Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM1-TuA

Next Generation ALD Semiconductors

Moderators: Neeraj Nepal, U.S. Naval Research Laboratory, **Junjie Zhao**, Zhejiang University

1:30pm **EM1-TuA-1 Real-time Optimization of Gallium Oxide and Aluminum Gallium Oxide Thin Film Growth via Plasma-Enhanced Atomic Layer Deposition Using In-situ Spectroscopic Ellipsometry***, Yousra Traouli, Ufuk Kilic, Mathias Schubert, Eva Schubert,* University of Nebraska - Lincoln

Ultrawide bandgap metal oxide semiconductor materials have attracted significant interest for high-power, high-frequency, and extreme-environment applications due to their large breakdown fields and thermal stability under harsh operating conditions. In this work, we investigate the growth dynamics of gallium oxide (Ga_2O_3) and aluminum gallium oxide $(Al_xGa_{1-x})_2O_3$ thin films deposited by plasma-enhanced atomic layer deposition (PE-ALD). The deposition process was monitored in real-time using *in-situ* spectroscopic ellipsometry (SE).

Ga_2O_3 ultrathin films were grown using four trimethylgallium pulses with a total exposure time of 20 msec during the metal-precursor half-cycle, followed by a remote oxygen plasma (75 sec, 300 W). Ternary $(Al_xGa_{1-x})_2O_3$ films were deposited using a hybrid ALD process that alternate trimethylaluminum (60 msec)/H_2O (60 msec) cycles for Al_2O_3 and trimethylgallium/oxygen-plasma cycles for Ga_2O_3. While the substrate temperature is maintained at 250° C, argon was used Argon as the carrier gas during the introduction of precursor material (60 sccm) and plasma process (200 sccm) with process pressure of 0.25 Torr.

To interpret the time-resolved SE data, a dynamic dual-box model approach was employed, providing insight into surface processes such as precursor adsorption and ligand removal [1,2]. Periodic oscillations in surface roughness and subsurface layer thickness were observed, reflecting the cyclic nature of molecule attachment and ligand desorption. To maintain accurate analysis of the *in-situ* SE data,the complex dielectric functions of Ga_2O_3 and $(Al_xGa_{1-x})_2O_3$ thin films were determined over the spectral range of 0.74–5.04 eV using selected *in-situ* SE data at different film thickness. The growth rates of Ga_2O_3 and Al_2O_3 were 0.918 Å/cycle and 0.575 Å/cycle, respectively. Additionally, by performing *ex-situ* SE measurements in a spectral range from 0.64 eV to 9 eV at select angles of incidence from 45° to 75° by 10° steps, we extracted the broad spectral range complex dielectric function at room temperature and identify the higher order band-to-band transitions based on critical point model dielectric function analysis.

Complementary characterization techniques, including X-ray diffraction, X-ray photoelectron spectroscopy, and atomic force microscopy, were used to assess film crystallinity, composition, and surface morphology.

Overall, this study demonstrates the *in-situ* SE technique as a powerful tool for recipe optimization and for revealing in-cycle growth kinetics during PE-ALD of Ga_2O_3 and $(Al_xGa_{1-x})_2O_3$ thin films.

[1] Kilic, Ufuk, et al. Sci. Rep. 10.1 (2020): 10392.

[2] Traouli, Yousra, et al. J. Vac. Sci. Technol. 42.5 (2024).

1:45pm **EM1-TuA-2 Conductive Si-Doped Ga_2O_3 via Thermal ALD Followed by Thermal Annealing***, Benjamin Greenberg,* U.S. Naval Research Laboratory*; Katie Gann,* National Research Council Fellow Residing at U.S. Naval Research Laboratory*; Boris Feigelson, Alan Jacobs, Jeffrey Woodward, Daniel Pennachio, Emma Rocco,* U.S. Naval Research Laboratory

Monoclinic β-Ga_2O_3 has a rare combination of ultrawide bandgap (~4.8 eV) and extrinsically controllable electron density, *n*, between ~10^{16} and ~10^{20} cm^{-3}, making it a strong candidate for high-power, high-frequency, and optoelectronic applications. There have been numerous reports of β-Ga_2O_3 thin film growth via metalorganic chemical vapor deposition (MOCVD), thermal atomic layer deposition (ALD), and plasma-enhanced atomic layer deposition (PEALD), including Ga_2O_3:Ge with $n > 10^{20}$ cm^{-3} via MOCVD[1] and Ga_2O_3:Si with $n > 10^{18}$ cm^{-3} via PEALD followed by thermal annealing.[2] In the case of thermal ALD, conformal growth on substrates with high aspect ratio (AR) has been demonstrated, including Si trenches with AR = 11,[3] although doping of the conformal Ga_2O_3 was not investigated. For the development of high-performance, high-AR Ga_2O_3 devices, there remains a need for thermal ALD processes for doped Ga_2O_3 that can simultaneously achieve high *n* and high conformality.

In this work, we demonstrate thermal ALD of Ga_2O_3:Si using trimethylgallium (TMG), bis(t-butylamino)silane (BTBAS), and ozone as precursors, employing supercycles consisting of *x* TMG/O_3 cycles and 1 BTBAS/O_3 cycle. Amorphous Ga_2O_3:Si is deposited on Si(100), α-Al_2O_3(0001), and insulating β-Ga_2O_3:Fe(010) substrates at 220 °C, and some films are then crystallized via thermal annealing under N_2. Comparing as-grown Ga_2O_3:Si with *x* = 15 to undoped Ga_2O_3, Si incorporation is confirmed by an increase in the growth-per-cycle (GPC) from 0.69 to 0.73 Å/cyc and a decrease in the refractive index from 1.92 to 1.84. The as-grown films are electrically insulating, but thermal annealing experiments reveal that low electrical resistivity is possible after crystallization. Ga_2O_3:Si (*x* = 400, thickness = 28 nm) grown on β-Ga_2O_3:Fe and annealed at 900 °C for 10 min exhibits $n = 8.4 \times 10^{18}$ cm^{-3} (dopant activation = 8.8%) and an electron mobility, μ, of 49 $cm^2V^{-1}s^{-1}$ for a resistivity, ρ, of 1.4×10^{-2} Ω-cm. Interestingly, ρ becomes immeasurably high ($\rho > 1$ Ω-cm) when the annealing temperature is increased to 1000 °C. X-ray diffraction (XRD) and transmission electron microscopy (TEM) indicate that annealing at 900 °C produces an epitaxial β-Ga_2O_3:Si layer on top of the β-Ga_2O_3:Fe that spans approximately half of the film thickness (with lower crystalline quality in the top half of the film), whereas annealing at 1000 °C produces fully epitaxial β-Ga_2O_3:Si. The high ρ of the fully epitaxial β-Ga_2O_3:Si—and potential strategies for attaining conformal, conductive β-Ga_2O_3:Si on various substrates—will be discussed in light of known challenges presented by Ga_2O_3 crystallization, including the possible formation of Ga vacancies[4] and γ-Ga_2O_3 en route to β-Ga_2O_3.[5]

1. Alema *et al.*, *APL Mater.* 9, 091102 (2021)
2. Zhang *et al.*, *Surf. Coat. Technol.* 435, 128252 (2022)
3. Comstock & Elam, *Chem. Mater.* 24, 4011 (2012)
4. Gann *et al.*, *J. Appl. Phys.* 138, 115302 (2025)
5. Wouters *et al.*, *APL Mater.* 12, 011110 (2024)

2:00pm **EM1-TuA-3 Low-Temperature Self-Limiting Growth of Crystalline III-Nitride Films: How Far Can We Go?***, Necmi Biyikli,* University of Connecticut **INVITED**

2:30pm **EM1-TuA-5 Piezoelectric and ferroelectric $Al_{1-x}Sc_xN$ by plasma-enhanced ALD***, Gilbert B. Rayner Jr., Noel O'Toole, Nathaniel Nelson,* Kurt J. Lesker Company*; Bangzhi Liu,* The Pennsylvania State University*; Jeffrey Shallenberger,* The pennsylvania State University*; Gregory Muha, Piush Behera, Suraj Cheema,* Massachusetts Institute of Technology*; Blaine Johs,* Film Sense*; Nastazia Moshirfatemi,* General Technical Services, LLC*; Daniel Drury, Brendan M. Hanrahan,* Army Research Directorate, DEVCOM Army Research Laboratory*; Glen R. Fox,* Fox Materials Consulting, LLC*; Nicholas A. Strnad,* Army Research Directorate, DEVCOM Army Research Laboratory

Wurtzite aluminum–scandium nitride ($Al_{1-x}Sc_xN$) thin films are promising for next-generation electronic and sensing technologies. However, achieving precise composition and uniform coverage on complex three–dimensional architectures remains challenging. Here, we demonstrate the growth of $Al_{1-x}Sc_xN$ by plasma–enhanced atomic layer deposition (PEALD) under ultrahigh purity conditions (UHP-C) using a supercycle sequence composed of alternating AlN and ScN constituent processes. The PEALD process utilized trimethylaluminum (TMA), bis(ethylcyclopentadienyl) scandium chloride [$ClSc(EtCp)_2$] and N_2−H_2 plasma as co-precursors at substrate temperatures ranging from 215−300 °C.

A 60.3 nm-thick PEALD $Al_{0.83}Sc_{0.17}N$ film grown at 300 °C on a {111}-oriented platinum bottom electrode on Si (100) exhibited clear ferroelectric switching. The film showed switched polarization ($2P_r$) of 163 μC/cm^2 and 139 μC/cm^2 for negative and positive pulsing, coercive fields of 5.5 MV/cm and -4.8 MV/cm, and a dielectric constant of 12.8−13.8 at 100 kHz under ±10 V. The effective longitudinal piezoelectric coefficient ($d_{33,f}$) of the $Al_{0.83}Sc_{0.17}N$ film was measured to be -23.6 pm/V and 22.1 pm/V for the N- and metal-polarities, respectively.

Structural analysis revealed that the film on {111} platinum was fully c-axis (0001) oriented out-of-plane, indicating high crystalline quality even along the sidewalls of three–dimensional features. When deposited on single–crystal gallium nitride, the $Al_{0.83}Sc_{0.17}N$ adopted a highly ordered in-plane and out-of-plane arrangement consistent with epitaxial growth. Films deposited over narrow trenches showed uniform, conformal coverage. These results demonstrate that PEALD enables high–quality $Al_{1-x}Sc_xN$ suitable for advanced three–dimensional electronic and sensing applications.

2:45pm **EM1-TuA-6 Low Temperature PEALD of Epitaxial AlN Without Atomic Layer Annealing**, ***Jeffrey Woodward**, David Boris, Michael Johnson, Daniel Pennachio,* U.S. Naval Research Laboratory*; Michael Mathews,* NRC postdoctoral fellow residing at U.S. Naval Research Laboratory*; Emma Rocco,* U.S. Naval Research Laboratory*; Katie Gann,* NRC postdoctoral fellow residing at U.S. Naval Research Laboratory*; Ben Sekely,* NRC postdoctoral fellow stationed at U.S. Naval Research Laboratory*; Tatyana Feygelson, Jonathan Levine-Miles,* U.S. Naval Research Laboratory*; Jennifer Hite,* University of Florida*; Michael Mastro,* U.S. Naval Research Laboratory*; Henry Chuang,* Boston University*; Virginia Wheeler, Scott Walton,* U.S. Naval Research Laboratory

AlN is a wide-bandgap semiconductor with exceptional thermal conductivity, temperature stability, and piezoelectric properties, making it a promising material for high power and high frequency electronics, deep ultraviolet optoelectronics, and microelectromechanical systems. While AlN PEALD has been the subject of extensive research, it typically results in amorphous or polycrystalline films, which have inferior electrical properties compared to epitaxial AlN. Most reports of epitaxial AlN growth by PEALD involve the use of atomic layer annealing (ALA), in which an Ar plasma exposure is incorporated into each cycle to induce crystallization of the surface.[1] While the effectiveness of ALA is proven, its use also increases cycle duration, which significantly prolongs total process time and can promote impurity incorporation. For these reasons, the growth of epitaxial AlN without ALA is desirable, though this is challenged by the complexity of controlling the plasma properties to achieve suitable growth conditions.[2]

In this work, we demonstrate the growth of 30-50 nm thick epitaxial AlN films on Al_2O_3, GaN, and Ga_2O_3 at 300 °C using PEALD without ALA or thermal annealing. The PEALD process uses the commonly-employed combination of trimethylaluminum (TMA) and $N_2/H_2/Ar$ plasma, and is performed in a standard commercial reactor with remote inductively coupled plasma (ICP) source.Plasma diagnostics were used to identify favorable plasma regimes which produce ion energy and flux characteristics comparable to those of plasmas used in ALA. The films were characterized using x-ray reflectivity (XRR), high resolution x-ray diffraction (HRXRD), in-plane grazing incidence diffraction (IP-GID), atomic force microscopy (AFM), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), and optical measurements. The growth per cycle (GPC) and density ranged from 0.90–1.03 Å and 2.998–3.173 g/cm^3, respectively, depending on substrate, with deposition on GaN resulting in the highest GPC and density.The topography of the films closely replicated that of the underlying material with roughness from 0.25–1 nm by AFM and 0.83–2 nm by XRR, indicating that the deposition was highly conformal. The epitaxial nature of the AlN (i.e., exhibiting a highly ordered crystalline structure with well-defined orientational relationship to the substrate) is confirmed by HRXRD and IP-GID, which show the films to be single phase and orientation with 6-fold azimuthal rotational symmetry. While the AlN films on Al_2O_3 and Ga_2O_3 are wurtzite phase with significant mosaicity, the AlN on GaN is metastable zincblende phase with low tilt disorder, as evidenced by narrow out-of-plane rocking curves with FWHM= 0.149 degrees (537 arcseconds). Results of AlN PEALD on nanocrystalline diamond (NCD) and single crystal diamond (SCD) will also be presented.

[1] H. Y. Shih et al., Sci. Rep. **7**, 39717 (2017)
[2] D. R. Boris et al., J. Vac. Sci. Technol. A **42**, 033008 (2024)

3:00pm **EM1-TuA-7 Enabling Blister-Free, Crystalline AlN Thin Films on 200 mm Si Wafers by PE-ALD Using a Microwave Electron Cyclotron Resonance Plasma Source**, ***Shiv Bhudia,*** TUM School of Natural Sciences, Technische Universität München; Silicon Austria Labs GmbH, Austria*; Tai Nguyen,* Silicon Austria Labs GmbH, Austria*; Dominik Hartmann,* Evatec AG, Switzerland*; Marco Deluca, Julian Pilz,* Silicon Austria Labs GmbH, Austria

Aluminum nitride (AlN) is an important material for optoelectronics,[1] energy harvesting, and surface-acoustic-wave transducers and resonators.[2–5] It also enables devices operating at high frequencies and in thermally and chemically harsh environments.[6] This interest stems from its combination of a wide bandgap, high thermal conductivity, favorable lattice constant, and piezoelectric properties. In most applications, (002)-textured wurtzite films are required to achieve the desired device performance.[7] Furthermore, when fabricating 3D nanostructures such as microelectromechanical systems (MEMS),[8] memory devices,[9] and through silicon via (TSV) technology,[10] conformal growth and atomic-scale control are essential. Atomic layer deposition (ALD) has been proven to be an enabling deposition method under these conditions.

However, obtaining AlN films with crystal quality comparable to that of other deposition techniques remains challenging for ALD on Si substrates,[11–13] as oxygen and carbon impurities can significantly degrade crystallinity. Surface blistering is also a critical reliability issue in ALD and PE-ALD AlN,[14] yet systematic wafer-scale studies are scarce in literature. Moreover, the use of electron cyclotron resonance (ECR) plasma sources for AlN growth has received limited attention to date.[15]

In this work, AlN films are deposited on 200 mm Si(111) wafers using plasma-enhanced atomic layer deposition with trimethylaluminum (TMA) and NH_3 plasma as reactants. A novel ALD module (Evatec PEALD) is used for film deposition, employing a microwave ECR source for plasma generation. The effects of substrate temperature (200-400 °C) and plasma power (50-200 W) on film properties and blister formation are investigated. It is found that a combination of high power and substrate temperature leads to the formation of blisters on the edge region of the wafer.Applying a combination of characterization techniques, the number of blisters as a function of process parameters could be quantified (0-10 % of wafer area), and the defect formation mechanism was identified as likely caused by stress-induced effects. Fine-tuning of the substrate temperature and plasma power enables the suppression of these defects, resulting in damage-free, crystalline, and chemically pure films on 200 mm Si(111) substrates.

In a nutshell, this work presents effective mechanisms for producing PEALD AlN thin films with preferential c-axis orientation on 200 mm wafers, highlighting the importance of plasma source and parameter selection and giving insights into the suppression of film blistering effects.

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