Plasma Science and Technology Division
Room B130 - Session PS+2D+SE+TF-FrM

Plasma Deposition and Plasma-Enhanced Atomic Layer Deposition

Moderators: David Boris, U.S. Naval Research Laboratory, Chenhui Qu, University of Michigan

8:20am **PS+2D+SE+TF-FrM1 Plasma-based Synthesis of 2D Materials for Devices on Flexible Substrates***, N.R. Glavin,* Air Force Research Laboratory*; **Christopher Muratore,*** Department of Chemical and Materials Engineering, University of Dayton **INVITED**

Synthesis of flexible two-dimensional electronic devices using low-cost, naturally abundant materials (e.g., MoS_2) directly onto inexpensive polymeric materials at economically viable scales enables use of their unique characteristics in grand challenge areas of energy, healthcare, and national security. Recently-proven approaches for low temperature, plasma-based 2D synthesis suitable for flexible substrates developed by the authors include growth of amorphous materials with subsequent photonic annealing to access crystalline domain sizes up to several microns. This approach has been demonstrated for synthesis of large area ultrathin monolithic layers as well as MoS_2/WS_2/BN multilayers with pristine interfaces, allowing interrogation of intrinsic properties of 2D materials and their heterostructures as they apply to diverse optoelectronic devices, with a current focus on molecular sensing. Advantages of plasma-based approaches will be discussed in terms of detailed kinetic studies of crystal formation and compositional evolution on the substrate surface. Correlations of structure, especially defect densities, to materials properties and device performance will be discussed in the context of diverse device applications including photodetectors and molecular sensors.

9:00am **PS+2D+SE+TF-FrM3 Homogeneous Ternary Oxides of Aluminum with Silicon, Molybdenum, and Niobium by Plasma Enhanced ALD by Sequential Precursor Pulses***, **Steven Vitale,*** MIT Lincoln Laboratory

Deposition of ternary oxide films by ALD is well known. In the vast majority of cases ternary films are deposited by sequential deposition of thin layers of the constituent binary oxides, such as Al_2O_3 / SiO_2. This nanolaminate approach allows for precise control of the global film stoichiometry and is a good solution for many applications, including optical coatings where the wavelength of light is much greater than the nanolaminate thickness thus the film appears quasi-uniform. The nanolaminate approach is less desirable for electronic applications which are sensitive to surface defect sites in the material which may acts as charge traps. For these applications a truly homogenous film which does not possess internal interface states is preferred. True homogenous ternary oxide growth by sequential precursor pulses before the oxidation step is much less well explored. In this work we grow homogeneous ternary oxides of $Al_xSi_yO_z$, $Al_xNb_yO_z$, $Al_xMo_yO_z$ by plasma enhanced ALD using sequential precursor pulses. The stoichiometry of the films is measured by XPS. Using this data we propose models of how the precursors interact with the surface under competitive adsorption. It is found that trimethyl aluminum (TMA) is so strongly adsorbed to the surface at unity surface coverage that ternary oxide growth is not possible if the surface is first exposed to TMA. However if the surface is exposed to the Si, Nb, or Mo precursor first, ternary oxide growth is achieved. The growth kinetics for the three films are markedly different, however, and we explain this through models of the adsorption energy of each precursor.

9:20am **PS+2D+SE+TF-FrM4 Piezoelectric Response of ZnO Thin Films Grown by Plasma-Enhanced Atomic Layer Deposition***, **Julian Pilz,** T. Abu Ali,* Graz University of Technology, Austria*; P. Schäffner, B. Stadlober,* Joanneum Research Forschungsgesellschaft mbH, Austria*; A.M. Coclite,* Graz University of Technology, Austria

ZnO is a direct band gap semiconductor with attractive piezoelectrical, optical, and electrical properties, particularly appealing for a variety of functional devices. Especially the utilization of piezoelectric properties of ZnO nanostructures for transforming mechanical to electrical energy has attracted much research interest. For most of these so called nanogenerators, solution based deposition methods have been applied to create the desired nanostructures, often lacking a precise control of the deposition parameters. Atomic layer deposition, on the other hand, allows conformal and uniform deposition on high aspect ratio structures with Å-level thickness control.

In this study, we investigate the piezoelectric response of ZnO thin films on flexible substrates as a starting point for piezoelectric nanostructures. The films are grown by plasma-enhanced atomic layer deposition (PE-ALD) to thicknesses below 100 nm by adapting diethylzinc and O_2-plasma as reactants. In comparison to thermal ALD (where diethylzinc and water are used as reactants), PE-ALD allows the deposition of films with higher resistivity, an important property to minimize the leakage of piezoelectric charges. Commercially available Polyethylenterephthalat (PET) coated with Indium Tin Oxide (ITO) serves as the flexible substrate and bottom electrode, respectively. The deposition of ZnO thin films is carried out at substrate temperatures between room temperature and 100 °C, as a change in preferential crystal orientation from (100) to (002) can be observed in this temperature range. The macroscopic piezoelectric characterization is performed in a home-built stamp station, in which a defined periodic force is exerted onto the samples and the generated piezoelectric charges are measured. Out of this, the longitudinal piezoelectric coefficient d_{33} can be obtained. Preliminary results show d_{33} coefficients > 7 pC/N, which is comparable to literature results. The piezoelectric characterization is made for the different samples to understand how the d_{33} coefficient changes for films deposited at different substrate temperatures and thus having different crystal orientation. Since the [002] is the polar axis in the ZnO wurtzite crystal structure, films with preferred orientation in this direction are therefore expected to show higher d_{33} coefficients.

The work lays the basis for developing functional piezoelectric generators and sensors in thin film form. However, the concepts can be easily transferred to depositions on lithographically defined templates in order to create nanostructured ZnO, which exhibits increased piezo response.

10:00am **PS+2D+SE+TF-FrM6 Plasma-enhanced Molecular Layer Deposition of Boron Carbide from Carboranes***, **Michelle M. Paquette,** R. Thapa, L. Dorsett, R. Bale, S. Malik, D. Bailey, A.N. Caruso,* University of Missouri-Kansas City*; J.D. Bielefeld, S.W. King,* Intel Corporation

Atomic layer deposition (ALD) research has exploded in this era of electronic miniaturization, smart materials, and nanomanufacturing. To live up to its potential, however, ALD must be adaptable to many types of materials growth. To extend the reach of this layer-by-layer deposition framework, researchers have begun to explore molecule based processes. Still relatively rare, existing molecular layer deposition (MLD) processes are limited and typically based on the condensation of "linear" 2D or "brush-type" organic polymer chains. To this end, icosahedral carborane ($C_2B_{10}H_{12}$) molecules provide an interesting target. Carboranes have been used in the plasma-enhanced chemical vapor deposition of boron carbide films for low-k interlayer dielectrics, neutron detection, and a variety of protective coatings. These are symmetric twelve-vertex molecules, known to form close-packed monolayers and to possess labile H atoms at each of the vertices capable of cross-linking in the presence of heat, plasma, or other energy source. As such, the carborane molecule is particularly intriguing as a novel MLD precursor for 3D growth, possessing unique symmetry, reactivity, and volatility properties not commonly encountered in traditional organic molecules. However, a challenge in developing a layer-by-layer process lies in achieving the selective coupling chemistry required, which in the case of molecular reagents requires typically exotic bis-functional derivatives. Herein we describe progress in developing a plasma-enhanced molecular layer deposition process based on carborane derivatives, where the plasma is exploited to create the surface functionalization necessary for selective coupling and to cross-link carborane layers. We investigate the deposition of several carborane derivatives on different functionalized surfaces with the application of various types of plasmas toward achieving controlled layer-by-layer growth of thin boron carbide films.

10:20am **PS+2D+SE+TF-FrM7 Gas Phase Kinetics Optimization Study for Scaling-up Atmospheric Pressure Plasma Enhanced Spatial ALD***, **Yves Creyghton,*** Holst Centre / TNO, The Netherlands, Netherlands

DBD plasma sources have been successfully integrated in spatial ALD equipment for low-temperature ALD (<120 °C) of metal-oxides. Applications involving (semi)conductive substrates require remote plasma operation. Radical losses during transport from remote plasma limit substrate speeds or demand excessive plasma flow rates. Proximity remote plasma sources were developed with sufficient radical flux even at low gas flow rates. The sources were demonstrated for ALD of InZnO for high mobility thin film transistors. Further optimization asks for deeper understanding of radical kinetics. In this contribution experimental and calculated data will be presented which allow insight in the radical gain and

loss processes. A reference temperature of 100 °C and gas flows in the range 2-10 slm (for a 4 cm wide source) were applied. Alumina depositions were carried out using TMA and 2% O_2-N_2 plasma gas. Deposited layers obtained for different relative height positions of the plasma source were analyzed. Growth per cycle (GPC) values indicate a strong decay of plasma reactivity for gaps > 0.5 mm. As O_3 --should not decay over such small distance, this indicates that the process is radical based. Surprisingly the GPC also shows a peak value at 0.1 mm (Fig. 1). O_3 and NO_x were measured in the plasma exhaust gas as a function of % O_2 (Fig. 2). The 1-2% O_2 for maximum NO appears to correspond with the optimal gas composition for both high GPC values and refractive index values close to 1.58 indicating high layer quality. This result suggests NO plays a role in downstream plasma radical formation. Further understanding of the role of plasma species such as N, metastable N_2(A) and NO has been obtained by modelling. Kinetic data sets for optimization of O_3 production have been implemented in a CFD model for the transport of plasma species from the remote plasma. For the analysis of modelling results, the reaction volume has been divided in 3 parts (1) the plasma ionization zone itself, (2) the flow dominated plasma source aperture and (3) the diffusional transport dominated surface reaction zone. The dominating reactions for gain and loss of O radicals differ much between zones (Fig. 3). As the main O radical formation in zone (2) is due to metastable excited N_2(A), in zone (3) reactions between N radicals and NO are the main source of O radical generation. In both zones, the main O radical loss process is due to generation of O_3. The experimentally validated model has been used for finding improved plasma process settings (source geometry, frequency, flow) allowing the further optimization of high-throughput plasma enhanced spatial ALD of metal oxides.

10:40am **PS+2D+SE+TF-FrM8 Taking Plasma ALD to the Next Level: From Fundamental Understanding to Selective 3D Processing**, *T.F. Faraz, K. Arts,* Eindhoven University of Technology, The Netherlands, Netherlands*; L. Martini, R. Engeln, H.C.M. Knoops,* Eindhoven University of Technology, The Netherlands*; **Erwin Kessels**,* Eindhoven University of Technology, The Netherlands, Netherlands **INVITED**

Current trends in semiconductor device manufacturing impose extremely stringent requirements on nanoscale processing techniques, both in terms of accurately controlling material properties and in terms of precisely controlling nanometer dimensions. Plasma-based processing remains key in next-generation device manufacturing with plasma-enhanced atomic layer deposition (PE-ALD or plasma ALD) being a method that has obtained a very prominent position in obtaining ultrathin films with atomic scale precision [1]. In this contribution the state-of-the-art of PE-ALD will be presented including latest insights into reaction mechanisms as well as some developments in plasma ALD equipment and emerging applications. Aspects such as the role of (energetic) ions, conformality in high aspect ratio structures, and selective processing will be discussed [2].

[1] H.C.M. Knoops, T. Faraz, K. Arts, and W.M.M. Kessels, J. Vac. Sci. Technol. A 37, 030902 (2019)

[2] T. Faraz, K. Arts, S. Karwal, H.C.M. Knoops, and W.M.M. Kessels, Plasma Sources Sci. Technol. 28, 024002 (2019).

11:20am **PS+2D+SE+TF-FrM10 Computational Investigation of Plasma Enhanced ALD of SiO_2**, *C. Qu,* University of Michigan*; P. Agarwal, Y. Sakiyama, A. LaVoie,* Lam Research Corporation*; **Mark J. Kushner**,* University of Michigan

Plasma enhanced atomic layer deposition (PE- ALD) of dielectric films typically consists of two steps – precursor deposition and oxidation. For example, in a SiO_2 PE-ALD process, the Si-containing precursor is often deposited in the feature without use of plasma while the oxidation step is performed by an oxygen containing plasma. In principle, the surface kinetics of both steps are self-terminating. Although the plasma step is performed using gas pressures of several to 10 Torr, in addition to O-atoms the fluxes onto the wafer contain energetic particles in the form of ions, photons, hot-neutrals and excited states. When performing PE-ALD in high aspect ratio (HAR) features, transport of these species into the feature determine the quality of the deposition. Optimizing the PE-ALD depends on control of these fluxes.

In this work, results from a computational investigation of reactor and feature scale processes in idealized PE-ALD of SiO_2 will be discussed. Reactor scale simulations of a capacitively coupled plasma sustained in Ar/O_2 mixtures were performed using the Hybrid Plasma Equipment Model (HPEM); and provided fluxes and energy distributions of radicals, ions, excited states and photons onto the wafer. Feature scale simulations were performed with the Monte Carlo Feature Profile Model (MCFPM). The idealized ALD process consists of a non-plasma first step using an Si-R (R indicates organic) precursor. The second step uses fluxes from the Ar/O_2 plasma to remove the organic and oxidize the Si site. The base-case features are moderate to high aspect ratio (AR = 7-20) vias and trenches. The metrics to evaluate the process are surface coverage of Si, O, R, stoichiometry, defect density, surface roughness and deposition rate.

In self-terminating processes, many of these metrics should scale with pt, where p is the probability of reaction and t is the step length. For example, a given surface coverage of Si-R or Si-O should depend on first order on pt. However, as deposition proceeds and a feature fills, the effective AR increases. When coupled with conductance limited transport into the feature, with increasing AR the value of pt to produce a given surface coverage increases. As the deposition proceeds and AR increases, stoichiometry and defect density begins to have a dependence on height inside the feature, as surfaces deep in the feature receive less exposure to the reactive fluxes. The consequences of ion- and photon-induced damages will also be discussed.

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11:40am **PS+2D+SE+TF-FrM11 Analyzing Self-limiting Surface Reaction Mechanisms of Metal Alkyl Precursors and Nitrogen Plasma Species: Real-time In-situ Ellipsometric Monitoring of III-nitride Plasma-ALD Processes**, ***Ali Okyay***, OkyayTech Inc., Turkey*; A. Mohammad, D. Shukla, S. Ilhom,* University of Connecticut*; B. Johs,* Film Sense LLC*; B.G. Willis, N. Biyikli,* University of Connecticut

ALD-grown films are vastly characterized via ex-situ measurements to quantify various material properties. However, gaining insight into the saturating surface reactions and growth mechanisms is only possible with real-time in-situ process monitoring of individual ALD cycles. While several in-situ measurement techniques have been employed in ALD research, in-situ ellipsometry stands out as one of the best options for real-time monitoring surface reactions. The promising potential of in-situ spectroscopic ellipsometry has already been demonstrated for a number of materials grown by remote plasma-ALD. Here, we verify that cost-effective multi-wavelength ellipsometer (MWE) can also be used effectively for real-time in-situ analysis of plasma-ALD growth cycles. We demonstrate for the first time that real-time dynamic in-situ MWE measurements convey not only accurate film deposition rate, but as well resolve single chemisorption, ligand removal, and nitrogen incorporation events with remarkable clarity. Moreover, forcing the limits for fitting the acquired in-situ MWE data, we were able to track the evolution of the optical constants of III-nitride films along the ALD cycles which indeed showed thickness-dependent behavior.

Our main motivation behind this study was twofold: (i) Analyze and compare the self-limiting growth characteristics of binary III-nitride (AlN, GaN, and InN) thin films via real-time in-situ ellipsometry and to gain insight into the ALD surface reaction mechanisms including chemical adsorption, ligand removal, and nitrogen incorporation steps. (ii) Performance evaluation of our custom designed ALD reactor featuring improved hollow-cathode plasma source by comparing our results with previous plasma-ALD grown III-nitrides.

Despite using the conventional alkyl metal precursors (trimethyaluminum, trimethyl/ethylgallium, trimethylindium) utilized also widely in MOCVD epitaxial growth, their solid-gas surface interactions with nitrogen plasma species shows notable differences, particularly with respect to substrate temperature, plasma power, plasma exposure time, and plasma gas composition. In terms of substrate temperature, AlN exhibited crystallinity at lower temperatures when compared to GaN and InN. Even at 100 °C, AlN showed crystalline behavior whereas GaN displayed amorphous character up to 200 °C. While $Ar/N_2/H_2$ composition is optimal for AlN, N_2/H_2 and Ar/N_2 mixtures proved to be better for GaN and InN. InN experiments revealed that the inclusion of H_2 gas led to mixed phase growth with substantial c-In_2O_3 phase. The possible surface reaction mechanisms that lead to these different growth behaviors will be discussed in detail.

12:00pm **PS+2D+SE+TF-FrM12 Tribological Properties of Plasma Enhanced Atomic Layer Deposition TiMoN with Substrate Bias**, ***Mark Sowa**,* Veeco ALD*; A.C. Kozen,* University of Maryland*; N.C. Strandwitz, T.F. Babuska, B.A. Krick,* Lehigh University

In our previous study, we demonstrated a tertiary plasma enhanced atomic layer deposited transition metal nitride (TiVN) with exceptional wear rates and friction coefficients. We have extended that work with an investigation of another tertiary transition metal nitride system, $Ti_xMo_yN_z$. For films deposited at 250°C and 300W on a Veeco CNT G2 Fiji PEALD system, we have demonstrated how the ratio of TiN:MoN cycles (1:0, 2:1, 1:1, 1:2, 0:1)

provides linear control of the Ti:Mo in the resulting film. Through application of an 13.56MHz RF substrate bias (0-188V) during the plasma step, ion bombardment energy of the substrate can be varied, providing a means for tweaking the films physical and chemical characteristics which in turn are shown to impact the resulting film's tribological properties. As PEALD metal nitrides have broader interest than wear layers and to gain insights on the interrelationships of the mechanical properties, the processing details, and other film properties, we also report on the resulting film composition/impurities, density, crystallinity, optical properties, resistivity, and morphology.

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