National Institute of Standards and Technology*; E. Jahrman,* National Institute of Standard and Technology*; J. Maslar,* National Institute of Standards and Technology

Low-temperature (<400 °C) deposition of transition metal dichalcogenide (TMD) films has been proposed as a potential route for fabricating diffusion barrier structures in field effect transistors and other electronic devices. Atomic layer deposition (ALD) is well-suited to this application due to its low thermal budget and high conformality, enabling its integration into back-end of line processing. Several publications have described the deposition of layered MoS_2 films by ALD, most commonly using $MoCl_5$ and H_2S as precursors[1–4]. Inorganic precursors may be desirable for their high thermal stability and the lack of organic ligands, which often are a source of impurities in deposited films. However, $MoCl_5$ is a low-volatility solid under typical delivery conditions and can readily form oxychlorides upon exposure to moisture. Delivery challenges associated with $MoCl_5$ are reflected in the large variety of delivery methods and conditions reported in the literature, for instance a vessel temperature range of 70 °C to 210 °C. Deposition studies using $MoCl_5$ and H_2S also show inconsistent results with respect to MoS_2 morphology, grain size, and composition, with no deposition reported under some conditions[5]. This lack of reproducibility could stem from variations in $MoCl_5$ flux observed under different delivery configurations. To address this possibility, we monitored the flow of $MoCl_5$ and H_2S as a function of delivery conditions using direct absorbance measurements. We measured vapor phase spectra of neat $MoCl_5$ and its common oxychlorides using an ultraviolet-visible (UV-vis) spectrometer under static conditions. To evaluate precursor delivery under flow, we

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[1] **AVS Nellie Yeoh Whetten Awardee**

implemented in-line gas analyzers each consisting of a broadband source, a filter for wavelength selection, and an avalanche photodiode. We evaluated the delivery rates of $MoCl_5$ and H_2S injected from vapor draw and direct draw vessels, respectively. In addition to vapor phase measurements, we used real-time spectroscopic ellipsometry to characterize precursor adsorption under varying delivery conditions. Using results from these measurements, we will discuss the reproducibility of $MoCl_5$ and H_2S delivery rates and potential implications for MoS_2 deposition.

[1] R. Browning et al., Mater. Res. Express **2**, 035006 (2015).

[2] A. Valdivia et al. Vac. Sci. Technol. Vac. Surf. Films **34**, 021515 (2016).

[3] L. Liu et al., Nanotechnology **28**, 195605 (2017).

[4] W. Ahn et al., Phys. Status Solidi RRL – Rapid Res. Lett. **15**, 2000533 (2021).

[5] M. Mattinen et al., Adv. Mater. Interfaces **4**, 1700123 (2017).

3:40pm **TF+AS-ThA-5 Temperature-Time-Thickness (TTT) Topography Maps: A Parameter Space Visualization Approach for ALD Processes***, **S. Novia Berriel**, C. Feit, U. Kumar,* University of Central Florida*; A. Arunachalam,* University of Texas at Dallas*; S. Seal,* University of Central Florida*; K. Basu,* University of Texas at Dallas*; P. Banerjee,* University of Central Florida

In atomic layer deposition (ALD), an optimized process is characterized by its stability, predictability, and self-limiting nature. Each of these characteristics is quantified individually with separate sets of experiments. For stability, temperature is varied while holding pulse time constant. Similarly, a process's self-limiting nature is determined by saturation curves, varying the pulse time (i.e., dose) of the precursors while holding temperature constant. These data are usually presented in such as way as to imply no interdependency between them. This is a limited view of process optimization that will only yield partial understanding of deposition characteristics. We propose the information held in the interdependencies of these parameters can lead to improved process development and better control of final film properties.

We have used in situ spectroscopic ellipsometry to capture temperature-time-thickness (TTT) topography maps of ALD processes. The TTT contour plots are 3D visualization maps that demarcate dose saturation times, temperature windows, and corresponding growth rates. Based on a methodology recently published by our group[1], we demonstrate TTTs of several thermal ALD processes including CeO_2, Al_2O_3, ZnO, TiO_2, as well as plasma enhanced ALD (PEALD) of TiO_2. These topographies collectively show stability, adsorption, and reaction (i.e., thermodynamic) characteristics of the precursor reactant molecules. TTT curves are also obtained as single-substrate experiments, thus reducing process development times and resource consumption. We propose a comprehensive database of TTT diagrams can be used for improved process development and can eventually provide guidance towards the development of precursors finely tuned to the requirements of ALD processes.

[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.

4:00pm **TF+AS-ThA-6 Surface Functionalization of Cu with Inhibitors to Enable Area-Selective Atomic Layer Deposition***, **Andrew Kaye**, S. Agarwal,* Colorado School of Mines

Area-selective atomic layer deposition (AS-ALD) is a bottom-up fabrication technique that can address challenges related to conventional lithography in the fabrication of integrated circuits. Cu is the predominant interconnect metal while SiO_2 is used as the dielectric. In this work, we explore the growth of a dielectric on SiO_2, with Cu as the nongrowth surface. Using *in situ* reflection-absorption infrared spectroscopy (RAIRS) we previously showed that thiols are effective inhibitors for Cu, and readily adsorb onto the surface by reducing the native CuO_x layer. However, thiols have a low vapor pressure and thermal stability on Cu. With these inhibitors, the Cu surface can be re-dosed between ALD cycles, which is essential in plasma-assisted ALD processes. Moreover, the inhibitor readily desorbs from the non-growth surface after AS-ALD, which eliminates surface cleaning steps that are normally required with self-assembled monolayers. Recently, several small molecule inhibitors for Cu have been reported in the AS-ALD literature including alkynes, aniline, and pyridine.

For alkynes, we show that a H_2 plasma cleaning step is required to reduce the native CuO_x layer on the Cu surface. When Cu wafers left in atmospheric conditions are exposed to an H_2 plasma, RAIRS shows that surface carbonates are removed, which indirectly confirms the presence of surface CuO_x. Specifically, we show that after we optimized the H_2 plasma cleaning duration at 200 °C, 5-decyne adsorbs on the Cu surface. The adsorption of 5-decyne is apparent from the appearance of –C=C– and –C≡C– stretching vibrations in the ~1600 and ~2200 cm^{-1} regions, respectively. In addition, we also observed the CH_x stretching and bending modes in the ~2900 and ~1400 cm^{-1} regions, respectively. Adsorption of 5-decyne on PVD and CMP Cu was observed over the temperature range of 28 to 150 °C. As the substrate temperature increased for the PVD Cu surface, the intensity of the –C=C– mode decreased while the –C≡C– mode increased, indicating that chemisorption is favored at lower temperatures while strong physisorption is favored at higher temperatures. At higher temperatures, the CH_x stretching and bending mode intensities decreased, indicating lower 5-decyne adsorption. ALD of Al_2O_3 on Cu with 5-decyne as an inhibitor was tested with dimethyl aluminum isopropoxide (DMAI) and H_2O. Even at sub saturation doses of DMAI, AS-ALD was not observed. We will also compare 5-decyne as an inhibitor with aniline and pyridine, which have been demonstrated as more promising candidates.

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