Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM2-WeM

Energy-enhanced ALD

Moderators: John Conley, Oregon State University, **Jean-François de Marneffe**, IMEC

10:45am **EM2-WeM-12 Let There Be Light: Photo-Assisted ALD of Pt Using $Pt(acac)_2$ and O_3**, ***Robin Petit***, *Kinanti Aliyah, Matthias Minjauw, Ruben Blomme, Arno Depoorter, Seppe Van Dyck,* Ghent University, Belgium*; Martin Rosenthal,* ESRF, France*; Zeger Hens, Christophe Detavernier, Jolien Dendooven,* Ghent University, Belgium

Global trends such as the transition to green hydrogen production and advancements in microelectronics are increasing the demand for high performance Pt-based electrodes. ALD enables Pt deposition in various morphologies, from size-controlled nanoparticles to continuous thin films, by tuning the nucleation behaviour and the number of ALD cycles. In thermal and plasma-enhanced Pt ALD, nucleation depends on parameters such as temperature, precursor dose, co-reactant choice, and substrate pretreatments.

This work focuses on photo-assisted ALD (photo-ALD), which uses ultraviolet (UV) illumination as an additional parameter to control growth. Building on our earlier study using $MeCpPtMe_3$ and O_2, where photon-precursor interactions enabled lower temperature Pt growth with shorter nucleation delays [AVS-ALD2024], we developed a new Pt photo-ALD process using $Pt(acac)_2$ and O_3 under 365 nm illumination. $Pt(acac)_2$ is a more economically viable precursor due to its straightforward synthesis and established large-scale production.

Continuous illumination at 100°C results in metallic Pt (Fig. 1a) and increased Pt loading compared to thermal ALD. To investigate nucleation and growth, in-situ X-ray fluorescence (XRF) and grazing-incidence small angle X-ray scattering (GISAXS) were performed at the European Synchrotron Radiation Facility (ESRF). Tracking the Pt growth kinetics with XRF reveals an enhanced nucleation with illumination (Fig. 1b). GISAXS indicates that, at similar Pt loading, photo-ALD produces smaller particles with higher areal density, while thermal ALD yields larger particles with wider spacing (Fig. 2). SEM images confirm these trends and show a broader size distribution for thermal ALD, indicating more disordered growth where nucleation and particle growth occur simultaneously (Fig. 3).

To understand the impact of photon-precursor interactions during each ALD step, the timing of the illumination is varied, showing that illumination during the $Pt(acac)_2$ half-cycle is critical to achieve photo-enhancement, yet reaction with O_3 remains necessary for further ALD growth. Notably, enhanced growth occurs not only when illuminating the precursor in the gas phase: illuminating surfaces bearing adsorbed $Pt(acac)_2$ and then dosing additional precursor, before the O_3 step, also increases Pt uptake relative to thermal ALD. Ongoing spectroscopy studies aim to clarify the effect of illumination on the precursor ligands.

In summary, our work shows that UV-illumination promotes Pt nucleation for both $MeCpPtMe_3$- and $Pt(acac)_2$-based ALD, providing insights that support the development of photo-ALD for other metals and advance the technique toward practical applications.

11:00am **EM2-WeM-13 Microwave Enhanced Atomic Layer Deposition (MW-ALD) of Ta2O5**, ***Jessica Haglund***, Oregon State University*; John Conley, Jr.,* Oregon State Univesity

A limitation of some ALD processes is the required low deposition temperature. Low temperature can allow incorporation of residual impurities from unreacted precursors which in turn may degrade electrical, physical, and optical properties. A way to reduce impurities and improve film quality while still maintaining a low thermal budget is known as energy enhanced ALD (EE-ALD), in which extra energy is incorporated into the ALD cycle to improve the film while it is growing. EE-ALD using *in-situ* treatments with either rapid thermal, flash lamp, plasma, or UV exposure have all demonstrated improvements over standard ALD films.[2-10] We recently demonstrated a new EE-ALD technique we call microwave enhanced ALD (MW-ALD) using Al_2O_3.[11] Here we present MW-ALD results on Ta_2O_5 and compare with MW-ALD of HfO_2 and Al_2O_3.

MW-ALD of Ta_2O_5 was performed at 120 and 200 °C using $Ta(OEt)_5$ and H_2O using a Picosun R200 modified with a custom MKS microwave generator and helical antenna. 400 W MW exposures (without plasma generation) were performed following the $Ta(OEt)_5$ purge, starting 15 s into the 120 s N_2 purge and lasting for 30 s. Film thickness and refractive index were analyzed using a mapping Film Sense FS-1 ellipsometer.

On Pt substrates, MW exposure at both 120 and 200 °C resulted in improved uniformity, an increase in median Ta_2O_5 thickness from 8.1 to 8.7 nm, and a slight increase in refractive index. For Si substrates, MW exposure at 200 °C also improved uniformity but had the opposite impact, reducing Ta_2O_5 median thickness from 5.7 to 4.7 nm. For HfO_2 (TEMA-Hf/H_2O), MW pulses during the TEMA-Hf purge resulted in a ~50% increase in thickness and an increase in refractive index, while MW during the H_2O purge had minimal impact. For Al_2O_3 (TMA/H_2O), MW exposure during the TMA pulse improved film quality compared to exposure during the H_2O pulse.Additional investigation of MW exposure during other parts of the ALD cycle, thicker depositions, and electrical data on MOS and MIM devices will be presented at meeting.

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11:15am **EM2-WeM-14 Electron-Enhanced Atomic Layer Deposition of Tunable TiCxNy Ternary Nitride Films Using Tetrakis(dimethylamido)titanium with Ammonia Reactive Background Gas**, ***Zachary Sobell***, *Andrew Cavanagh, Steven George,* University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) of amorphous tunable titanium carbonitride (TiC_xN_y) films was obtained at low temperatures. Amorphous ternary nitrides are important as diffusion barriers for back-end-of-the-line metallization in microprocessor fabrication. The TiC_xN_y EE-ALD was achieved using sequential exposures of tetrakis(dimethylamido)titanium (TDMAT) and low energy electrons in the presence of a continuous NH_3 reactive background gas (RBG) (**Figure 1**). The composition of the TiC_xN_y films was tuned by varying the NH_3 background pressure and the electron exposure time. The TiC_xN_y EE-ALD was performed utilizing a hollow cathode plasma electron source (HC-PES). The HC-PES delivered a high electron flux into background gases at pressures up to several mTorr. TDMAT was used as the source of Ti, C, and N. The NH_3 RBG served both as a source of additional N and a method for the removal of C from the TiC_xN_y films. The TiC_xN_y EE-ALD film growth was monitored using in situ ellipsometry. The TiC_xN_y EE-ALD was conducted at temperatures of 30-130°C using NH_3 pressures of 0 to 3 mTorr.

The C content in the TiC_xN_y films could be tuned using the NH_3 RBG pressure (**Figure 2**). Lower NH_3 pressures led to the incorporation of more C into the TiC_xN_y films. The C:Ti ratio varied from ~0.3 to ~0.05 as measured by XPS at a constant electron exposure time of 10 s. Electron exposure time was also used to modulate the C content in the TiC_xN_y films (**Figure 3**). Shorter electron exposures led to more C incorporation. The C:Ti ratio varied from ~2 to ~0.1 as measured by XPS at a constant NH_3 background pressure of 2 mTorr. In situ 4-wavelength and ex situ spectroscopic ellipsometry were able to estimate electrical resistivities for the TiC_xN_y films. Resistivity decreased from >2000 μΩ-cm to ~200 μΩ-cm with decreasing C content. XRR measurements were able to determine film densities. The film density for TiN films was 4.6 g/cm^3 and the film density decreased with increasing C content.

The C content in the TiC_xN_y films could also be varied using a CH_4 RBG. Carbon could be added by carbon EE-CVD using electron exposures together with CH_4 RBG. The carbon could also be removed using electron exposures together with NH_3 RBG. However, the C content in TiC_xN_y films was difficult to control using a supercycle approach with TiN EE-ALD and carbon EE-CVD.

11:30am **EM2-WeM-15 Pulsed Excimer Laser Processing to Promote Room-Temperature Crystallization of ALD HfO_2 Films**, ***T. Jude Kessler***, *Hans Cho, John P. Murphy, Sarah Brittman, Saikat Mukhopadhyay,* 1. US Naval Research Laboratory*; Peter Litwin,* 2. NRC Research Associateship Program*; Bradley De Gregorio, Virginia Wheeler, F.K. Perkins, Margo Staruch,* 1. US Naval Research Laboratory

Ferroelectric hafnia compounds, including Hafnium Oxide (HfO_2), are of interest to realize advanced neuromorphic devices. The metastable, polar

orthorhombic phase of HfO_2 is required to achieve the necessary ferroelectric device properties. Typically, this phase is stabilized at elevated temperatures, a significant barrier to producing thin films by atomic layer deposition (ALD). The lower deposition temperature of ALD enables direct, conformal integration of HfO_2 films on a variety of materials at any fabrication step but produces non-ferroelectric amorphous or monoclinic phase. Excimer Laser Annealing (ELA) has an edge over conventional annealing because it uses short laser pulses to heat only a thin surface layer, which rapidly cools due to a sharp thermal gradient with the underlying material. This process creates a heating and cooling cycle with insufficient time for the elevated state of the thin film to relax, promoting crystallization and stabilization of metastable phases. Thus, in this work, we apply ELA process to crystallize ALD HfO_2 films and determine the parameters that produce the ferroelectric, orthorhombic phase.

Ultrathin (10-20 nm), amorphous HfO_2 films were deposited by plasma enhanced atomic layer deposition on thermal SiO_2 substrates at 200°C using TEMAHf and Ar/O_2 plasma. To enhance the absorption of the pulsed laser, all films were capped with 50nm PEALD TiN. Films were processed using 20ns ELA pulses from 308nm broad bandwidth XeCl Coherent COMPex 201 laser homogenized by a fly's eye system illuminating a 5mmx5mm square with gaussian temporal profile onto the film surface. Parametric ELA testing was initially conducted, varying fluence and number of pulses, to determine the experimental range with sufficient energy to alter the film without causing delamination or photochemical ablation. Experiments investigating the influence of raster pattern and fluence on resulting HfO_2 structure were then performed.

Initial results show that controlling the ELA process parameters, we can both crystallize and influence the phase of HfO_2 films produced. Crystalline films were achieved without any observed damage to the film or underlying surface, exemplifying an advantage of ELA. Using TEM and glancing-incidence x-ray diffraction (GIXRD), we identified the ability to stabilize films with either orthorhombic, tetragonal, or a combination of both phases. Under the right parameters, films were single phase without any residual amorphous or monoclinic phase. Details establishing process-structure-property relationships using this promising technique to achieve relevant and scalable ferroelectric films will also be discussed.

11:45am **EM2-WeM-16 Thermally Activated Atomic Layer Annealing (ALA): A Plasma Free Approach to Densification of Hafnia Thin Films**, ***Dushyant Narayan***, *Thi Thu Huong Chu, Dan Le, Minjong Lee, Doo San Kim, Soham Shirodkar, Jean-Francois Veyan, Jiyoung Kim,* The University of Texas at Dallas

As device length scales continue to scale and transition from 2D planar to 3D structures, device architectures require precise control of step coverage and involve increasingly stringent requirements on electronic performance of high-k dielectrics. One of the immediate challenges is achieving growth of high-k dielectric materials with low defectivity and high density in high-aspect-ratio (HAR) structures within a low thermal budget. In this regard, Atomic layer annealing (ALA) methods offer low-temperature deposition with superior film quality compared to conventional thermal ALD, which has been reported for nitride-based materials such as AlN, and GaN.[1-3]These ALA methods typically utilize plasma to transfer energy to the film during growth to facilitate the migration of adatoms on the surface and also eliminate unreacted ligands, leading to a more organized and compact thin film.[4] However, plasma based methods suffer from serious limitations in high-aspect ratio structures, where plasma recombination effects can limit the concentration of plasma radicals in trenches.

In this work, we will discuss a chemical approach to densification which we term Thermal-ALA. This method is plasma-free, enabling deposition in HAR structures, and introduces a chemical annealing step into the reaction chamber after each deposition cycle. Here, we will present *in-situ* characterization of the reaction mechanisms involved in this process via Reflective Absorption Infrared Spectroscopy (RAIRS) as well as *ex-situ* characterization of the resulting film properties. By varying the dose of oxidant and substrate temperature we show that resulting hafnia films grown with this technique have improved wet-etch rate (WER), density, and can even crystallize during deposition at substrate temperatures as low as 300 °C. By demonstrating this technique, we show that densification of hafnia thin films can be achieved with purely thermal and chemical techniques, thereby providing another engineering parameter by which film properties can be controlled.

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