ALD Fundamentals: Growth and Characterization
Room HB Plant Ballroom - Session AF2-WeM

Plasma-enhanced ALD of Nitrides

Moderators: Andrew Cavanagh, University of Colorado at Boulder, **Craig Huffman**, Oxford Instruments

10:45am **AF2-WeM-12 Low-Temperature Plasma-Enhanced Atomic Layer Deposition of Crystalline Gan Thin Films Using Monovalent Organogallium Precursor**, ***Fumikazu Mizutani***, *Nobutaka Takahashi,* Kojundo Chemical Laboratory Co., Ltd., Japan

GaN thin films are promising wide-gap semiconductors, and the low-temperature atomic layer deposition (ALD) of high-quality crystalline GaN films is being actively investigated. In ALD of GaN, trimethylgallium (TMG; $Ga(CH_3)_3$), triethylgallium (TEG; $Ga(C_2H_5)_3$) are widely used. However, there have been almost no reports on obtaining high-purity crystalline GaN films at temperatures below 350 °C.

We have developed a novel liquid precursor (GaCp*; pentamethylcyclopentadienyl gallium) for the ALD of high-purity Ga_2O_3 films [1]. A film with almost no impurities was obtained using ABC-type ALD at a low temperature of 200 °C consisting of precursor adsorption, ligand elimination, and surface oxidation processes. Here, we report the results of investigating a similar ABC-type ALD process to obtain high-purity crystalline GaN at 200 °C.

GaN films were deposited at 200 °C on 150 mm Si wafers with native oxide films using a FlexAL system (Oxford Instruments) with a remote plasma generator and an in situ spectroscopic ellipsometer. In one ALD cycle, GaCp* was used as a precursor, and H_2 plasma followed by N_2 plasma was used as the reactant. In this process, the aromatic anion ligand Cp* was desorbed by H_2 plasma, and the surface Ga was nitrided by N_2 plasma.

Self-limiting reactions were observed for GaCp*, H_2 plasma, and N_2 plasma pulse times of 0.5, 20, and 20 s, respectively. Next, we measured the GPC of ALD using the pulse times. The relationship between the number of ALD cycles and film thickness was linear, with a GPC of 0.023 nm/cycle. The sample, which was deposited in 600 cycles and had a film thickness of approximately 14 nm, was subjected to impurity analysis by GDOES and observation of crystallinity by cross-sectional TEM.

GDOES analysis showed that almost no C impurities were detected, suggesting that the ligands were sufficiently removed by H_2 plasma. Clear lattice fringes were observed in the cross-sectional TEM image, indicating that the GaN thin film was highly crystalline. In this study, deposition was performed on a native oxide film of silicon, but it is expected that epitaxial films can be deposited on templates such as sapphire.

The reason why high-purity, highly crystalline GaN could be deposited even at a low temperature of 200 °C is thought to be because GaCp* is a monovalent precursor, meaning that monovalent GaCp* is more advantageous for ligand elimination than trivalent TMG and TEG.

Reference[1] F. Mizutani, S. Higashi, M. Inoue, and T. Nabatame, J. Vac. Sci. Technol. A 38, 022412 (2020).

11:00am **AF2-WeM-13 Plasma-Enhanced Growth of Low-κ Amorphous Boron Nitride: From 25 °C to 400 °C**, ***Daehyun Ko***, *Fu-Chun Sheu, Luwen Li, Xun Zhan,* UT Austin*; John Carroll, Sergio Gamez-Puente, Hu Li, Peter Ventzek, Jianping Zhao,* Tokyo Electron America*; John Ekerdt, Jamie Warner,* UT Austin

The International Roadmap for Devices and Systems (IRDS) highlights the critical need for new dielectric materials that reduce permittivity and meet reliability requirements for future interconnect architectures. As interconnect dimensions scale into the sub-25 nm regime, conventional silicon-based dielectrics face significant challenges in mitigating parasitic capacitance and crosstalk while satisfying the rigorous mechanical and barrier requirements for integration. Amorphous boron nitride (a-BN) has emerged as a promising alternative for these applications because it offers a unique combination of low permittivity, high mechanical strength, and excellent chemical stability.

In this work, we demonstrate the plasma-enhanced growth (100 MHz capacitively coupled plasma) of a-BN onSiO_2/Si(001) using borazine ($B_3N_3H_6$) as a single-source precursor. We explore a wide processing window, ranging from room temperature (25 °C) to 400 °C. Growth is governed by weak, reversible physical adsorption and plasma exposure time. During a growth cycle, borazine is adsorbed on the substrate, the chamber is purged/evacuated, and an Ar plasma is ignited. The plasma activates the adsorbed borazine by dissociating the B-H and N-H bonds and breaking open the ring structure. *In situ* X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) analyses confirm the formation of stoichiometric, sp^2-bonded films with exceptional purity (<1 at.% carbon) and no resolvable B-C or B-O bonding features over a 25 to 400 °C window. By rigorously defining the thickness of a-BN (~14 nm) grown at 25 °C via cross-sectional scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) of the fabricated metal-insulator-metal (Au/a-BN/SiO_2/Si) capacitors, we extracted a dielectric constant of ~2.94, validating the potential of a-BN for back-end-of-line integration.

We further investigated the temperature dependence of film properties by extending the growth window from 100 °C to 400 °C. Although Fast Fourier transform (FFT) analysis confirms the emergence of short-range lamellar ordering at elevated temperatures, transmission electron microscopy (TEM) and EELS confirm the preservation of a global amorphous phase and an sp^2-bonded network throughout this transition. Consistent with this, X-ray reflectivity (XRR) reveals a linear increase in film density with temperature, reaching ~2.10 g cm^{-3} at 400 °C. This densification correlates with enhanced environmental stability, offering a tunable pathway to synthesize high-quality a-BN dielectrics optimized for diverse thermal budgets.

11:15am **AF2-WeM-14 Comparing the Effect of H_2 and N_2 Plasma on Boron Nitride Surface During Plasma Enhanced Atomic Layer Deposition Using Density Functional Theory**, ***Tsung-Hsuan Yang***, *Jianping Zhao, Peter Ventzek,* Tokyo Electron America

Boron nitride (BN) has emerged as a promising candidate for next–generation semiconductor and dielectric materials due to its wide bandgap, chemical stability, and compatibility with advanced device architectures. However, the intrinsic inertness of BN surfaces presents challenges for thin–film growth and surface functionalization, particularly when using conventional precursors such as boron trichloride (BCl_3) or borazine ($B_3N_3H_6$), which exhibit limited surface reactivity. Plasma-assisted processes employing hydrogen (H_2) or nitrogen (N_2) are therefore commonly used to activate BN surfaces, although the underlying reaction mechanisms remain poorly understood.

In this work, density functional theory (DFT) calculations are used to investigate the reaction mechanisms and energetics of H_2 and N_2 plasma interactions with boron nitride surfaces. Plasma environments are modeled using atomic hydrogen and nitrogen radicals to represent the highly reactive plasma species. Adsorption configurations, reaction pathways, and activation barriers are analyzed to elucidate key differences between hydrogen- and nitrogen-based plasma treatments.

Our results show that hydrogen radicals preferentially interact with surface nitrogen sites, leading to hydrogen termination and, in some cases, B–N bond dissociation. In contrast, nitrogen radicals promote nitrogen incorporation and surface restructuring through B–N bond formation and the generation of N_2-like dimer species. These distinct reaction pathways produce markedly different surface chemistries, which influence subsequent precursor adsorption and thin–film growth behavior. Based on the calculated energetics, we identify process conditions under which plasma species can selectively tailor surface reactivity, enabling control over film geometry, stoichiometry, and structural evolution.

11:30am **AF2-WeM-15 Precise and Narrow Ion-Energy Distributions in Plasma-Enhanced ALD of Nitrides Using Tailored-Waveform Biasing**, *Arthur de Jong, Silke Peeters, Harm Knoops, Erwin Kessels,* ***Adrie Mackus***, Eindhoven University of Technology, Netherlands

Plasma-enhanced ALD (PEALD) is a powerful approach for the low-temperature growth of nitride thin films, where controlled ion bombardment can be used to tailor film composition, density, and functional properties. In previous work, we have demonstrated that radiofrequency (RF, 13.56 MHz) substrate biasing provides beneficial ion-energy effects during PEALD, enabling improved electrical and structural properties of a range of dielectrics and conductive nitrides [1,2]. However, the achievable process window can benefit from more precise, narrow, and independent control over the ion energy.

In this contribution, we demonstrate tailored-waveform (TW) substrate biasing at 200 kHz as an advanced ion-energy control scheme [3] for PEALD, offering narrow and well-defined ion-flux energy distribution functions (IFEDFs) without increasing the plasma density [4]. We apply this approach to the PEALD of several technologically-relevant metal nitrides, including AlN_x, TaC_xN_{1-x}, TiN_x, and NbN_x, using Ar–N_2–H_2 plasma mixtures.

By systematically tuning the ion energy via TW biasing, clear and material-specific structure–property relationships are observed. For AlN_x, an increased refractive index and reduced oxygen incorporation are achieved, while for conductive nitrides (TaC_xN_{1-x}, TiN_x, and NbN_x) significant reductions in electrical resistivity are obtained. These results are consistent with, and extend beyond, earlier RF-bias PEALD studies, highlighting the role of controlled low-energy ion bombardment in densification, impurity suppression, and microstructural optimization.

Overall, tailored-waveform biasing provides substantially narrower and better-defined ion-energy distributions, transforming ion energy during ALD into a high-precision knob for materials design.

This work was carried out in collaboration with Oxford Instruments and Prodrive Technologies. An Oxford Instruments FlexAL ALD reactor in the TU/e NanoLab was retrofitted with a Prodrive Technologies prototype low-frequency tailored waveform generator.

[1] T. Faraz *et al*., *Tuning material properties of oxides and nitrides by substrate biasing during plasma-enhanced atomic layer deposition*, ACS App. Mater. Interfaces 10, 13158 (2018).

[2] S. A. Peeters *et al*., Ultrathin superconducting TaC_xN_{1-x} films prepared by plasma-enhanced atomic layer deposition with ion-energy control., App. Phys. Lett. 123, 132603 (2023).

[3] T. Faraz et al., *Precise ion energy control with tailored waveform biasing for atomic scale processing*, J. Appl. Phys. 128, 213301 (2020).

[4] T. Faraz *et al*., *Tailored waveform biasing in atomic and molecular plasmas for atomic-scale processing*, submitted.

11:45am **AF2-WeM-16 Characterizing Inductively Coupled Plasmas in $Ar/N_2/H_2$ Mixtures for Plasma Enhanced Atomic Layer Deposition***, **David Boris**, Jeffrey Woodward, Virginia Wheeler, Michael Johnson, Mackenzie Meyer, Scott Walton,* U.S. Naval Research Laboratory

Low temperature plasmas containing mixtures of Argon, Nitrogen, and Hydrogen are widely used in the plasma enhanced atomic layer deposition of crystalline metal nitrides (e.g. AlN) at low temperatures (<500C) [1,2,3].Generally, the addition of H_2 is beneficial in that it facilitates the removal of precursor ligands and leads to films with low carbon content (<1%). In addition, if the process conditions are properly chosen, highly crystalline metal-nitride films can be grown in $Ar/N_2/H_2$ mixtures.However, the effects of H_2 addition on the downstream plasma properties near the substrate are not well understood in remote, inductively coupled plasma (ICP) geometries.As such, a better understanding of the downstream plasma properties in this gas chemistry will be the focus of this presentation.

In this work, we use a combination of Langmuir probes, a retarding field energy analyzer, and optical emission spectroscopy (OES) to examine the effects of varying process parameters on the physical characteristics of $Ar/N_2/H_2$ plasmas generated in a remote, 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 species density, plasma density, plasma potential, and the energy and flux of ions at the substrate.Of particular interest is the effect H_2 has on the ion flux and ion energy distribution at the substrate. These changes in plasma properties are then tied to changes in the characteristics of AlN thin films grown via plasma-enhanced ALD using a remote ICP employing $Ar/N_2/H_2$ gas mixtures. This work was supported by the NRL Base program through the Office of Naval Research.

[1] N. Nepal, et al Appl. Phys. Lett. 103, 082110 (2013)

[2] M. J. Sowa, et al J. Vac. Sci. Technol. A 34, 051516 (2016)

[3] M. F. J. Vos, et al J. Phys. Chem 122, 39 (2018)

Author Index

Bold page numbers indicate presenter