Thin Films Division
Room A124-125 - Session TF+AS+EL+PS+RA-ThA

Characterization of Thin Film Processes and Properties
Moderators: Richard Vanfleet, Brigham Young University, Virginia Wheeler, U.S. Naval Research Laboratory

2:20pm **TF+AS+EL+PS+RA-ThA-1 Phase Separation in III-V Semiconductor Thin Films**, *Mark Twigg*, N Mahadik, N Kotulak, S Tomasulo, M Yakes, U.S. Naval Research Laboratory **INVITED**
Phase separation in III-V semiconductor alloys remains a problem that limits the performance of electronic materials. As the first stage in a comprehensive program addressing this issue, we have begun investigating an alloy system in which only the group III elements differ: InGaAs. Lattice-matched InGaAs alloy films were deposited at three temperatures (400, 450, and 500C) by molecular beam epitaxy on a (001) InP substrate.

According to kinetic instability theory, the critical temperature for spinodal phase separation in InGaAs is 814C, a temperature well above the growth temperatures used in this study [1,2]. Dark-field (DF) cross-sectional transmission electron microscopy (XTEM), using the composition sensitive g=002 reflection, was used to determine the amplitude of composition modulations averaged over the thickness of the XTEM sample. The amplitude of composition modulation was found to decrease with increasing growth temperature, yielding values of 0.6, 0.4, and 0.3 atomic percent for the growth temperatures 400, 450, and 500C, respectively, a trend in accord with kinetic instability theory. X-ray reflectivity and 2-dimensional small angle x-ray measurements also indicate that the 400C growth shows significantly greater phase separation than the 450 and 500C growths. Atom probe tomography indicates that the amplitude of composition modulation for the 400C growth is approximately 1 atomic percent, a value that compares favorably with the 0.6 atomic percent measured by DF XTEM.

The range of wavelengths for lateral composition modulation is found to extend from approximately 3 to 30 nm. According to the literature, such wavelengths have been found to depend on growth temperature for a number of III-V semiconductor alloys, in agreement with predictions based on surface diffusion. Measurements of the composition modulation wavelength as a function of temperature have been performed by analyzing DF XTEM images recorded using the g=220 diffraction vector, from XTEM samples with the glue line along the rapidly-diffusing [110] direction. Fast Fourier Transform (FFT) power spectra recorded from each image allowed the dominant composition modulation wavelengths to be determined. Analyzing these wavelengths as a function of temperature yields the same activation energy (0.55 eV) as that found in surface diffusion measurements for In adatoms on the (001) InGaAs surface [3]; thereby confirming the role of surface diffusion in phase separation driven composition modulations.

[1] F. Glas, Phys. Rev.B, 62, 7393 (2000).

[2] I. P. Ipatova, V. G. Malyshkin, and V. A. Shchukin, J. Appl. Phys. 7198 (1993).

[3] Stevens et al., J. Appl. Phys. 121, 195302 (2017).

3:00pm **TF+AS+EL+PS+RA-ThA-3 In-Situ Spectroscopic Monitoring of Methylamine-Induced Hybrid Perovskite Phase Transitions**, *Jonathan Meyers*[1], L Serafin, J Cahoon, University of North Carolina at Chapel Hill
Lead halide perovskites have shown remarkable promise for use in thin film optoelectronic devices such as photodetectors, light-emitting diodes, and solar cells. Methods for casting thin films of perovskite have been extensively studied, and great improvements have been made in an effort to improve device efficiency and stability. A few reports have suggested some benefits to processing or post-processing techniques in a methylamine (MA) atmosphere, including healing grain boundary defects to create pinhole free films with grains on the order of tens of microns and improving crystallinity. The process can be observed spectroscopically as the MA induces a reversible phase change which bleaches the dark perovskite film. In this work, we perform the MA-treatment in a vacuum reactor while monitoring in-situ the UV-visible spectral response correlated with temperature and MA partial pressure. Clear evidence is found for the existence of a solid intermediate phase in transitioning from $MAPbI_3(s)$ to $MAPbI_3 \cdot xMA(l)$ and back again. We construct a phase diagram and

demonstrate that the critical partial pressure of the phase transition changes from 10 to 500 torr between 25 and 120 °C. By tuning the kinetics of film crystallization, compact films with domains up to 80 μm can be produced.

3:20pm **TF+AS+EL+PS+RA-ThA-4 Angle-Resolved HAXPES Analysis of Al_xO_y and Cu_xO_y Layers formed by Metal Salt Diffusion into a poly 2-vinylpyridine (P2vP) Polymer Layer**, *Pierre Mani*, Universidad Autonoma de Ciudad Juarez, México; *M Snelgrove*, Dublin City University, Ireland; *P Rueff*, Synchrotron SOLEIL, France; *R Lundy*, Trinity College Dublin, Ireland; *J Bogan, R O´Connor*, Dublin City University, Ireland; *J Enríquez*, Universidad Autonoma de Ciudad Juarez, México; *M Morris*, Trinity College Dublin, Ireland; *G Hughes*, Dublin City University, Ireland
This work is motivated by the desire to develop a semiconductor device patterning technology based on precursor infiltration into block copolymer materials. Developing an understanding of the preferential infiltration of metal precursors into one of the polymer blocks is of critical importance to advance this patterning approach. In this study, metal salts were used as a means to diffuse metal ions into poly 2-vinylpyridine (P2VP) polymer brush layers (~4 nm), which had been deposited by spin coating onto silicon substrates. Thin P2VP films infused with aluminum nitrate and copper nitrate by a wet chemical process were analyzed with angle resolved hard x-ray photoelectron spectroscopy (AR HAXPES). This photoemission based technique gives a lot information about a variety of core levels.[1] The large sampling depth of HAXPES measurements (20-30nm) enabled details of the chemical composition of the thin film to be characterized and subsequent angle-resolved HAXPES measurements offered a robust analysis of the interfaces and discrete layers that are present in the films. These measurements displayed evidence of bonding interactions between the elements in the polymer film and the infiltrated salts, which assists in developing an understanding of the infiltration process which needs to be optimized for device fabrication applications.[2]

[1] P. G. Mani-Gonzalez, M. O. Vazquez-Lepe, F. Espinosa-Magaña, and A. Herrera-Gomez J. Vac. Sci. Technol., A 31, 010601 (2013).

[2] C. Cummins and M. A. Morris. Using block copolymers as infiltration sites for development of future nanoelectronic devices: Achievements, barriers, and opportunities. Microelectron Eng., 195:74–85, 2018.

4:00pm **TF+AS+EL+PS+RA-ThA-6 Obtaining Smooth Surfaces and Measuring Surface Roughness**, *Steven M. George*, University of Colorado at Boulder **INVITED**
Smooth surfaces are important in many areas including friction, adhesion, optics and film growth. Smooth surfaces can be obtained from rough surfaces using chemical mechanical polishing (CMP). Rough surfaces can also be smoothed using atomic layer deposition (ALD) if the conformal ALD film thickness is comparable with the lateral length scale of the roughness. In addition, rough surfaces can be smoothed using isotropic thermal atomic layer etching (ALE) if the ALE etch depth is comparable with the width of the surface asperities. Quantifying the degree of surface roughness after CMP, ALD or ALE is challenging. Surface roughness can be obtained using atomic force microscope (AFM) or x-ray reflectivity (XRR) measurements. However, the AFM and XRR techniques do not always agree. Some of the inconsistencies are attributed to the different lateral length scales for the AFM and XRR measurements. Using both AFM and XRR to characterize surface roughness is recommended for reliable measurements. In addition, XRR measurements for surface roughness should include both specular and diffuse off-specular scattering.

4:40pm **TF+AS+EL+PS+RA-ThA-8 Characterizing Ultra-thin Layer Growth and Area Selective Deposition using High Resolution Low Energy Ion Scattering (LEIS)**, *Thomas Grehl*, IONTOF GmbH, Germany; *P Brüner*, ION-TOF GmbH, Germany; *V Pesce, B Pelissier, R Gassilloud, C Vallée*, Laboratoire des Technologies de la Microélectronique (LTM), France
When depositing ultra thin films of only very few nm of thickness, the characterization of the early stages of film growth is crucial for the quality of the film. For example, the initial thickness distribution before layer closure, created by the nucleation mechanism, will often remain after the film is complete. To analyze these early stages of growth requires very surface sensitive analytical techniques with good detection limits.

Specifically for area selective deposition, the demand for characterization increases even further. The deposition processes get more complex, involving atomic layer or plasma etching to remove nucleation on blocked areas. This also requires means of characterization, determining the effects of etching steps on the film being created, possible contamination and the level of success of the blocking.

[1] **National Student Award Finalist**

One technique specifically suited for this application is Low Energy Ion Scattering (LEIS). By scattering noble gas ions from the surface of the sample, the mass of the atoms in the outer atomic layer is determined non-destructively. Due to specific charge exchange processes, the peaks in the scattering spectrum correspond only to the outer atomic layer, making LEIS the most surface sensitive technique to determine the elemental composition of a surface.

In addition, information from deeper layers is available in two ways: First of all, features in the spectrum contain information about the first few nm of the sample – especially for heavier elements, the in-depth distribution can be determined non-destructively. For more complex systems or light elements, sputter depth profiling can be applied as well.

In this presentation, we will illustrate the main features of LEIS on ALD films. The main part will be on an area selective deposition (ASD) process for Ta_2O_5 films on TiN or Si. Here, plasma-enhanced ALD (PE-ALD) and various plasma or ALE like etching processes, all using fluorine-containing compounds, are used to develop a super-cycle scheme for ASD. We show the effect of the different etching methods and use sputter depth profiling to determine the distribution of F – a light element not accessible to non-destructive depth profiling in LEIS. An important result is the distribution of F close to the surface, in the bulk of the film, or at the interface.

Besides this, some further sample systems will be used to highlight the use of LEIS for ultra-thin film characterization.

5:00pm **TF+AS+EL+PS+RA-ThA-9 Real-Time Monitoring of Aluminum Oxidation Through Wide Band Gap MgF_2 Layers for Protection of Space Mirrors**, B Johnson, T Avval, G Hodges, K Membreno, D Allred, *Matthew Linford,* Brigham Young University

Because of its extraordinary and broad reflectivity, aluminum is the only logical candidate for advanced space mirrors that operate deep into the UV. However, aluminum oxidizes rapidly in the air, and even a small amount of oxide (as little as a nanometer) can have a noticeable, detrimental impact on its reflectivity at short wavelengths. Thin films of wide band gap materials like MgF_2 have previously been used to protect aluminum surfaces. Here we report the first real-time, spectroscopic ellipsometry (SE) study of aluminum oxidation as a function of MgF_2 over layer thickness, which ranged from $0 - 6$ nm. SE data analysis was performed vis-à-vis a multilayer optical model that included a thick silicon nitride layer. The optical constants for evaporated aluminum were initially determined using a multi-sample analysis (MSA) of SE data from MgF_2 protected and bare Al surfaces. Two models were then considered for analyzing the real-time data obtained from Al/MgF_2 stacks. The first used the optical constants of aluminum obtained in the MSA with two adjustable parameters: the thicknesses of the aluminum and aluminum oxide layers. The thicknesses obtained from this model showed the expected trends (increasing Al_2O_3 layer thickness and decreasing Al layer thickness with time), but some of the Al_2O_3 thicknesses were unphysical (negative). Because the optical constants of very thin metals films depend strongly on their structures and deposition conditions, a second, more advanced model was employed that fit the optical constants for Al, and also the Al and Al_2O_3 thicknesses, for each data set. In particular, the Al and Al_2O_3 thicknesses and optical constants of Al were determined in an MSA for each of 50 evenly spaced analyses in each four-hour dynamic run performed. The resulting optical constants for Al were then fixed for that sample and the thicknesses of the Al and Al_2O_3 layers were determined. While the first and second models yielded similar Al and Al_2O_3 thickness vs. time trends, the film thicknesses obtained in this manner were more physically reasonable. Thicker MgF_2 layers slow the oxidation rate of aluminum. The results from this work should prove useful in protecting space mirrors prior to launch. Detailed surface/material analysis by X-ray photoelectron spectroscopy will also be shown, as well as more advanced SE modeling.

5:20pm **TF+AS+EL+PS+RA-ThA-10 Visualization of Ultrafast Charge Motion in Thin Films via THz Emission Spectroscopy**, *Aaron Lindenberg,* Stanford University **INVITED**

We describe a method for probing ultrafast time-dependent currents in thin films and heterostructures by recording the associated emitted electromagnetic fields. This detection scheme offers direct sensitivity to the flow of charges at the atomic-scale and enables a real-time probe for investigating ultrafast charge transfer processes at molecular interfaces. Applied to transition metal dichalcogenide heterostructures having a staggered (Type-II) band alignment, we observe a burst of electromagnetic radiation at terahertz frequencies following above gap excitation. The emitted electric field transients encode information about the charge transfer within the heterostructure. The polarity of the emitted field reflects the direction of the charge transfer and the polarity is reversed as the order of the bilayer within the heterostructure is altered. We find that the charge transfer proceeds at an ultrafast rate (~100 fs) indicating a remarkable efficiency for the charge separation across these atomic-scale bilayers.

We will also describe initial experiments and coupled theoretical efforts probing charge separation and ultrafast photovoltaic responses in multiferroic BFO periodic domain structures. We show that charge separation occurs dominantly at the domain walls and provide a quantitative estimate of the efficiency of this process.

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