Emerging Materials
Room Auditorium - Session EM1-WeA

Emerging Materials

Moderators: Nathanaelle Schneider, CNRS-IPVF, Charles H. Winter, Wayne State University

1:30pm **EM1-WeA-1 Self-Limiting Growth of Monocrystalline GaN Films via Sequential Triethylgallium and Forming Gas Plasma Cycles in Hollow-Cathode Plasma-ALD Reactor**, *D. Shukla, S. Ilhom, A. Mohammad, B. Willis,* University of Connecticut*; A. Okyay,* Stanford University*;* ***Necmi Biyikli,*** University of Connecticut

Low-temperature synthesis efforts for high-quality GaN thin films using plasma-assisted ALD utilized various reactor configurations featuring different plasma sources. While our early GaN growth experiments using quartz-based ICP sources resulted in nanocrystalline/amorphous films with elevated oxygen impurities, shifting to stainless-steel based hollow-cathode plasma source revealed polycrystalline GaN films with preferred (002) orientation. Upon further modification of plasma source and reactor chamber design, eventually we achieved single-crystal GaN film growth on sapphire substrates. In this presentation we share our experimental findings on the epitaxial growth of GaN films using hollow-cathode plasma-assisted ALD (HCPA-ALD).

The films were deposited using triethylgallium (TEG) and forming gas (95/5% N_2/H_2) plasma as metal precursor and nitrogen co-reactant, respectively. Growth experiments have been performed at 240 °C substrate temperature and 150 W rf-power. Both in-situ and ex-situ ellipsometry were employed to monitor the surface reactions, measure the thickness variation, and optical properties of the films. When compared to reference films grown on Si(100) substrates, growth-per-cycle (GPC) values obtained for GaN films on sapphire substrates showed a notable increase. Grazing-incidence XRD measurements revealed polycrystalline films on Si substrates while GaN/sapphire samples showed no crystal peak. When theta-2theta scans were done, we observed a strong single peak at (002) orientation, confirming the monocrystalline character of these GaN films. High-resolution transmission electron microscopy (HR-TEM) revealed the epitaxial relationship of the GaN layers grown on sapphire substrates. We attribute this significant improvement in crystal quality to the synergistic impact of customized HCPA-ALD reactor, large-diameter third-generation hollow-cathode plasma source, and optimized growth conditions with low-hydrogen forming gas plasma chemistry. With further improvement, we aim to achieve device quality electrical properties that can be used for prototype device fabrication.

1:45pm **EM1-WeA-2 ALD of $In_{1-x}Ga_xN$**, ***Henrik Pedersen****, P. Rouf, C. Hsu,* Linköping University, IFM, Sweden

Alloying group 13-nitrides to ternary phases allows tuning of the bandgap from 6.2 eV for pure AlN down to 0.7 eV for pure InN. The bandgap of $In_{1-x}Ga_xN$ can theoretically span from UV to IR (3.4–0.7 eV), including the whole visible light range by varying x, making it promising material for optoelectronic applications. However, the ability to vary the composition of $In_{1-x}Ga_xN$ is limited by the theoretically predicted metastability of $In_{1-x}Ga_xN$ for $0.05 < x < 0.95$, which leads to phase separation into their binary materials. The deposition of $In_{1-x}Ga_xN$ is also hindered by the low thermal stability of InN, which decomposes into In metal and N_2 at around 500 °C, making traditional CVD approaches ill-suited. We have recently shown that ALD is a promising technique to deposit InN thin films with excellent structural quality,[1] ALD is therefore a promising alternative to CVD for $In_{1-x}Ga_xN$ with x close to 0.5. In our efforts to deposit $In_{0.5}Ga_{0.5}N$ we have explored two ALD approaches:

By using a short period superlattice, with alternating monolayers of GaN and InN, $In_{0.5}Ga_{0.5}N$ deposition was attempted from repeated *n* InN and *m* GaN monolayers (*n*=*m*= 1, 2, 3…) using triethyl gallium (TEG), trimethyl indium (TMI) and ammonia plasma at 320 °C. This approach afforded single-crystalline $In_{1-x}Ga_xN$ with tunable x between 0.3 and 0.7 by varying the ratio between *n* and *m*. The crystalline quality of $In_{1-x}Ga_xN$ prepared by this multilayer approach ALD is remarkably better than that prepared by conventional continuous CVD and earlier reported ALD work using a multilayer approach with thicker layers of InN and GaN in the multilayer.

By mixing solid Ga(III) and In(III) triazenides in the same evaporator and co-subliming the two metal precursors $In_{1-x}Ga_xN$ was deposited using a single, mixed metal pulse and NH_3 plasma at 350 °C.[2] $In_{1-x}Ga_xN$ was successfully deposited using this approach and the value of x could be tuned by changing the sublimation- and deposition temperatures, and the ratio of the two metal precursors. An $In_{1-x}Ga_xN$ film with x = 0.5 was deposited and found to have a band gap of 1.94 eV. The $In_{1-x}Ga_xN$ film grew epitaxially on 4H–SiC(0001) without need for a buffer layer and without phase segregation or decomposition of the $In_{1-x}Ga_xN$ into the binary materials or In droplets.

Our results reveal a promising potential of ALD over conventional growth techniques to prepare ternary group 13-nitrides with tunable composition at low temperature, which provides the possibility to grow heterostructures with metastable alloys for device application.

Refs.

1. Hsu et al. *Appl. Phys. Lett.* **2020**, *117*, 093101.
2. Rouf et al. *J. Mater. Chem. C* **2021**, *9*, 13077.

2:00pm **EM1-WeA-3 Atomic Layer Doped Epitaxial β-Ga_2O_3 Films Grown via Supercycle and Co-dosing Approaches at 240 ℃***,* ***Saidjafarzoda Ilhom,*** *A. Mohammad, D. Shukla, B. Willis,* University of Connecticut*; A. Okyay,* Stanford University*; N. Biyikli,* University of Connecticut

Wide and ultrawide bandgap (WBG/UWBG) semiconductors make the backbone of high-power high-frequency electronics, used in electric vehicles, 5G and beyond wireless communication systems, and smart power grids. However, the relatively complex growth reactors and typical growth temperatures around 1000 °C lead to increased production costs. Gallium oxide (Ga_2O_3) is an emerging UWBG semiconductor showing superior material properties particularly ideal for harsh environment (high temperature, high-energy radiation, corrosion) applications. Reducing the growth and doping process temperatures for Ga_2O_3 would potentially enable a wider integration platform towards post-CMOS integration and flexible electronics.

Hence, we report on the low-temperature as-grown crystalline β-Ga_2O_3 films on Si, glass, and sapphire via hollow-cathode plasma-enhanced atomic layer deposition (HCPA-ALD). The films were deposited using triethylgallium (TEG) and Ar/O_2 plasma as metal precursor and oxygen co-reactant, respectively. Additionally, we have employed in situ atomic layer doping to n-type dope β-Ga_2O_3 films where tris-dimethylaminosilane (TDMAS) and tetrakis-dimethylaminotin(IV) (TDMASn) were utilized as the dopant precursors. Growth experiments have been performed at 240 °C under 50 W rf-power. The doping process was carried out via both supercycle (ABC-type ALD-cycle) and co-dosing methods. Additionally, eachunit ALD-cycle was followed by an in-situ Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20 seconds at 250 W rf-power. Both in-situ and ex-situ ellipsometry were employed to measure the thickness and optical properties of the films. X-ray diffraction (XRD) of the sample on sapphire revealed epitaxial β-Ga_2O_3 films with monoclinic β-phase. On the other hand, GIXRD of the samples grown on Si and glass displayed polycrystalline β-Ga_2O_3 films. Further outcomes from our ongoing optical and electrical characterizations will provide additional insight to overcome the challenges in achieving device quality undoped and doped β-Ga_2O_3 layers at low growth temperatures. A significant effort will be devoted for the comparison of Si and Sn-doping strategies, and if needed, ex-situ thermal annealing studies will be carried out for doping activation.

2:15pm **EM1-WeA-4 Closing in on Room-Temperature Metal-Insulator-Transitions for Next Generation Electronics by Epitaxial Nickelate ALD***,* ***Linn Rykkje****, H. Sønsteby, O. Nilsen,* University of Oslo, Norway

Complex oxides exhibiting metal-insulator transitions (MITs) are exemplar materials systems with strong correlation and emergent functional phenomena. Particularly the rare-earth nickelates (*RE*NiO_3, with trivalent rare-earth *RE* = La, Pr, Nd, …, Lu) are of interest as their MITs occur concomitantly with a structural transition. Underlying their rich phase diagram and the MIT's physical origin is a complex interplay of interactions; though it remains an unsolved puzzle in fundamental research, the exotic properties rooted in it have great potential for electronics applications.

Among the *RE*NiO_3s, the MIT temperature of $NdNiO_3$ (T_{MI} = 200 K) is the closest to room temperature. Tuning the T_{MI} can be carried out using strain or by partial substitution of Nd with larger RE cations (see phase diagram). A more significant challenge, however, has been to develop a synthesis route that stabilizes Ni^{3+} and provides sufficient control under industrially relevant conditions. For instance, high temperatures and ultrahigh vacuum (UHV) typically facilitate epitaxy, but are incompatible with monolithic device integration.

In this talk we show that with ALD – since long embraced by the electronics industry – we can grow high-quality epitaxial $NdNiO_3$ thin films with excellent control of thickness, uniformity, and chemical composition. This is achieved at low temperatures (225 °C) without constraints to the substrate geometry or need for UHV. Thin films of stoichiometric composition show low resistivities at room temperature and a sharp MIT, which are desired properties of a functional electronic switch in future neuromorphic architectures. Quaternary oxide thin films of the form (*RE*,Nd)NiO_3 have been successfully deposited using ALD with the aim of tuning the T_{MI} close to 273 K. Further chemical and electrical characterizations are needed, however, to establish and control the effect of partial *RE* substitution on the T_{MI}.

Although much of the fundamental behavior of the *RE*NiO_3s remains contested, their potential for applications is undisputed; in fact, many members are already found in various device concepts. The success in using low-temperature ALD to grow high-quality $NdNiO_3$ (stoichiometric and cation substituted) thin films with a sharp MIT could promote the implementation of such switching-materials in next-generation electronics. A complex oxide field-effect transistor may thus be more within reach than previously anticipated, offering a viable alternative and/or complement to Si-based circuitry. Based on fundamentally different mechanisms, this could pave the path for a greener and more sustainable integrated circuit technology in the future.

2:30pm **EM1-WeA-5 Plasma-Enhanced Atomic Layer Deposition of Spinel Ferrite $CoFe_2O_4$ and $NiFe_2O_4$ Thin Films***, **Mari Napari,*** University of Southampton, UK*; M. Heikkila,* University of Helsinki, Finland*; S. Kinnunen, J. Julin,* University of Jyvaskyla, Finland*; T. Prodromakis,* University of Southampton, UK

Thin films of insulating ferro- and ferrimagnetic complex oxides with high Curie temperatures, such as spinel ferrites, are essential for many emerging applications utilising room temperature spin-polarisation and magneto-optical effects, e. g. spintronics and sensors [1]. There is a need for a synthesis method for high quality magnetic oxides with large scale processing compatibility. Here, we have developed PEALD processes for two spinel ferrite materials, $CoFe_2O_4$ (CFO) and $NiFe_{2.5}O_4$ (NFO) using ferrocene and cobalt(III)- or nickel(II) acetylacetonate as precursors in direct plasma PEALD at 250°C. The CFO films were deposited with 1:2 Co:Fe ratio, while the NFO films were grown iron-rich to ensure that the ferrimagnetic property is not hampered by a parasitic antiferromagnetic nickel oxide component [2]. Stoichiometry of the grown ternary oxide films was confirmed with time-of-flight elastic recoil detection analysis measurements, which also showed that the low light element impurity content of the films (H < 2.0 at. -%, C < 0.3 at. -%,) originates mainly from the acetylacetonate sources. According to the X-ray diffraction measurements of 40 nm thick films, the PEALD CFO and NFO have the desired (inverse) spinel structure, and the films grown on sapphire substrates are strongly (111) oriented already as-deposited. Helium ion microscopy and atomic force microscopy both showed that the films are continuous and free of aggregations. The oriented CFO films on sapphire have a very smooth surface (r_{rms} < 0.3 nm) but the NFO with a same thickness has a higher surface roughness (r_{rms} > 1.5 nm), which is in accordance with the previous observations of the ALD-grown iron-rich NFO [3]. In addition to the growth and structural characteristics we will present the results of the magnetic property measurements of the films.

[1] Hirohata et al. IEEE Trans. Magnetics 5 (2015) 0800511

[2] Napari et al. InfoMat 2 (2020) 769

[3] Bratvold et al. J. Vac. Sci. Technol. A 37 (2019) 021502

2:45pm **EM1-WeA-6 Engineering Maxwell-Wagner Polarization in $Al_2O_3/TiO_2/Al_2O_3$ Nanolaminates Grown by Atomic Layer Deposition***, **Partha Sarathi Padhi,*** Raja Ramanna Centre for Advanced Technology, India*; R. Ajimsha, S. Rai, P. Misra,* Raja Ramanna Centre for Advanced Technology, India

Recently multilayered nanolaminates (NLs) of two dielectrics with conductivity contrast exhibiting giant dielectric constant owing to interface induced Maxwell–Wagner (M-W) relaxation have emerged as potential candidate for high density storage capacitors. The M-W polarization can be engineered precisely by controlling the thicknesses of sublayers and number of interfaces. We report growth of Al_2O_3/TiO_2 (ATA) NLs on Si and Au/Si substrates using atomic layer deposition, wherein M-W relaxation induced high dielectric constant was realized and engineered by tuning sublayer thicknesses. Trimethylaluminum (Al $(CH_3)_3$) and Titanium tetrachloride ($TiCl_4$) were used as source for Al and Ti respectively, while deionized water (H_2O) was used as source for oxygen. Depositions were carried out at 200 °C and the average growth per cycle for TiO_2 and Al_2O_3 was ~ 0.4 and 1.6 Å respectively. The thickness of Al_2O_3 and TiO_2 layers were kept same in a given NL and was reduced from ~ 2.4 to 0.17 nm in different NLs keeping the total stack thickness fixed at ~ 60 nm. X-ray reflectivity curves from these NLs with intense Bragg peaks and clean Kiessig fringes, as shown in Fig. 1, confirmed the multilayer structures with uniform thickness along with distinct interfaces. The dielectric properties of ATA NLs were studied in Au/ATA/Au device configuration using impedance spectroscopy in frequency range of $10–10^6$ Hz. The dielectric constant of ATA NLs at 10 Hz was found to increase from ~ 23 to 290 with decreasing sublayer thicknesses from ~ 2.4 to 0.17 nm (Fig. 2(a)), while the dielectric loss was initially found to reduce from ~ 0.8 to 0.06 with reduction in sublayer thicknesses down to ~ 0.48 nm and then increased up to ~ 0.24 with further reduction in sublayer thicknesses down to ~ 0.17 nm (Fig. 2(b)). The dielectric constant of ~ 290 obtained for the ATA NL with ~ 0.17 nm sublayer thickness is significantly larger than that of both Al_2O_3 (K ~10) and TiO_2 (K ~ 20) and is proposed to be due to M-W type dielectric relaxation caused by space charge polarization across the interfaces of Al_2O_3/TiO_2. Temperature dependent dispersion in dielectric constant and loss of ~ 0.48 nm ATA NL clearly revealed two sets of thermally activated relaxations, confirming existence of interfacial M-W relaxation (Fig. 3). The ATA NLs of sublayer thickness ~ 0.17 nm showed high capacitance density of ~ 43.1 fF/μm^2, low loss of ~ 0.24 at 10 Hz, low EOT of ~ 0.8 nm, high breakdown field of ~ 0.265 MV/cm, low leakage current density of ~ 8.5 x 10^{-4} A/cm^2 at 1V and cut-off frequency of ~ 12KHz which are promising for development of next generation high density storage capacitors.

3:00pm **EM1-WeA-7 Plasma Enhanced Spatial ALD of Silver and Copper Thin Films at Atmospheric Pressure using B_2O_3 Seed Layers***, **Tim Hasselmann**, B. Misimi,* University of Wuppertal, Germany*; N. Boysen,* Ruhr University Bochum, Germany*; D. Rogalla,* RUBION, Ruhr University Bochum, Germany*; D. Theirich,* University of Wuppertal, Germany*; A. Devi,* Ruhr University Bochum, Germany*; T. Riedl,* University of Wuppertal, Germany

Due to their excellent electrical and optical properties[1,2] silver and copper thin films are used in various (opto-)electronic devices, e.g. as semi-transparent electrodes[3,4]. Both of these metals have already been deposited using PE-ALD which provides a precise thickness control and homogeneous film growth at low temperatures [5–9]. However, since metals have a relatively high surface energy and thus tend to grow according to the Volmer-Weber-Mode[10], most of the films consist of isolated islands instead of a percolated and conductive layer. Two possibilities to overcome these issue are the increase of the growth rate, since a correlation between growth rate and nucleation and thus percolation was observed, where a higher growth rate leads to earlier percolation[6,8] and the use of seed layers to enhance the wetting of the deposited metal on the surface[11].

In this work, we provide detailed growth studies of Ag and Cu thin films grown from [Ag(NHC)(hmds)], [Ag(fod)(PEt_3)] and [Cu(NHC)(hmds)] precursors by spatial PE-ALD at atmospheric pressure. Interestingly, we find a significant effect of B_2O_3 seed layers on the growth of both metal films, compared to neat Si substrates. Specifically, for Cu films a substantially increased growth per cycle (GPC) of $2.1x10^{14}$ Cu atoms cm^{-2} is found with a 10 nm thick B_2O_3 seed layer compared to a GPC of $3.3x10^{13}$ Cu atoms cm^{-2} on neat Si substrates. At the same time the B_2O_3 seed layer strongly affects the percolation threshold and continuity of the grown metal layers. A comparison of Ag layers with a similar areal density of Ag atoms (~ $3x10^{17}$ Ag atoms cm^{-2}) shows that on top of a B_2O_3 seed layer the Ag film is percolated with a high electrical conductivity, whereas its analogue on neat Si consists of separate islands and is found electrically insulating.

Detailed studies on the growth mechanism in dependence of the B_2O_3 seed layer will be presented and its potential use in area-selective ALD of metals will be discussed.

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3:15pm **EM1-WeA-8 Silicon-Based Polymer-Derived Ceramic Coatings by Post-Processing of Pre-Ceramic MLD Thin Films***, **Kristina Ashurbekova**, M. Knez,* CIC nanoGUNE, Spain

Si-based polymer-derived ceramics (PDCs) belong to an emerging class of advanced materials that provide high strength, hardness, corrosion protection and heat dissipation, even upon use in extreme environments like high temperatures or chemically reactive plasma conditions. For example, wet-chemically synthesized aluminum doped SiOC PDCs retained their mechanical properties up to 1900°C in addition to an increased creep and corrosion resistance [1].

In the present work, MLD-deposited siloxane-alumina (SiAlCHO) thin films have been used as pre-ceramic polymers for a polymer-derived amorphous silicoaluminum oxycarbide (SiAlCO) synthesis by high-temperature post-processing. Pre-ceramic SiAlCHO films were grown by applying sequential surface reactions between 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (V4D4) and trimethylaluminum [2]. To increase the mass yield during the polymer-to-ceramic transformation, cross-linking of the growing chains is desired. For this purpose, we introduced di-tert-butyl peroxide into the MLD process to cross-link the chains through their vinyl groups. The resulting film exhibited improved properties, such as 12% higher film density and enhanced thermal stability, if compared to the non-cross-linked film [3].

The fabrication of the final SiAlCO PDCs coatings was carried out by pyrolyzing the SiAlCHO MLD films in an Ar atmosphere and in vacuum at 900^{o}C. The Raman spectra showed D and G peaks at 1350 cm^{-1} and 1590 cm^{-1}, respectively, thereby indicating the formation of free sp2-hybridized carbon in the resulting PDCs film. The in situ sp2-carbon, formed by decomposition of Me and Vi groups in the SiO2MeVi moieties within the SiAlCO PDC film was identified by X-ray photoelectron spectroscopy (XPS). The spectra showed presence of C=C sp2 bonds and C-H bonds at the interface of free carbon nanoclusters. The elimination of a part of the organic groups is confirmed with the XPS survey scan data, where the Si:C ratio in the film after pyrolysis was reduced from 1:3 to 1.5:1. Transmission electron microscopy confirmed that the PDC film remained amorphous and defect-free after pyrolysis. Interestingly, annealing a 5 nm thick SiAlCO PDC film in vacuum at 900°C showed the formation of a conformal graphene shell on the surface of the amorphous SiAlCO PDC (Supplementary Fig. 1). This MLD-derived conformal SiAlCO PDC thin film showed exceptional uniformity, linear shrinkage, and thermal stability up to 1100°C.

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