ALD Fundamentals
Room Jan & Hubert Van Eyck - Session AF2-MoA

Plasma Enhanced ALD

Moderators: Sumit Agarwal, Colorado School of Mines, Seung Wook Ryu, SK Hynix

1:45pm **AF2-MoA-2 Ion Energy Distribution and Fluxes for a Newly-Designed Remote Plasma Source for ALD for GaN Devices***, **Harm C.M. Knoops,*** Oxford Instruments Plasma Technology, Netherlands*; K Arts, J Buiter, L Martini,* Eindhoven University of Technology, Netherlands*; T Hemakumara,* Oxford Instruments Plasma Technology, Netherlands*; M Powell,* Oxford Instruments Plasma Technology, UK*; A Kurek, Y Shu,* Oxford Instruments Plasma Technology, Netherlands*; E Kessels,* Eindhoven University of Technology, Netherlands*; C Hodson, A O'Mahony,* Oxford Instruments Plasma Technology, Netherlands

Gallium nitride devices have been found to benefit from low-damage remote plasma ALD processing to not exceed energy and flux levels leading to device damage. At the same time plasma species concentrations and impact energies in these processes must be sufficient to allow for high throughput and high-quality film deposition. This contribution will outline ion energy distribution functions and flux levels for a remote plasma ALD reactor, Oxford Instruments Atomfab™. This tool includes a new, RF-driven, remote plasma source. The source design is optimized for ALD on GaN High Electron Mobility Transistors (HEMTs) for substrates up to 200 mm in diameter and allows for Al_2O_3 cycles of less than one second.

The plasma source has been evaluated using a retarding field energy analyzer (RFEA). As expected from a remote plasma, a strong reduction of the ion flux was observed when increasing the pressure. A roughly exponential decrease in ion flux as a function of pressure was observed for plasmas generated in Ar and also in O_2/Ar mixtures. The average ion energy also generally decreases with pressure, although the effect is less obvious. For example, the plasma source of Atomfab at 100 W plasma power and ~375 mTorr pressure gives modest ion energies (<50 eV) and very low ion flux ($<10^{13}$ cm^{-2} s^{-1}). Furthermore, the short plasma exposure time required for Atomfab to reach saturation (0.25 s plasma), means that the ion energy dose per ALD cycle is relatively low. By increasing plasma power and decreasing pressure, the ion flux can be increased to the 10^{14} cm^{-2} s^{-1} range if desired.

To validate that these conditions were suitable for GaN HEMT devices, ALD depositions were carried out using a standard Atomfab configuration. Al_2O_3 layers were grown on GaN HEMTs at 300 °C where the best electrical device performance was obtained by including an NH_3 plasma pre-treatment (100 mV hysteresis and 125 mV dispersion). Interestingly, this was achieved using a <1 s cycle time, while maintaining a refractive index >1.63 and a film thickness non-uniformity <±1.0% over the wafer. General characteristics and plasma aspects of this new remote plasma source will be discussed together with their impact on ALD processing.

2:00pm **AF2-MoA-3 Plasma-Enhanced Atomic Layer Deposition of Cobalt and Cobalt Nitride: What Controls the Incorporation of Nitrogen?***, **Gerben van Straaten**, R Deckers, M Vos, E Kessels, A Creatore,* Eindhoven University of Technology, Netherlands

Cobalt is a transition metal with a wide range of applications, including as a catalyst for the Fischer-Tropsch reaction, as a contact material in spintronic devices and as a potential replacement for copper in IC interconnects. In many of these applications, precise control over the thickness of the Co film is required and this can be obtained via Atomic Layer Deposition (ALD). ALD of Co thin films and nanoparticles can be achieved using a variety of Co precursors together with NH_{3-} plasma[1]. However, nitrogen has been identified earlier in literature, as a species that can be incorporated into Co films from the NH_3 plasma during ALD[2]. Here we demonstrate that nitrogen incorporation is a major factor affecting the resistivity of Co thin films and thus their performance for interconnect applications. At the same time, incorporation of nitrogen in the film also leads to the formation of cobalt nitrides, which are materials with interesting magnetic and catalytic properties.

Analysis of the N content in ALD-deposited Co shows that the nitrogen incorporation process is strongly temperature-dependent. In particular, we find a critical temperature of 290° C: below this temperature CoN_x is deposited, while above it we obtain metallic Co with traces of N. This opens up possibilities for the controlled deposition of both Co and CoN_x using the same process. To gain more insight into the formation of CoN_x during ALD, we analyzed the effect of NH_3 plasma exposure on cobalt and show that an inductively coupled NH_3 plasma can incorporate nitrogen into the top 4 nm of a Co thin film. By combining Temperature Programmed Desorption (TPD) with in-situ Spectroscopic Ellipsometry (SE) we show that the cobalt nitride is metastable and that it decomposes in two stages: surface-bound nitrogen starts to leave at 170° C, while nitrogen present deeper in the film starts to leave around 260° C and leads to the complete removal of all nitrogen from the film.

Detailed analysis of the film surface after NH_3 plasma exposure reveals that it is initially passivated by nitrogen atoms but that free adsorption sites are generated by N_2 desorption at elevated temperatures. This yields further insight into the mechanism by which the Co precursors adsorb on the Co and CoN_x surfaces. Based on these insights we formulate a reaction mechanism for Co ALD which includes a competition between nitrogen incorporation and desorption and the effect on Co precursor adsorption.

[1] M. F. J. Vos, G. van Straaten, W. M. M. Kessels, and A. J. M. Mackus, *J. Phys. Chem. C*, p. acs.jpcc.8b06342, Sep 2018

[2] H.-B.-R. Lee and H. Kim, *Electrochem. Solid-State Lett.*, vol. 9, no. 11, p. G323, Nov 2006

2:15pm **AF2-MoA-4 Recent Advances in Hollow Cathode Technology for Plasma Assisted ALD***, **K. Scott Butcher**, V Georgiev, D Georgieva,* Meaglow Ltd, Canada

In the past, hollow cathode plasma sources were primarily used in the Semiconductor Industry as sputter sources, however we have developed a range of gas-based sources that have been widely adopted for plasma assisted atomic layer deposition. This has largely been because of reduced oxygen contamination evident with these plasma sources when depositing non-oxide films (eg. [1]) though other advantages include high radical flux and relatively low ion damage. There have now been over forty journal papers published in relation to our hollow cathode sources. In this presentation we talk about some of the recent advances in their design, in particular the introduction of aluminum cathodes, which, like our titanium cathodes, are compatible with deposition on silicon. Aluminum is a relatively soft metal, and its resistance to sputtering might be questioned, however Langmuir probe measurements and other observations reveal that for operation below a certain power density, compatible with our third-generation designs, a protective dielectric coating is produced in the first few moments of operation with either nitrogen or oxygen plasmas. These hard coatings help to protect the underlying aluminum while providing an added advantage of decreased electron recombination at the cathode walls.

Finally, we have been able to demonstrate scalability to 12" diameter with our newest designs, and lower pressure operation than was available with our second-generation sources.

[1] J. Mater. Chem. C. 2 (2014) 2123.

2:30pm **AF2-MoA-5 Detection of Oxygen Vacancies in H_2-Plasma Enhanced Atomic Layer Deposited (PEALD) Ferroelectric Hafnia Zirconia Thin Films***, **H. Alex Hsain**,* NC State University*; G Walters,* University of Florida*; Y Lee, J Jones,* NC State University*; T Nishida,* University of Florida

Oxygen vacancies are suggested to be one of the main driving factors in stabilizing the unexpected polar orthorhombic phase (*Pca2₁*) in ferroelectric hafnia.[1] They also play a key role in the so called "wake-up" effect in which the remnant polarization of a ferroelectric device increases with repetitive electric field cycling.[2] Studies have suggested that the wake-up effect is caused by a redistribution of oxygen vacancies.[3] As a result, devices must be preconditioned with a set number of wake-up cycles in order to achieve the desired properties which comes at the expense of the device lifetime. There is an urgent need to detect – and control – the oxygen vacancy concentration in hafnia-based devices. For the first time, we report a direct method of detecting oxygen vacancies in ferroelectric hafnia-zirconia ($Hf_{0.5}Zr_{0.5}O_2$) thin films using depth profiling X-Ray Photoelectron Spectroscopy (XPS).

Recently, Walters et al. found that inclusion of an H_2-plasma step after oxidation can significantly decrease the wake-up effect.[4] We fabricate films via Plasma-Enhanced Atomic Layer Deposition and study the effect of H_2-plasma time duration on ferroelectric properties. We find that increasing H_2-plasma exposure time from 0 to 5 seconds increases the switched polarization from 0 to 27 $\mu C/cm^2$. Upon further exposure to H_2 plasma, the films display a distinct "pinched" hysteresis loop showing that the films become anti-ferroelectric. To reveal the mechanism by which H_2 plasma dramatically changes the ferroelectric properties, we use XPS to characterize the chemical and stoichiometric nature of HZO films.

Elemental quantification indicates a significant reduction in oxygen content in the HZO/TiN layer with higher exposure of H_2-plasma suggesting that H_2-plasma can directly reduce HZO into sub-oxides and form oxygen vacancies. The deconvolution of the O 1s peak in plasma-treated films suggests a shift toward lower binding energy which would occur in the presence of oxygen vacancy formation in the films.[5] Inspection of the Hf 4d and Zr 3d spectra also reveal a shift toward lower binding energy for films exposed to the highest plasma time. Grazing Incidence X-Ray Diffraction (GIXRD) corroborates these findings by a peak shift from 30.5° toward lower 2θ which supports the stabilization of the polar orthorhombic phase in intermediate H_2 plasma exposure times. Our study suggests that H_2-plasma enhanced ALD in conjunction with XPS could be a promising route for designing a wide array of HZO functional devices using defect engineering.

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3:00pm **AF2-MoA-7 Effect of an Electric Field on the Material Properties of Hafnium Oxide Thin Films Deposited by Plasma Enhanced Atomic Layer Deposition**, ***Vivek Beladiya**, A Szeghalmi,* Friedrich Schiller University, Germany

HfO_2 is widely used metal-oxide in semiconductors and optics due to high dielectric constant and high refractive index. The HfO_2 thin films were deposited using plasma enhanced atomic layer deposition at 100 °C using tetrakis(dimethylamino)hafnium and oxygen plasma. Additionally, substrate biasing up to -100 V was applied during the oxygen reaction step. The HfO_2 thin films of various thickness from 30 nm to 100 nm were deposited. The mechanical, optical, structural and chemical properties of hafnium oxide were investigated.

The mechanical stress in the ~30 and ~100 nm HfO_2 film changed from tensile to compressive when an average-bias voltage of -50 V was applied. The increase in the refractive index was observed with an increase in average-bias voltage. The high refractive index of 2.03 were observed when ~30 nm and ~100 nm HfO_2 thin films were deposited using an average-bias voltage of -50 V. The XRD measurement showed an increase in crystallization of ~100 nm HfO_2 thin films when average bias voltage was increased to -50 V. Thus crystallization can be the reason for induced stress in the HfO_2 thin films. The AFM and XRR measurements showed an increase in surface roughness with the increase in average-bias voltage. Nano-crystalline hillocks were observed in AFM images of HfO_2 thin film deposited with average-bias voltage of -50 V. The density of the films increased and reached a maximum value of 9.07 g/cm³, when average-bias voltage was increased to -50 V. The FTIR measurement showed a decrease in OH impurity into the film with an increase in average-bias voltage.

It is shown that substrate biasing can be an effective technique to modify properties of HfO_2 thin films and good quality films can be realized at low temperature.

3:15pm **AF2-MoA-8 Study of the Surface Species During Thermal and Plasma-Enhanced Atomic Layer Deposition of Titanium Oxide Films using In-situ IR-Spectroscopy and Iin Vacuo X-ray Photoelectron Spectroscopy**, ***Sofie Vandenbroucke,*** Ghent University - IMEC, Belgium*; E Levrau, M Minjauw, M Van Daele,* Ghent University, Belgium*; E Solano,* Ghent University, Belgium, Spain*; R Vos,* IMEC, Belgium*; J Dendooven, C Detavernier,* Ghent University, Belgium

Understanding ALD reaction mechanisms is key to optimize the quality of thin metal oxide films for various applications. One class of precursors that are of particular interest for the deposition of metal oxide films are the alkylamine precursors. They are liquid at room temperature, have a relatively high vapor pressure, are easily oxidized and do not contain halogen atoms. However, they can leave C, N and H impurities in the film due to the low thermal stability of the ligands.

In situ Fourier Transform Infrared Spectroscopy (FTIR) is often used to study the surface species present during each ALD half-cycle. However, peak identification can be inconclusive and no quantification based on relative peak intensities is possible. The use of a complementary technique such as in vacuo X-ray Photoelectron Sprectroscopy (XPS) might tackle this problem. Peak identification by XPS is more unambiguous and the technique is known for the quantification of chemical groups, but compared to FTIR the detection limit is higher and the sensitivity to low abundant surface groups thus lower. This unique combination of surface techniques is very powerful and relevant for studying surface reactions and surface treatments in general.

In this work, in situ FTIR and in vacuo XPS are used as complementary techniques to gain more insight in the ALD growth of TiO_2 from the alkylamine precursor tetrakis(dimethylamino)titanium (TDMAT) in combination with water vapor, water plasma or oxygen plasma. For the thermal process using water vapor, a typical ligand exchange reaction mechanism was observed. For the plasma enhanced ALD processes a decomposition and combustion reaction could be detected as a secondary reaction mechanism. Surface species such as imines (N=C) and isocyanate (N=C=O) were observed by in situ FTIR for both plasma processes (Figure 1). In addition, nitrites (NOx) could be distinguished during the oxygen plasma process using in vacuo XPS (Figure 2). A schematic overview of all surface species present during ALD growth can be seen in Figure 3.

The resulting films of the thermal process were found to contain a higher amount of C and N impurities compared to the plasma enhanced processes, despite the presence of a secondary decomposition and combustion reaction for the latter. For the water vapor process 2 % of N and 7 % of C impurities were observed with in vacuo XPS, while the films produced with the water plasma process showed only 2 % of N and 3 % of C impurities. Remarkably, only 1% of N and no C impurities were found for the oxygen plasma process.

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