Thin Films
Room 115 - Session TF2-FrM

Thin Films: Characterization and Fundamentals

Moderators: Mark Losego, Georgia Institute of Technology, **Virginia Wheeler**, U.S. Naval Research Laboratory

10:30am TF2-FrM-10 Variable-Angle, Spectroscopic Ellipsometry Studies of the Repeated Application of First Contact Polymers on Optical Surfaces, *Joshua Vawdrey*, Brigham Young University; *J. Hamilton,* University of Wisconsin, Platteville; *D. Allred,* Brigham Young University

First Contact Polymer™ (FCP) is an adhesion-based, cleaning polymer that has been shown to remove molecular and particulate contamination from surfaces. Applying, allowing to dry, and then peeling off a layer of FCP from a contaminated surface embeds and removes contaminants. While a single peel-off has been observed to be effective at removing both particulate and molecular contaminants, the effect of consecutive fresh applications and peel-offs on the same surface has not been extensively studied. This is important since FCP is used to protect optical surface in storage. Using variable-angle, spectroscopic ellipsometric (VASE) data, modeled with J.A. Woollam Inc. software, CompleteEase, we addressed the questions: can surfaces be cleaned multiple times recovering the same clean surface each time? And what formulations are suitable for hygroscopic materials like lithium fluoride? One set of thin-film materials studied were three that are important materials in silicon microelectronics: native oxide on "bare" silicon wafer pieces, CVD silicon nitride on silicon wafers, and thermal silicon dioxide on silicon wafers. In addition, surfaces important in thin-film optics including far ultraviolet (FUV) were examined. These were metal fluoride thin films on evaporated aluminum. At each iteration in the study, we removed the layer of FCP coating each sample, measured the surface at several different spots with VASE, reapplied FCP and stored the samples for a designated time. Control samples, which received no FCP but were stored with the others, were also measured iteratively. We observed a reduction in the top-layer thickness of both silicon and CVD silicon nitride on silicon samples after cleaning impure solvent residue off the surface- We interpret this as FCP can effectively remove physisorbed materials from such surfaces yielding atomically clean surface in the absence of can be absorbed layers. We observed that the apparent native oxide layer on both FCP-coated samples and control samples increased with time. This could be due to the deposition of adventitious carbon from the environment. There is a slight increase--about an eighth of an angstrom per repeated peel-off, in the apparent top-layer thickness of the native oxide on Si samples. Cleaning fluorides proved to be more challenging. This is due to affinity of some fluorides particularly LiF to water. We determined condition under which some fluorides can be effectively cleaned without trapping water. Coatings suitable for long-term storage of fluorides are still under investigation.

10:45am TF2-FrM-11 EnviroMETROS – A Novel Surface and Multilayer Thin Film Analysis Tool, *Paul Dietrich*, F. Mirabella, S. Boetcher, K. Kunze, O. Schaff, A. Thissen, SPECS Surface Nano Analysis GmbH, Germany

The new EnviroMETROS series transforms the realm of surface hybrid metrology by employing the key techniques of parallel detection angle resolved XPS (PARXPS) and multi-wavelength excitation. This method utilizes variable photon energies and emission angles operating under diverse environmental conditions for conducting chemical analyses of thin films and bulk materials. LEIS facilitates high surface sensitivity, while electronic characterization can be enhanced with UPS, IPES, and REELS. Integrated Raman and/or IR spectroscopy provide structural information, whereas XPS mapping and SEM/SAM contribute to elemental surface maps correlated with morphology.

The relevance of ultrathin films and 2D materials in modern devices is continuously increasing, prompting a growing interest in the chemical analysis of these multilayer systems and their surfaces. A thorough characterization of stoichiometries, composition, and depth distribution of elements is crucial. The novel EnviroMETROS series serves as an ideal tool for routine analysis in this research and development field. It combines large sample and wafer handling with a photoelectron spectrometer offering variable information depth. When combined with optical and other analytical techniques, it enables depth-dependent composition analysis with unparalleled precision, reliability, and repeatability.

11:00am TF2-FrM-12 Passivation of Indium Phosphide Substrate Evaluated by Atomic Force Microscopy, *Fabiano Borges*, Federal Institute of Sao Paulo, Brazil; *C. Almeida,* PUC-Rio, LabSem, Brazil; *A. Silva,* Unicamp, CCS, Brazil; *O. Berenguel, C. Costa,* CNPEM, LNNano, Brazil; *G. Vieira,* IEAv, Brazil; *J. Diniz,* Unicamp, CCS, Brazil

Passivation involves coating a material to make it passive, i.e., less affected by the environment. In this study, passivation is achieved by depositing an aluminium oxide layer with prior surface treatment. Four surface treatments are considered: oxidation only (O), nitriding only (N), oxidation followed by nitriding (ON), and nitriding followed by oxidation (NO). An InP substrate is heated and exposed to an environment enriched with oxygen and/or nitrogen to form a thin film over the InP surface. Following this, a 20nm thick layer of aluminium oxide is deposited using atomic layer deposition (ALD). Thus, six different samples were generated for analysis: four with surface treatments, one of pure InP without any added thin film, and one of InP with only an aluminium oxide layer as the control sample for reference. This process presumably enables electricity to reliably penetrate the conducting InP below the surface while overcoming the surface states that hinder electrical conduction in the semiconducting layers. Different techniques such as Photoluminescence Spectroscopy, Atomic Force Microscopy, Electrostatic Force Microscopy, and X-ray Photoelectron Spectroscopy can be used for evaluating these treatments' effectiveness. The simplest one, analysing AFM images [1] alongside their RMS roughness values [2], reveals that samples with lower RMS roughness also possess fewer defects at their surfaces [3]. By defining the RMS roughness value of the control sample as the reference, all other values are lower: pure InP has a 15% lower RMS roughness, N has 10%, O has 20%, NO has 15%, and ON 10%. This suggests that the O sample is the smoothest and likely possesses the lowest surface defect density.

References

[1] Klapetek, P. (2006). Quantitative Data Processing in Scanning Probe Microscopy. William Andrew Publishing. 2013.
[2] Nečas, D., Klapetek, P. Gwyddion: an open-source software for SPM data analysis, Cent. Eur. J. Phys. 10(1) (2012). 181-188.
[3] Streetman, B. G., Banerjee, S. (2006). Solid state electronic devices. 6th ed. Pearson/Prentice Hall.

Acknowledgments

11:15am TF2-FrM-13 Adsorption of Aromatic Molecules on Metal Surfaces for Area-Selective Deposition: A Dft Study, *Matías Picuntureo*, Universidad Tecnica Federico Santa Maria, Chile; *I. Tezsevin, M. Merkx,* Eindhoven University of Technology, Netherlands; *S. Semproni, J. Chen, S. Clendenning,* Intel; *A. Mackus,* Eindhoven University of Technology, Netherlands; *T. Sandoval,* Universidad Tecnica Federico Santa Maria, Chile

Area-selective deposition (ASD) is a bottom-up fabrication technique that enables the targeted growth of materials on specific regions of a patterned substrate. For applications like creating bottomless diffusion barriers in semiconductor devices, ASD allows for the selective deposition of a barrier material on the interlayer dielectric while avoiding the metal at the bottom of the trench. A key strategy in ASD involves using small molecule inhibitors (SMIs) to prevent undesired material deposition on the non-growth areas. Previous studies demonstrated the potential of aniline as an SMI for Ru and Co surfaces, where the benzene ring plays a crucial role in surface inhibition through chemical passivation and physical shielding.[1-2]

In this study, we expand on this work by investigating the adsorption of various aromatic molecules—aniline, benzaldehyde, benzene, phenol, and toluene—as potential SMI candidates on Cu(111), Ru(0001), Mo(110), and W(110) surfaces using density functional theory (DFT) calculations. We focus on (i) the differences in adsorption behavior across these metal surfaces and (ii) the effects of different substituent groups on SMI-metal interactions, employing adsorption energy decomposition and charge transfer analysis.

Our results show a strong correlation connecting the interaction energies and the charge transfer between SMIs and surfaces. Metals with higher d-band center positions exhibit more favorable interaction energies in line with the increased electron transfer from the metal to the molecule. A

detailed charge transfer analysis reveals that most electron transfer is directed towards the phenyl group, underscoring its central role in adsorption. For benzaldehyde, additional electron transfer to the aldehyde group is observed, likely due to back-bonding between metal d-states and the π* orbitals of the C=O group, leading to stronger adsorption energies. Structural deformation analysis indicates that adsorption-induced strain is effectively compensated by enhanced charge transfer in the most exothermic cases, resulting in increased interaction strength.

Overall, this study provides a fundamental understanding of SMI-metal interactions at the molecular level, offering valuable insights for optimizing ASD processes in advanced semiconductor applications.

[1]*Chem. Mater. 2020, 32, 18, 7788–7795*

[2]*J. Chem. Phys. 2024, 160, 204701*

11:30am **TF2-FrM-14 In Situ Synchrotron GISAXS Studies of the Roles of Reactive and Energetic Species in Plasma-Enhanced Atomic Layer Deposition of InN**, *Jeffrey Woodward, D. Boris, M. Johnson, M. Meyer,* U.S. Naval Research Laboratory*; S. Rosenberg,* Lockheed Martin Space – Advanced Technology Center*; Z. Robinson,* SUNY Brockport*; S. Johnson,* Honeywell International*; N. Nepal,* U.S. Naval Research Laboratory*; K. Ludwig,* Boston University*; C. Eddy,* ONR Global*; S. Walton,* U.S. Naval Research Laboratory

The *in situ* characterization of atomic layer deposition (ALD) processes is challenged by the highly contaminating metal precursors, relatively high pressures, and harsh process environments which preclude the use of powerful electron-based techniques employed for ultrahigh vacuum growth methods.An alternative approach is to utilize hard x-ray techniques which are compatible with arbitrary pressures and allow for the placement of source and detector outside the reactor.Among such techniques, grazing incidence small-angle x-ray scattering (GISAXS) using synchrotron radiation is particularly well-suited to the study of ALD due to its exceptional surface sensitivity and ability to probe nanoscale structure in real time.[1]The application of GISAXS for the investigation of plasma-enhanced ALD (PEALD) is especially compelling when combined with *a priori* knowledge of the plasma properties, as even relatively simple plasmas may contain a broad range of species which influence the growth and resulting film properties.[2]

In this work, we investigate the growth kinetics of indium nitride (InN) PEALD using *in situ* GISAXS in a custom reactor.The InN films are grown on GaN using trimethylindium and N_2/Ar plasma as the metal precursor and reactant.Different regimes of plasma species generation are explored and are characterized by optical emission spectroscopy (OES) and Langmuir probe measurements.These plasma diagnostics are supported by modeling with the 2D Hybrid Plasma Equipment Model (HPEM), which is used to predict the fluxes of various reactive plasma species to the sample, including atomic N and metastable N_2.The growth mode is observed to be correlated to the concentration of atomic N, with high concentrations promoting island growth and low concentrations promoting layer-plus-island growth.Under conditions of high atomic N production, both the mean island radius and critical thickness for island formation are found to increase with ion flux. Furthermore, the mean InN island distance is 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.After identifying the low atomic N plasma condition as optimal, we then explore the influence of plasma exposure time from slightly undersaturated to optimized and excessive conditions.The InN growth mode is found to be layer-plus-island for all cases, with increased plasma exposure promoting redistribution of material from small surface features to large ones.

[1] H. Pedersen *et al.*, Cryst. Growth Des **23**, 7010-7025 (2023)
[2] J. M. Woodward *et al.*, J. Vac. Sci. Technol. A **40**, 062405 (2022)

11:45am **TF2-FrM-15 Thermal Atomic Layer Deposition of Low Resistivity Metallic Films for High Aspect-Ratio Via Seed**, *Dane Lindblad,* Forge Nano*; I. Stateikina, M. Guilmain,* MiQro Innovation Collaborative Centre (C2MI), Canada*; S. Harris,* Forge Nano*; X. Gaudreau-Miron,* MiQro Innovation Collaborative Centre (C2MI), Canada*; A. Dameron, M. Weimer,* Forge Nano

Scaling interconnects to increase device density is a critical bottle neck for a range of applications from complementary metal oxide semiconductor (CMOS) to microelectromechanical (MEMS) switches and other devices. Commonly, Cu is the interconnect metal of choice to fill vias but comes with significant challenges. A diffusion barrier is applied to ensure Cu leakage does not cause electrical breakdown between vias and a metal seed layer is required to ensure smooth and dense Cu electroplating. Uniform seed resistivity, correlated to thickness, is critical to produce low resistivity, void-free interconnects. Unfortunately, state-of-the-art processes for high quality metallic films are limited to line-of-sight techniques like chemical vapor deposition (CVD) or physical vapor deposition (PVD), limiting possible device pitch and architectures. When the aspect ratio increases above ~10:1 or there is a line-of-sight obstruction at least one of these layers are missing, resulting in insufficiently thin seed for Cu electroplating nucleation. This creates a void or thickness gradient resulting in pinch-off at the top and ultimately high line resistance or device failure. Fortunately, atomic layer deposition (ALD) can produce high density, low resistivity metal films for both Cu diffusion barrier and Cu electroplating seed applications. Here we report on a total solution using thermal ALD. Plasma enhanced ALD (PEALD) can produce quality metallic films at a reasonable thermal budget, unfortunately plasma processes have a limit to aspect ratios that can be coated conformally and have the added risk of surface plasma damage. Our all-thermal ALD solution has been demonstrated on Si vias ranging from 4:1 to 25:1 aspect ratio, an example of Cu electroplated in this solution is shown in Figure 1. First, a SiO_2 ALD film is deposited as a dielectric barrier, then a thin TiN layer is applied as a Cu diffusion barrier, followed by a low resistivity Ru film for Cu adhesion. A novel TiN thermal ALD process at 300°C has been developed alongside a high-quality Ru film with resistivity values <20 uΩ·cm which can be deposited on SiO_2, HfO_2, Pt, and TiN. When compared to PVD, the ALD stack produces dense, void free nucleation of Cu that remains well adhered to the Si via. Conversely, the PVD stack has voids at the bottom of the trench from poor adhesion of electroplated Cu and narrowing at the top from a resistivity gradient within the trench. This comparison demonstrates that the Ru seed provides sufficient adhesion for Cu electroplating and that the resistivity of the ALD Ru/TiN stack is low and consistent enough for conformal and dense Cu electroplating.

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