Atomic Scale Processing Mini-Symposium
Room 116 - Session AP1+EM+PS+TF-WeM

Energy-Enhanced Atomic Layer Processing

Moderators: Ashley Bielinski, Argonne National Laboratory, USA, **John F. Conley, Jr.**, Oregon State University

8:00am AP1+EM+PS+TF-WeM-1 Low-Temperature Synthesis of Crystalline In$_x$Ga$_{1-x}$N Films via Plasma-Assisted Atomic Layer Alloying, *S. Allaby, F. Bayansal, H. Silva, B. Willis, Necmi Biyikli,* University of Connecticut

Based on our first demonstration of crystalline III-nitride film growth via hollow-cathode plasma-assisted atomic layer deposition (HCP-ALD) at substrate temperatures as low as 200 °C, this technique is attracting increasing interest for the low-temperature deposition of various semiconductor layers. Despite its success for binary III-nitride films, ternary III-nitrides pose additional challenges including limitation on fine stoichiometry control, potential incompatibility of plasma gas mixtures, and complexity of in-situ ellipsometry analysis of the growing film. In this work, we share our experimental findings on the self-limiting growth of In$_x$Ga$_{1-x}$N films on SiO$_2$/Si, quartz, and sapphire substrates using digital alloying technique in an HCP-ALD reactor at 200 °C.

The In$_x$Ga$_{1-x}$N alloy films were deposited using conventional metal-alkyl precursors (triethylgallium, trimethylindium) and two different nitrogen plasmas (N$_2$/H$_2$, N$_2$/Ar) as metal precursor and nitrogen co-reactant, respectively. GaN and InN unit ALD cycle parameters have been determined using the saturation curves for each binary compound. Digital alloying technique was used by forming ALD supercycles with the following GaN:InN cycle ratios: (9:1), (6:1), (3:1). The targeted indium concentrations ranged within (10% – 50%) range. In$_x$Ga$_{1-x}$N alloy films with different stoichiometries and thickness values around 50 nm were synthesized to further characterize the structural, chemical, optical, and electrical film properties.

In-situ ellipsometry was employed to monitor the surface ligand-exchange reactions and plasma surface interactions. XRD, XRR, XPS, spectroscopic ellipsometer, UV/Vis spectroscopy, and Hall-effect measurements are carried out to characterize the crystal structure, average crystal grain size, film density, stoichiometry (Ga:In ratio), impurity content, complex refractive index, optical bandgap, film resistivity, carrier concentration and electron mobility, respectively. The experimental results will be discussed along with faced challenges, potential solutions and follow-up studies.

8:15am AP1+EM+PS+TF-WeM-2 Comparison of Low Temperature Methods for Crystallization of Vanadium Oxide Produced by Atomic Layer Deposition, *Peter Litwin,* Naval Research Laboratory, USA*; M. Currie, N. Nepal, M. Sales, D. Boris, S. Walton, V. Wheeler,* US Naval Research Laboratory

Crystalline VO$_2$ (c-VO$_2$) undergoes a phase transformation between two crystalline states near room temperature ($\approx$ 68 °C), which is accompanied by a metal-to-insulator transition (MIT). This favorable MIT in stoichiometric c-VO$_2$ is of interest for numerous applications such as passive thermal regulation (e.g. energy efficient windows), thermal sensors, and passive radio frequency components. Current VO$_2$ films deposited by thermal atomic layer deposition (ALD) processes are amorphous and require a high temperature post-deposition annealing step ($\geq$ 400 °C) to crystallize, which often limits the application space of ALD VO$_2$ due to thermal budget constraints. Thus, the development of processes to produce ALD c-VO$_2$ without the need of a high-temperature annealing step are desired.

Two possible routes to c-VO$_2$ are plasma-enhanced ALD (PEALD) and femtosecond laser processing (fsLP). PEALD offers increased kinetics through the simultaneous delivery of a flux of both energetic and reactive plasma species to the growth surface, allowing for deposition and crystallization at lower processing temperatures. However, the enhanced reactivity of oxidizing-plasma sources poses challenges not present in thermal ALD processes of VO$_2$. For example, the oxidation state of the V in the metal-organic precursor is less of a driver for stoichiometric control often resulting in the more stable V$_2$O$_5$ with plasma processes. In fsLP, crystallization is initiated as a result of non-equilibrium excited-state dynamics in the film occurring on sub-ps timescales. This produces a combination of athermal and thermal annealing expected to promote the formation of c-VO$_2$, even under ambient conditions. Both methodologies maintain sub-200 °C temperature windows which facilitate the use of c-VO$_2$ in a wider range of applications. For example, high-temperature annealing

of VO$_2$ on metal substrates often results in the dewetting of VO$_2$ films; both PEALD and fsLP are potential solutions.

Here we report on investigations into the efficacy of PEALD and fsLP to produce c-VO$_2$. A focal point of the PEALD studies is correlating plasma properties, including plasma power, Ar/O$_2$ ratio, system pressure, and total gas flow during the plasma step, with the control of the VO$_x$ stoichiometry and crystallinity. We demonstrate control of the amorphous to crystalline transition as a function of PEALD parameters and comment on control of the V^{4+}/V^{5+} ratio. fsLP is shown effective at producing c-VO$_2$ from amorphous ALD films under ambient conditions. We also discuss the ability of the technique to produce c-VO$_2$ on polymer and metal substrates, an application space often incompatible with high-temperature annealing.

8:30am AP1+EM+PS+TF-WeM-3 Temperature-Dependent Dielectric Function of Plasma-Enhanced ZnO Atomic Layer Deposition using in-Situ Spectroscopic Ellipsometry, *Yousra Traouli,* U. Kilic, University of Nebraska-Lincoln, USA*; M. Schubert,* University of Nebraska - Lincoln*; E. Schubert,* University of Nebraska-Lincoln, USA

In this study, *in-situ* spectroscopic is employed to real-time monitor the growth of ZnO thin films fabricated by plasma-enhanced atomic layer deposition for different temperatures. The process involves dimethylzinc, Zn(CH$_3$)$_2$, organometallic precursor and oxygen plasma as the primary reactant and co-reactant, respectively. We investigate the cyclic surface modifications and growth mechanisms of ZnO for different substrate temperatures. Subsequently, the deposition chamber is then used as an thermal annealing chamber to investigate the evolution of dielectric function of ZnO ultra-thin films for different temperature values (22°C ≤ T ≤ 300°C).

Hence, the temperature-dependent complex dielectric function spectra of ZnO ultra-thin film is obtained. Complementary x-ray photoelectron spectroscopy, x-ray diffraction, and atomic force microscopy are also used to provide the compositional, structural, and morphological characteristics of the ZnO films, respectively. These findings highlight the critical role of precise thermal management in ALD processes for tailoring the dielectric properties of ZnO thin films. The insights gained from this study are crucial for the development and optimization of ZnO PE-ALD recipe but also for optoelectronic devices, ensuring enhanced performance and reliability.

8:45am AP1+EM+PS+TF-WeM-4 Optical Properties and Carrier Transport Characteristics of NiO Films Grown via Low-Temperature Hollow-cathode Plasma-assisted Atomic Layer Deposition, *Fatih Bayansal, S. Allaby, H. Mousa, H. Silva, B. Willis, N. Biyikli,* University of Connecticut

While there is an abundance of as-grown unintentionally doped n-type semiconductor materials, only a few alternative materials exhibit p-type conduction without requiring additional high-temperature doping processes. NiO is of particular interest mainly due to its relative stability and promising performance as hole-transport layers in emerging solar cell device structures. However, the stability of film properties including carrier concentration and mobility of NiO needs to be substantially improved for its use as reliable transistor channel layers. While low-temperature thermal, plasma, and ozone-assisted ALD efforts have resulted in NiO films with p-type behavior, degrading film properties over time and at higher temperatures, and low hole mobility values prevent the usage of these layers for devices.

To enhance film properties in low-temperature as-grown NiO layers, our study conducts a comprehensive investigation on plasma-enhanced ALD (PEALD) of NiO films on Si, SiO$_2$/Si, glass, sapphire, and quartz substrates. This process utilizes nickelocene (NiCp$_2$) and O$_2$ plasmas within a plasma-ALD reactor featuring a stainless steel-based hollow-cathode plasma (HCP) source, equipped with an in-situ ellipsometer. 800-cycle deposition runs at 100 – 250 °C substrate temperatures were carried out to achieve at least 30 nm thick films for further characterization.

The resulting as-grown crystalline (*c*-NiO) films are characterized for their optical and electrical properties. Films grown at 200 °C exhibited higher refractive index values reaching 2.3, which is in good agreement with reported values for the best polycrystalline NiO films in the literature. NiO films deposited on sapphire and quartz substrates showed strong absorption in the UV region (l=190-380 nm) yet demonstrated minimal absorption in the visible and near-IR regions. As a result of the analysis using the Tauc relation, it was found that the band gaps of all films were close to the bulk value of 3.6 eV. Furthermore, we will also present the results of Hall-effect measurements conducted at room temperature to determine the film resistivity, type of conduction mechanism, Hall mobility, and carrier concentration. The long-term stability of the NiO films will be investigated at ambient and higher temperature annealing conditions.

9:00am AP1+EM+PS+TF-WeM-5 Characterizing Inductively Coupled Plasmas in Ar/SF₆ Mixtures for Atomic Layer Deposition, *David Boris, V. Wheeler,* U.S. Naval Research Laboratory; *M. Sales,* NRC Research Associateship Program; *L. Rodriguez de Marcos, J. Del Hoyo,* NASA Goddard Space Flight Center; *A. Lang,* U.S. Naval Research Laboratory; *E. Wollack, M. Quijada,* NASA Goddard Space Flight Center; *M. Meyer,* NRC Research Associateship Program; *S. Walton,* U.S. Naval Research Laboratory

Low temperature plasmas containing sulphur hexafluoride (SF_6) are particularly rich plasmas from the perspective of gas phase chemistry and plasma physics.They possess a wide range of positive and negative ion (SF_x^+, SF_y^-, F^-, F_2^+, etc.) and reactive neutral species (SF_x, F, F_2, etc.) that play important roles in materials processing applications ranging from semiconductor etching [1] to the formation of fluoride based optical thin films[2]. Understanding the physical mechanisms at play in these plasmas is often challenging and requires a comprehensive approach employing multiple diagnostic tools.

In this work, we use a combination of Langmuir probes and optical emission spectroscopy to examine the effects of varying process parameters on the physical characteristics of Ar/SF_6 plasmas generated in a remote, inductively coupled plasma (ICP) geometry.In particular, a range of applied RF powers,gas flows, and pressures are explored with a focus on the resulting changes in atomic F density, plasma density, plasma potential, and the ratio of positive to negative ions in the plasma.These changes in plasma properties are then tied to changes in the material characteristics of aluminum tri-fluoride (AlF_3) thin films grown via plasma-enhanced ALD using a remote ICP employing Ar/SF_6 gas mixtures. This work is supported by NASA Astrophysical Research and Analysis (APRA) grant 20-APRA20-0093/ N0017322GTC0044. This work was also partially supported by the NRL Base program through the Office of Naval Research.

[1] D.C. Messina et al, J. Vac. Sci. Technol. A 41, 022603 (2023)

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9:15am AP1+EM+PS+TF-WeM-6 Dynamic Global Model of Cl₂/Ar Plasmas: In-Depth Investigations on Plasma Kinetics, *Tojo Rasoanarivo, C. Mannequin,* Institut des Matériaux de Nantes Jean ROUXEL - Nantes Université, France; *F. Roqueta, M. Boufnichel,* ST Microelectronics, France; *A. Rhallabi,* Institut des Matériaux de Nantes Jean ROUXEL - Nantes Université, France

Plasma processes such as Atomic Layer Etching (ALE) using Cl_2/Ar gas mixture are often reported in the literature as chlorine chemistry is suitable for a wide variety of materials [1]. ALE is a cyclic process and Cl_2 and Ar plasmas are implemented for the adsorption and activation steps, respectively, through alternating feedgas overtime or overspace. However, these studies mostly focus on experimental approaches and modeling investigations are scarce. Some others ALE recipes rely on plasma kinetics through specific recipes [2] and to better understand plasma/surface interactions at atomic scale, we must first precisely investigate plasma behavior especially during the switching durations.

In most cases, global models have been well implemented to determine the plasma composition at specific plasma reactor parameters, with good computational time effectiveness [3] in steady-states conditions [4]. We have implemented the dynamic mode to investigate the plasma kinetics during the transitions between the modifying Cl_2 plasma and the Ar activation plasma.

We closely investigate the influence of the switch duration between the Cl_2 to/from Ar feedgas, for different RF powers. We found that under a critical switch duration there is a competition between the plasmas kinetics mainly governed by electrons collisions with the neutrals and the physical residence time depending of the working pressure. For short switch duration from Cl_2 rich plasma toward Ar plasma, we observed discrepancies compared to equivalent steady-state composition on chlorine species. These differences are associated with longer characteristics time reactions than the switch duration. In the case of RF power source switch, we observed for switch duration lower than 100 ms, overshoots of the electron temperature (T_e). These stiff T_e variations observed are assumed to originate from quasi-instantaneous electrons acceleration before first collisions with neutrals.

These results may be used to predict plasma behavior during ALE transitions steps or for fast-paced plasma etching processes.

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9:30am AP1+EM+PS+TF-WeM-7 Precise Growth and Removal of Carbon Films by Electron-Enhanced Chemical Vapor Deposition (EE-CVD) and Chemical Vapor Etching (EE-CVE), *Z. Sobell, Steven George,* University of Colorado at Boulder

Electron-enhanced chemical vapor deposition (EE-CVD) was used to grow carbon films at T < 70 °C. EE-CVD employs a continuous flux of low energy (~100 eV) electrons that are incident on the sample through a methane (CH_4) reactive background gas (RBG). Electron-enhanced chemical vapor etching (EE-CVE) was also used to etch carbon films at < 70 °C. EE-CVE employs a continuous flux of low energy electrons that are incident on the sample through an oxygen (O_2), ammonia (NH_3), or hydrogen (H_2) RBG. Both EE-CVD and EE-CVE were accomplished with precise rate control.

The EE-CVD and EE-CVE used an electron beam from a hollow cathode plasma electron source with currents on the sample of ~30 mA over ~10 cm^2. The electron beam can desorb surface species by electron stimulated desorption. The electron beam also travels through the RBG in the reactor at pressures of ~1-3 mTorr. Electron induced dissociation can form radicals and ions that facilitate the growth or removal of the carbon film. In addition, a negative voltage (-30 V) on the substrate (sample bias) was observed to greatly enhance both the deposition and etching of carbon films. The negative voltage is believed to pull positive ions to the substrate to enhance the growth or removal.

With no applied sample bias, carbon deposition proceeded at ~22 Å/min for a CH_4 flowrate of 10 SCCM (Fig. 1). The introduction of a sample bias of -30 V increased the deposition rate by >20 times to ~480 Å/min. In contrast, carbon deposition with a +30 V sample bias proceeded at a similar rate to carbon deposition with no sample bias. For etching of carbon films with a -30 V sample bias and RBG flow rates of 4 SCCM, O_2 produced the highest carbon etch rate at ~225 Å/min (Fig. 2). In contrast, NH_3 displayed a slower carbon etch rate of ~48 Å/min and H_2 had an even slower carbon etch rate of ~18 Å/min.

Raman spectroscopy was used to characterize the carbon films grown at different sample biases. At negative substrate voltage, the carbon films displayed faster growth, were more disordered (D:G peak ratio=2.29), and exhibited faster etching. At zero substrate voltage, the carbon films displayed slower growth, were more ordered (D:G peak ratio=1.18), and exhibited slower etching.

Many applications are possible for the EE-CVD and EE-CVE of carbon films. More ordered carbon films may find use as hard masks or diffusion barriers. Amorphous carbon films may be employed as channel materials. Carbon hard masks are currently removed with an O_2 plasma which also oxidizes the surrounding and underlying material. Using H_2 and electrons may allow for a single-step oxygen-less hard mask removal.

9:45am AP1+EM+PS+TF-WeM-8 Microwave Enhanced ALD of Al₂O₃, *Benjamin Kupp, J. Haglund, S. Witsell, J. Conley,* Oregon State University

The low deposition temperatures typical of ALD are advantageous for many applications. However, low deposition temperatures can allow incorporation of -OH groups or residual impurities from unreacted ligands which can lead to non-ideal stoichiometry and sub-optimal physical, optical, and electrical properties. Although increasing the deposition temperature and post deposition annealing can both help drive off impurities and improve film properties, the temperatures required may (i) move a process out of the ALD regime or (ii) exceed the thermal budget, respectively. To maintain a low ALD temperature while maximizing film properties, adding energy in-situ *during* each ALD cycle or supercycle can help drive/speed reactions and reduce impurity incorporation. For example, including rapid thermal annealing as part of the ALD cycle have been shown to improve density, stoichiometry, electrical, and optical properties that cannot be achieved by post deposition annealing alone [1-4]. Other reported in-situ energy enhanced EE-ALD methods include flash lamp annealing, plasma, UV, and laser exposure, electric fields, and electron-beams [5-15]. Here, we introduce microwave enhanced MWE-ALD.

Al_2O_3 films were deposited at 300 °C using TMA and H_2O in a Picosun R200 PE-ALD chamber integrated with a custom microwave antenna and an MKS SG 1024 solid state microwave (MW) generator. Film thickness and

refractive index, n, were modeled using a Film Sense FS-1 mapping ellipsometer. A 30 s in-situ 400 W MW exposure (*without* plasma generation) during either the TMA or H_2O purge part of each ALD cycle reduced film thickness by ~7% and ~ 25%, and increased n by ~2% and ~6%, respectively, across a 150 mm Si wafer as compared to a control without MWs (Fig. 1). Preliminary electrical measurements on MOS devices indicate an associated reduction in low field leakage. Additional electrical and analytical data will be presented, including MWE-ALD deposition temperatures.

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