Atomic Scale Processing Mini-Symposium
Room A107-109 - Session AP+PS+TF-WeM

Plasma Deposition and ALD Processes for Coatings and Thin Films

Moderators: Silvia Armini, IMEC, Belgium, **Jessica Kachian**, Intel Corporation

8:00am **AP+PS+TF-WeM-1 Recent Progress in Analysis of the Conformality of Films by Atomic Layer Deposition**, ***Riikka Puurunen,*** Aalto University, Finland **INVITED**

Conformality is a fundamental characteristic of atomic layer deposition (ALD) thin film growth technique. "Conformal" film refers to a film that covers all surfaces of a complex three-dimensional substrate with everywhere the same thickness and properties. ALD - invented independently by two groups in 1960s and 1970s - has since late 1990s been transformational in semiconductor technology. Apart from semiconductors, conformal ALD films find applications and interest in widely varied fields such as microelectromechanical systems, pharmaceutical powder processing, optical coatings, battery technologies and heterogeneous catalysts.

Conformality follows directly from the "ideal ALD" principles: growth of material through the use of repeated separate self-terminating (i.e., saturating and irreversible) gas-solid reactions of at least two compatible reactants on a solid surface. Obtaining conformality in practice is not self-evident, however. Reasons for deviation from conformality are multiple, ranging from mass transport limitations to slow reaction kinetics and various deviations from ideal ALD (e.g., by-product reactivity or a continuous chemical vapor deposition (CVD) component through reactant decomposition or insufficient purging). Incomplete conformality can also be intentional: a saturation profile inside a feature can be exposed, to enable an analysis of kinetic parameters of the reactions.

This invited talk will explore recent progress especially by the author and collaborators in understanding ALD conformality and kinetics, obtained via experiments and simulations. Experiments have been made with the recently commercialized (chipmetrics.com) silicon-based PillarHallTM lateral HAR test chips (channel height ~500 nm) and spherical mesoporous high-surface-area materials (average pore diameter ~10 nm, sphere diameter ~1 mm). Simulations are presented for 1d feature-scale models and optionally a recently developed 3d code for spheres. Two codes are available on GitHub: DReaM-ALD (diffusion-reaction model, DRM) and Machball (ballistic transport-reaction model, BTRM). Often it is assumed that diffusion during an ALD process in HAR features is by Knudsen diffusion and free molecular flow conditions prevail (Kn >>1). If so, a characteristic "fingerprint saturation profile" can be obtained, and the slope method (derived for DRM-ALD-Arts, GitHub) can be used to back-extract the lumped sticking coefficient. When diffusion is in the transition flow (Kn ~1) or continuum flow (Kn<<1), the shape of the saturation profile depends on process conditions and the slope method is not applicable.

8:40am **AP+PS+TF-WeM-3 ALD Temperature Cycling for Uniform Infilling of Macroscopic Nanoporous Solids**, ***Benjamin Greenberg****, K. Anderson, A. Jacobs, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

Uniform ALD infilling of macroscopic nanoporous solids with aspect ratio greater than 10^4 can require precursor dose times on the order of 10^3 seconds, at least four orders of magnitude longer than typical dose times for ALD on wafers. For ALD processes based on relatively stable precursors and straightforward chemistries, such as ALD of Al_2O_3 from trimethylaluminum (TMA) and H_2O, very long doses are generally harmless, but for some ALD processes, precursor decomposition and other side reactions are significant concerns. For example, at a deposition temperature of 180 °C, which has been chosen previously for ZnO ALD infilling to ensure rapid removal of H_2O from nanopores during purging,[1] diethylzinc (DEZ) decomposition[2] and surface Zn deethylation[3] may be substantial on the ~10^3 s timescale.

In this work, we investigate the potential of temperature cycling as a route toward rapid yet controlled infilling of macroscopic nanoporous solids. We infill Al_2O_3 nanoparticle compacts of ~1.5 mm thickness and ~100 nm pore size (aspect ratio > 10^4) with ZnO using DEZ and H_2O as precursors, and we cycle the substrate temperature between ~160 °C (during H_2O purges) and ~120 °C (during all other steps). DEZ infiltration is accomplished via static dosing, wherein DEZ vapor is held in the ALD chamber for >10^3 seconds with the pump valve closed so that, in principle, diffusion/reaction and saturation are observable as a rise (due to byproducts) and flattening of the ALD chamber pressure, respectively. The 120/160 °C cyclical-temperature process produces clear saturation signals in the pressure trace, whereas fixed-temperature processes carried out entirely at 120 or 160 °C do not, apparently due to incomplete H_2O removal at 120 °C and DEZ decomposition and/or other side reactions at 160 °C. We use a variety of characterization techniques, including SEM/EDS, XRD, and electrical conductivity measurements, to assess the uniformity and purity of the ZnO infills.

1. A. Cendejas, D. Moher, and E. Thimsen, J. Vac. Sci. Technol. A **39**, 012406 (2021).
2. J. D. Ferguson, A. W. Weimer, and S. M. George, J. Vac. Sci. Technol. A **23**, 118 (2005).
3. T. Weckman and K. Laasonen, J. Phys. Chem. C **122**, 7685 (2018).

9:00am **AP+PS+TF-WeM-4 Plasmonic Plasma Process for Room Temperature Growth of High-quality Ultra-thin Dielectric Films**, ***Takeshi Kitajima****, M. Miyake,* National Defense Academy, Japan*; K. Watanabe,* National defense Academy, Japan*; T. Nakano,* national defense Academy, Japan

Catalytic surface reactions utilizing gold nanoparticle plasmons have been utilized in various applications in recent years.[1] We have applied hot electrons supplied from gold nanoparticles to plasma surface reactions to use them to form high-quality ultrathin dielectric films at room temperature.[2] We focused on the mixed effect of visible light for plasmon excitation and plasma VUV emission and discovered the effect of green light excitation that promotes radical nitriding. Due to the mercury probe measurement and TEM imaging, the film grown have sperior dielectric feature and uniformity with less plasma induced damage in spite of nonuniform formation of gold nanoparticles.

In the growth sequence, Au was vapor-deposited on a SiO_2 / Si (100) substrate in an ultra-high vacuum chamber with an average thickness of 0.4 nm by electron beam deposition to form Au nanoparticles (C) on the surface. A 30 mTorr N_2-inductively coupled plasma was generated in the attached chamber, and the sample was irradiated with N radicals (R) that passed through a 30 line/inch SUS304 single mesh with the configuration shown in Fig. 1 (a) for 5 minutes. A filter and a white LED controlled the wavelength of light (L), and VUV light from N_2 plasma was mixed. The reaction condition consisting of the above is RLC. Figure 1 (b) shows the dielectric characteristics of the SiON film {leakage current and EOT (equivalent oxide film thickness) when 1 V is applied}. In green light suitable for Au plasmons, the hot electrons (~ 4 eV) generated by the deexcitation of plasmons enabled the bond conversion from Si-O to Si-N the ultra-thin SiON shows the same characteristics as the ideal SiON film. By mixing VUV, it is possible to increase the film thickness further and reduce leakage.

Cross-sectional TEM image of SiON film after plasmonic process is shown in Fig. 1 (c). Beneath the Au particle SiON film with wide range of uniformity is confirmed and the single crystal lattice of Si substrate is clearly identified.

From the above, it is considered that the reaction between the adsorbed N radicals and Si proceeded, and a quality SiON film was formed by superimposing the photoelectron emission from the VUV light on the hot electron injection from the gold nanoparticles by green light irradiation.

1 C. Clavero, Nat. Photonics 8, 95 (2014).

2 T. Kitajima, M. Miyake, K. Honda, and T. Nakano, J. Appl. Phys. 127, 243302 (2020).

9:20am **AP+PS+TF-WeM-5 Time Resolved Energy Diagnostics of HiPIMS Discharges With Positive Cathode Reversal**, ***Zachary Jeckell****, T. Choi, M. Hossain, D. Kepelyan, N. Vishnoi,* University of Illinois at Urbana Champaign*; B. Jurczyk,* Starfire Industries*; D. Ruzic,* University of Illinois at Urbana Champaign

This work investigates the temporal evolution of a high-power impulse magnetron sputtering (HiPIMS), with a positive cathode reversal, discharge by using the Hiden ANALYTICAL PSM probe that can measure the ion energies as well as perform charge to mass (q/m) measurements. This work builds off other diagnostic work done on the chamber such as time resolved electron energy distribution functions from our time resolved Langmuir probe technique, previous work with measuring ion energy distribution functions using the SEMION probe, as well as preliminary

measurements taken with the PSM probe. This work was performed on several different target materials such as Ag, Ti, ZnTe, and W. The diagnostic capabilities of the PSM allows for differentiation between the working gas and target material ions which enables us to calculate the ratio of target ions for a given condition. Previous work we have done has shown that at early stages of the positive cathode reversal there is an elevated population of metal ions and that the overall fraction of metal to working gas fraction is at its highest. Time and energy resolved mass spec data was collected on this system for a variety of conditions such as pulse lengths, pressures, and target material with the objective of developing a better understanding for the energetics at play. Additionally, by running the PSM with the filament on and a properly set repelling voltage it was possible to get a sense of the neutral energies as well. This required a deconvolution of the energy that the neutrals gain from the ionization from the filament. The goal was to use the results of those experiments to build a framework of understanding and to use that information to deposit better films, such as increasing the hardness of TiN, reducing the resistivity of N doped ZnTe, improving the crystallinity of W films or improving the optical properties of a Ag thin film.

9:40am **AP+PS+TF-WeM-6 Electron-Enhanced ALD of TiO_2, TiN, and TiCN at Low Temperature Using TDMAT Together with O_2 and NH_3 Reactive Background Gas***, Z. Sobell, A. Cavanagh,* ***Steven George,*** University of Colorado Boulder

Electron-enhanced atomic layer deposition (EE-ALD) was utilized for the growth of TiO_2, TiN, and TiCN films at T < 70 °C.Three Ti-based films were grown using sequential exposures of tetrakis(dimethylamido) titanium (TDMAT) precursor and electrons together with a continuous reactive background gas (RBG) (Figure 1). The electrons accelerated across a grid bias of 100 V desorb surface species by electron stimulated desorption.The electrons also dissociate the RBG as they travel to the substrate.The RBGs utilized to tune the film composition were oxygen (O_2) for TiO_2 and ammonia (NH_3) for TiN and TiCN.

TiO_2 EE-ALD was performed at T < 70 °C using TDMAT together with an O_2 RBG at ~1 mTorr. O_2 is believed to be dissociated by the electron beam, creating O radicals that add oxygen to form TiO_2 and remove N and C from the TDMAT precursor. XPS showed no detectable C or N in the TiO_2 films and a slightly O-rich stoichiometry. Oxygen-rich TiO_2 films may be more photochemically active due to bandgap narrowing and could be useful in photocatalysis.

TiN EE-ALD was conducted at T < 70°C using TDMAT together with an NH_3 RBG at a pressure of ~1 mTorr. NH_3 is believed to be dissociated by the electron beam, liberating H and NH_x radicals that facilitate Ti nitridation and C removal from the film. Electron exposures for 20 seconds led to the rapid nucleation of TiN films with purities of > 96% and ultralow resistivities of < 120 μΩ-cm. These films may be useful as diffusion barriers in backend interconnects.

Incomplete C removal resulted from shorter electron exposures during TiN EE-ALD using TDMAT with NH_3 RBG.This carbon residual provides a pathway for the deposition of TiCN, an important amorphous ternary nitride diffusion barrier.TiCN EE-ALD film growth and properties were explored for electron exposure lengths from 20 seconds to 0.5 seconds.Shorter electron exposures led to an increase of the C:Ti ratio from ~0.03 to ~0.33 as measured by x-ray photoelectron spectroscopy (XPS) (Figure 2).Shorter electron exposures also produced a decrease in film density from ~5.3 g/cm^3 to ~3.3 g/cm^3.In addition, shorter electron exposures yielded an increase in the film resistivity from < 120 μΩ-cm to ~2000 μΩ-cm as measured by ex situ spectroscopic ellipsometry (SE).Consequently, the enhanced diffusion barrier properties of TiCN EE-ALD films will be accompanied by higher film resistivities and lower film densities than TiN EE-ALD films.

11:00am **AP+PS+TF-WeM-10 A Non-Violent Approach to Remove SiN:H Surface Impurities (HCl) at Room Temperature***,* ***Tsung-Hsuan Yang****, T. Wang, G. Hwang,* University of Texas at Austin*; P. Ventzek, J. Zhao,* Tokyo Electron America, Inc.

Our research presents a non-violent approach to remove H^+/Cl^- pairs, a common reaction byproduct, after depositing chlorosilane-type Si precursors (such as dichlorosilane, SiH_2Cl_2) on a SiN surface. While previous studies have suggested the use of H radicals in NH_3 and CH_3NH_2 plasma to remove Cl impurities, these methods have limitations in high-aspect-ratio structures. The recombination rate of radicals may be too fast to reach the bottom of the trench, resulting in the accumulation of Cl and possibly the formation of a salt layer that inhibits further film growth. Through first-principles calculations, we propose an alternative solution by introducing polar molecules, such as NH_3, N_2H_4, CH_3NH_2, and $(CH_3)_2NH$. When these polar molecules are dosed onto the surface, they can first abstract the H^+ from the H^+/Cl^- pair to form a complex with Cl^-. Adjacent polar molecules then solvate the complex, forming a stable "microsolvation cluster." This cluster effectively captures Cl^- while weakening the interactions between Cl^- and surface amine groups, providing a pathway for HCl desorption with a lower energy barrier. Our calculations of free energy surface show that when the surface is saturated with CH_3NH_2 molecules, the energy barrier for HCl desorption can be significantly reduced at 300K. Based on these promising findings, we propose a novel and non-aggressive atomic layer deposition (ALD) scheme to grow SiN at low temperatures while achieving a higher growth rate.

11:20am **AP+PS+TF-WeM-11 Influence of Plasma Species on the Growth Kinetics and Properties of Epitaxial InN Films Grown by Plasma-Enhanced Atomic Layer Deposition***,* ***Jeffrey Woodward****, D. Boris,* U.S. Naval Research Laboratory*; M. Johnson,* Huntington Ingalls Industries*; S. Walton,* U.S. Naval Research Laboratory*; S. Rosenberg,* Lockheed Martin Space Advanced Technology Center*; J. Hite, M. Mastro,* U.S. Naval Research Laboratory

The controlled co-delivery of reactive and energetic plasma species during plasma-enhanced atomic layer deposition (PEALD) enables the growth of epitaxial layers at significantly reduced temperatures which are prohibitive to other methods. However, this capability is challenged by the complexity which arises from the reliance on plasma-surface interactions, and it is thus necessary to understand the influence of the plasma properties on the growth kinetics and resultant film properties. Among the III-nitride binary compounds, indium nitride (InN) is particularly well-suited for the investigation of the roles of reactive and energetic plasma species, as high-quality crystalline films can be achieved using trimethylindium (TMI) and a relatively simple N_2/Ar plasma rather than $N_2/Ar/H_2$ or NH_3/Ar plasmas which generate greater varieties of species. This was explored in recent studies of InN PEALD on gallium nitride (GaN) using *in situ* synchrotron x-ray scattering, which revealed that the growth mode is correlated with the relative density of atomic N, while coarsening behavior is influenced by ion flux.[1]

In this work, epitaxial InN films are grown by PEALD on GaN (0001) at approximately 320 °C using TMI and N_2/Ar plasma within various regimes of plasma species generation in order to investigate the influence on the resultant film properties. Optical emission spectroscopy and Langmuir probe measurements are used to correlate the production of atomic N and ions with the N_2 and Ar gas flows into the inductively coupled plasma (ICP) source. The InN films are characterized by atomic force microscopy (AFM), x-ray reflectivity (XRR), high-resolution x-ray diffraction (HRXRD), in-plane grazing incidence diffraction (IP-GID), synchrotron grazing incidence wide-angle x-ray scattering (GIWAXS), and x-ray photoelectron spectroscopy (XPS). The films are found to exhibit wurtzite phase and sixfold rotational symmetry with a clear epitaxial relationship to the GaN. Low fluxes of atomic N are found to promote larger domains, increased crystalline order, and smoother morphology compared to films grown with high atomic N fluxes. For the high atomic N flux condition, increasing ion flux is found to promote a very rough morphology containing large cluster-like features and decreased in-plane crystalline order, but increased out-of-plane crystalline order and a reduction in mosaic twist.

[1] J. M. Woodward *et al*., J. Vac. Sci. Technol. A **40**, 062405 (2022)

11:40am **AP+PS+TF-WeM-12 One Step Synthesis of Patterned Coatings Using Immobilized Filaments in an Atmospheric Pressure Dielectric Barrier Discharge. Effect of Gap and Power Pulsing.***, M. Brabant,* ***Annaëlle Demaude****, D. Petitjean,* Université Libre de Bruxelles, Belgium*; K. Baert, T. Hauffman,* Vrije Universiteit Brussel, Belgium*; M. Gordon,* University of California Santa Barbara*; F. Reniers,* Université Libre de Bruxelles, Belgium

Deposition of patterned coatings to generate hybrid surface properties often require a multi-step process, such as the use of masks or lithography [1]. We proposed recently a simple scalable method for the deposition of patterned coatings (morphological and chemical contrasts) [2]. As a case study, the deposition of propargyl methacrylate (PMA) based-coatings was realized, as, due to its structure (one double and one triple bond), this molecule allows very fast deposition, and can lead to hydrophobic coatings, without the need of fluorinated atoms. Moreover, we showed that, depending on the deposition conditions, one could obtain hybrid hydrophilic/hydrophobic patterns.

To test the flexibility and the limits of the method, we now investigate further this route and try to understand better the effects of the gap between the electrodes and of the pulsed/non pulsed injection of the power. The deposited coating was characterized using μ-XPS, FTIR and contact angle measurements, whereas the discharge was characterized

using a high intensity camera, electrical measurements (oscilloscope and Rogowski coil), and mass spectrometry. Due to the DBD configuration, the coating exhibits two distinct areas : the spot (S) area, corresponding to the coating deposited under the filament position, and the between spot (BS) area, corresponding to the coating deposited outside the filament position.

Filaments are immobilized thanks to beads fixed to one of the dielectrics, reducing locally the gap and therefore igniting specifically the discharge at these locations. Here the gap was fixed at 2, 2.5 and 3 mm. it is shown (using a high intensity camera, and electrical measurements) that an increase in gap leads to more energetic discharges inside the filaments. As shown by XPS, this leads to a lower preservation of the precursor structure for the “S”area coating. In parallel, due to higher voltages needed to light up the discharge, surface discharges take place between the filaments leading to subsequent deposition also between the spots located under the filaments.

Pulsing the power (in the ms range) leads to more localized filaments, to a global change in the plasma behavior and to a change in the coating chemistry [3] .

References :

[1]. A. Demaude *et al*., *Langmuir*, 2019, *35* (30), 9677–9683

[2] A. Demaude *et al*., *Advanced Science*. 2022, *9* (15), 2200237

[3] A. Demaude *et al*., *Plasma Chemistry and Plasma Processing*, submitted.

12:00pm **AP+PS+TF-WeM-13 Effect of Bias Pulsed Plasma Enhanced Atomic Layer Deposition for Void-Free SiO_2 Gap-Fill of High Aspect Ratio Trench Structures***, **Ye Ji Shin**, H. Kim, G. Yeom,* Sungkyunkwan University, Korea

In 3-dimentional (3D) device structures, cells are getting thinner and higher to increase the density of devices which resulted in High Aspect Ratio (HAR) structures. Gap-fill process is one of the processes that could affect the device performance of HAR trench structures. Void and seam are observed after the gap-fill process and they allow penetration of the chemical etchant used in subsequent processes, and which degrades isolation performance and increases leakage currents. To solve this issue, various processes such as thermal ALD processes with inhibitors, plasma enhanced ALD with substrate biasing, etc. have been used but, with increasing the aspect ratio of the structure, it is found to be difficult to fill the gap completely without void or seam in the trench. In this study, bias power with pulsing was introduced to PEALD processes for void and seam free SiO_2 gap-filling. Pulsed bias power with various pulse duty ratio from 30 to 75% were used and compared with continuous wave (CW) bias power and no bias power to identify the effect of bias pulsing. The results showed that, as the bias pulse duty ratio was decreased, void and seam were decreased and disappeared at HAR trench structures even with negative bowing. The pulse biasing with low duty ratio appeared to open the opening of the trench top while the pulse biasing with high duty ratio and CW biasing operation appeared to close the opening of the trench top possibly due to differences in combined effect of ion bombardment flux and deposition. Eventually, void-free SiO_2 gap-fill for HAR trench structures were obtained with bottom-up filling under the pulsed bias conditions. Detailed experimental results and analysis data will be shown in the presentation.

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