Sunday Afternoon, July 16, 2017

Nanostructure Synthesis and Fabrication
Room Plaza ABC - Session NS+EM-SuA

2D Materials (1:30-3:30 pm)/Laminate, Multicomponent, and Emerging Materials (4:00-5:30 pm)

Moderators: Jiyoung Kim, University of Texas at Dallas, Dennis Hausmann, Lam Research, Sumit Agarwal, Colorado School of Mines

1:30pm **NS+EM-SuA-1 Plasma-enhanced Atomic Layer Deposition of Large-area MoS_2: From 2-D Monolayers to 3-D Vertical Fins**, ***Akhil Sharma**, S Karwal, V Vandalon, M Verheijen,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, UK*; R Sundaram,* Oxford Instruments Plasma Technology*; W Kessels, A Bol,* Eindhoven University of Technology, Netherlands

Atomic layer deposition (ALD) might prove as a key enabler for tackling the current challenge of large-area growth of 2-D materials with wafer-level uniformity and digital thickness controllability. In this contribution, we have implemented plasma-enhanced ALD to synthesize large-area MoS_2 thin films with tuneable morphologies i.e. in-plane and vertically standing nano-scale architectures on CMOS compatible SiO_2/Si substrates. The large scale 2D in-plane morphology has potential applications in nanoelectronics, while the 3D fin structures could be ideal for catalysis applications such as water splitting.

The ALD process was characterized over a wide temperature range between 150°C - 450°C by using a combination of a metal organic precursor $[(NtBu)_2(NMe_2)_2Mo]$as Mo source and a H_2S based plasma as the co-reactant. A saturated growth rate of ~0.9 Å/cycle was observed within the parameter space investigated. The number of layers in the MoS_2 film could be controlled down to a mono-layer by tuning the number of ALD cycles. The precise variation in thickness was confirmed by Raman spectroscopy which showed a monotonic decrease in the frequency difference between the two characteristic modes for MoS_2 with decreasing layer thickness down to 21 cm^{-1} which corresponds to a monolayer. The photoluminescence spectroscopy data was in line with these results, showing a strong peak at ~1.9 eV corresponding to the direct band gap transition for the mono-to-few layered MoS_2. XPS showed that the films were pure and stoichiometric in nature with negligible trace amounts of carbon and oxygen contaminants. The HAADF TEM analysis of the films grown at 450°C showed that during the initial ALD cycles, MoS_2 islands extended in the lateral direction and merged to form a film which continued to grow in a layer-by-layer fashion until a certain thickness. Thereafter, an out-of-plane vertical growth mode started to dominate as shown by cross-sectional TEM analysis. The origin of this transition from in-plane to out-of-plane growth mode might be attributed to the enhanced precursor adsorption on high surface energy locations such as grain boundaries, kinks or ledges. Due to the crowding effects at these favourable adsorption sites, vertical growth of MoS_2 is observed.

These results show that ALD might be instrumental in realizing not only the large area growth of high-quality 2-D materials but can also be applied as a tool to control the morphology of thin films which might yield into interesting structures (including heterostructures) for various opto-electronics and catalysis applications.

1:45pm **NS+EM-SuA-2 Low-Temperature Atomic Layer Deposition of MoS_2 Films**, ***Michael Moody**, T Jurca, A Henning, J Emery, B Wang, J Tan, T Lohr, T Marks, L Lauhon,* Northwestern University

Molybdenum disulfide (MoS_2) is a widely-studied layered semiconductor with interesting fundamental optoelectronic properties and promising applications in the two-dimensional limit. If a suitable metal-organic precursor and reaction chemistry were available, atomic layer deposition (ALD) could extend the impact of fundamental work on this system by enabling growth of consistent, large-area films. Here we report the use of the volatile molybdenum complex, tetrakis(dimethylamido)molybdenum (MoTDMA) and H_2S for direct low-temperature ALD of MoS_2 films. Preliminary wet chemical screening revealed a high reactivity of MoTDMA with H_2S , suggesting suitable chemistry for MoS_2 ALD under mild conditions. Indeed, ALD growth of amorphous MoS_2 was subsequently achieved at temperatures as low as 60°C, a temperature compatible with polymer substrates and photolithographic patterning over multiple length scales. Associated with the high reactivity of this system is robust nucleation , even on layered materials with interlayer van der Waals bonding such as graphene and exfoliated MoS_2. Annealing of amorphous MoS_2 films results in continuous, semiconducting nanocrystalline films, as characterized by multiple structural techniques including GIXRD and HRTEM. This work provides a route to 2D materials via ALD and post-processing, and exploration of related compounds to further tailor reactivity and ALD window is in progress.

2:00pm **NS+EM-SuA-3 Dielectric-MoS_2 Interfaces Grown by Atomic Layer Deposition**, ***Steven Letourneau**,* Boise State University*; A Mane, J Elam,* Argonne National Laboratory*; E Graungard,* Boise State University

Molybdenum disulfide (MoS_2) has become a prototypical transition metal dichalcogenide (TMDC) atomic-layered material because of its unique materials properties. For example, bulk MoS_2 exhibits an indirect band-gap of 1.3 eV, while a single monolayer has a direct band-gap of 1.8 eV. Recently, nanometer scale transistor devices have been made with MoS_2 and graphene, yet much of this work relies on layered materials prepared using chemical vapor deposition (CVD) and mechanically exfoliation. Multiple reports have demonstrated the growth of MoS_2 via CVD, but only a few studies have reported MoS_2 growth using atomic layer deposition (ALD), which offers potential advantages for high volume semiconductor manufacturing. Here, we report the ALD of few-layer MoS_2 films using MoF_6 and H_2S on various ALD-grown dielectric surfaces and the ALD of metal oxides on the ALD MoS_2 films at temperatures between 100-300 °C. In particular, we used in-situ quartz crystal microbalance measurements to investigate the nucleation of MoS_2 ALD on oxide surfaces and vice versa. In general, self-limiting growth of MoS_2 was observed on a wide range of dielectric surfaces including alumina, magnesia, and hafnia. The ALD MoS_2 films were amorphous as-deposited, but crystallized into a layered atomic structure upon annealing at 800 °C. Using in-situ spectroscopy and electrical measurements, growth inhibition of MoS_2 was seen depending on the growth substrate. These studies provide insight into the low-temperature ALD of MoS_2 and provide guidance for the ALD of additional TMDC films.

2:15pm **NS+EM-SuA-4 Plasma-Enhanced Atomic Layer Deposition of sub-5 nm high- k Dielectrics on 2D Crystals**, ***Katherine Price**, F McGuire, A Franklin,* Duke University

Recently, 2D crystals have been targeted as the basis for enabling many exciting nanoelectronic and optoelectronic applications. One of the main challenges inhibiting the integration of 2D crystals is uniform deposition of a scalable, high-quality dielectric, which serves as an integral aspect of some devices (as with top-gated field-effect transistors (FETs)) or as a protection from ambient conditions for other devices. This problem arises from the chemically inert surface of 2D crystals, which prevents uniform growth of a dielectric film using atomic layer deposition (ALD). While thick ALD high-k films can be obtained on transition metal dichalcogenides (TMDs) through island growth, ultrathin films (< 5 nm) have not been possible without additional surface modification steps or the addition of a buffer layer. In this work, we show that a plasma-enhanced ALD (PEALD) process, compared to traditional thermal ALD, substantially improves nucleation on TMDs, such as MoS_2 and WSe_2, without hampering their electrical performance, and enables uniform growth of high-k dielectrics to sub-5 nm thicknesses. A custom-designed PEALD system (from Kurt J. Lesker Company) with a remote plasma sustained by Ar carrier gas was used for this study. Ultrathin high-k films, including Al_2O_3 and HfO_2, were successfully grown on mechanically exfoliated 2D crystals. A systematic comparison between PEALD (using O_2 precursor) and ALD (using H_2O precursor) revealed significant improvement in overall surface coverage and rugosity using PEALD. Back-gated FETs were used to study the electrical properties of the TMDs before/after ALD or PEALD. Interestingly, PEALD of HfO_2 resulted in an greater overall improvement in performance based on hysteresis and on-current compared to ALD of HfO_2. Mechanisms for the dramatic nucleation improvement and impact of PEALD on the 2D crystal structure were studied by x-ray photoelectron spectroscopy (XPS). XPS showed no evidence of oxidation that would adversely impact the electrical properties of the TMDs. To demonstrate the utility of the PEALD-enhanced nucleation, HfO_2 films as thin as ~3 nm were realized on MoS_2 and used in the gate stack of top-gated FETs, yielding robust performance for key metrics such as leakage current and gate control. In addition to providing a detailed analysis of the benefits of PEALD vs ALD on 2D crystals, this work reveals a straightforward approach for realizing ultrathin films of device-quality high-k dielectrics on 2D crystals without the use of additional nucleation layers or damage to the electrical performance.

2:30pm **NS+EM-SuA-5 Novel *in-situ* Electrical Characterization of the Atomic Layer Deposition Process on 2D Transition Metal Dichalcogenides Transistors*, Antonio Lucero*,** *J Lee, L Cheng, H Kim, J Lee, S Kim, J Kim,* University of Texas at Dallas

Two-dimensional transition metal dichalcogenide (TMD) materials are promising candidates for future, low-power semiconducting applications[1]. In spite of their numerous desirable characteristics, there are a number of challenges facing the implementation 2D TMDs into high performance transistors. Key among these problems is the development of a scalable gate dielectric deposition process due to the chemical inertness of the TMD surface[2]. In this report four deposition processes are studied using a novel, *in-situ* electrical characterization system.

Exfoliated MoS_2 backgated devices are loaded into an ultra-high vacuum (UHV) cluster tool which integrates a thermal ALD, a plasma enhanced ALD, and a plasma enhanced chemical vapor deposition with a UHV electrical probe station (Fig. 1). Thermal ALD of Al_2O_3, both alone and combined with nitrogen radical surface functionalization, hollow cathode nitrogen plasma surface functionalization, and ozone surface functionalization are studied. Samples are transferred between deposition and characterization chambers under UHV conditions, allowing “half-cycle” studies to be performed (Fig. 2). Common to all results, as well as *ex-situ* studies, the ALD process results in a reduction of the on-off ratio, an increase in drive current, and a large negative shift in the threshold voltage (V_{th}). The shift in V_{th} can be seen immediately after the functionalization step or from the first ALD pulse if no functionalization is performed. In the case of functionalization, the shift in V_{th} is attributed to the oxidation of the MoS_2 surface, a result of oxygen contamination during radical functionalization. The effect of surface dipoles, precursor adsorption and coverage, and nucleation during the ALD process will be discussed as they relate to the electrical characteristics of the device.

This work was supported by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST, and by NRF (No. 2015M3D1A1068061) in Korea. We thank TMEIC for providing the ozone generator and nitrogen radical generator used in this work.

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2. L. Cheng et al., *ACS Appl. Mater. Interfaces*, 6, 11834 (2014)

2:45pm **NS+EM-SuA-6 Deposition of MoS_2 and WS_2 from bis(tert-butylimido)-bis(dialkylamido) Compounds and 1-Propanethiol*, Berc Kalanyan*,** *J Maslar, W Kimes, B Sperling,* National Institute of Standards and Technology*; R Kanjolia,* EMD Performance Materials

Layered two dimensional (2D) transition-metal dichalcogenides (TMDs) are finding use in nanoelectronic and optoelectronic applications due to their thickness dependent optical and electrical properties. Scalable fabrication of TMD-based devices requires deposition routes that can produce continuous and uniform films with sub-nanometer thickness control. Atomic layer deposition (ALD) is a highly promising route for the synthesis of 2D TMDs and heterostructures due to digital thickness control achieved by sequential self-limiting chemistry. Another advantage of ALD is that thickness control and the structural development of the films can be decoupled by separating the deposition and crystallization steps. Existing ALD-like chemistries for TMD growth use metal halide and hydrogen sulfide sources. We report on the development of MoS_2 and WS_2 growth processes from metalorganic and thiol precursors, which offer halide-free chemistry and eliminate the safety hazards associated with H_2S.

We deposited thin films using $(N^tBu)_2(Nme_2)_2M$ and 1-propanethiol, where M={Mo,W}, at wafer temperatures of 200°C to 400°C on SiO_2/Si substrates. The amount of precursor injected was directly measured using inline non-dispersive infrared optical flow meters. Precursor saturation conditions were evaluated using optical flow measurements and X-ray photoelectron spectroscopy (XPS). As-deposited and sulfur annealed films were further evaluated using X-ray diffraction (XRD) and Raman spectroscopy. As-grown films were amorphous and included a mixture of a sulfide and a conductive phase, likely a nitride. For the Mo precursor, the onset of sulfur incorporation occurred around 300°C, similar to values reported for Mo_2N produced using ammonia1. Below 300°C, deposition was limited to a thin surface oxide. Higher temperatures resulted in an increase in growth rate, which also introduced a weak CVD component to the growth. Deposition rates were <0.5 Å/cycle at 350°C. Exposure studies revealed that relatively long saturation times for thiol were required to incorporate sulfur into the film, analogous to the NH_3 reaction for WN[2]. As-deposited films were successfully annealed to 2H-MoS_2 under a sulfur atmosphere, which also removed residual ligands, including nitrogen-containing groups. In this paper, we will also present similar results and process characteristics for the WS_2 route and discuss initial results from MoS_2/WS_2 nanolaminates.

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3:00pm **NS+EM-SuA-7 Direct Growth of Layered Boron Nitride Films on MoS_2 using Atomic Layer Deposition for 2D Based Nano-electronics*, Jaebeom Lee*,** *L Cheng, H Zhu, A Ravichandran, A Lucero, M Catalano, M Kim, R Wallace, L Colombo, J Kim,* University of Texas at Dallas*; Z Che,* The University of Texas at Dallas

Hexagonal boron nitride (h-BN), a graphene analogue with strong covalent bonding of boron and nitrogen, is an atomically thin two-dimensional (2D) dielectric material having interesting properties, such as atomic flatness, high stiffness, near lattice matching with graphene, and low surface energy. These unique properties have made h-BN a widely-studied dielectric as a substrate material and a gate dielectric for graphene based device. However, direct integration of h-BN with other 2D semiconductors, such as graphene and MoS_2, remains a major challenge because of their low surface reactivity which leads to poor surface nucleation of h-BN, thus preventing the synthesis of large area films with controllable thickness and grain size.

We used atomic layer deposition (ALD) using BCl_3 and NH_3 as precursors in the temperature range of 600~800 ℃ as shown in figure S1 to grow h-BN thin films. We evaluated the growth of layered BN on different substrates, such as Co, SiO_2, HOPG and MoS_2 and found that the nucleation mechanism depends on substrates. The distinct nucleation mechanisms of layered BN are likely attributed to the unique surface reactivities of the various substrates. Both Co and SiO_2 shows uniform nucleation sites, while growth on HOPG and MoS_2 showed growth mostly at the step edges due to the presence of dangling bonds and the inert nature of the basal plane. In order to increase the nucleation density we used O_3 pretreatment to functionalize the surface of MoS_2. The AFM images revealed enhanced nucleation of BN with an average grain size of ~ 20nm at a growth rate of ~ 0.22 Å/cycle. We also performed XPS measurements of the B 1s and N 1s peaks at 190.66 and 398.07 eV respectively, and the B:N ratio was estimated to be close to 1. The formation of layered BN was also verified further with the identification of satellite features at the higher binding energy shoulders of the XPS peaks, which is in good agreement with the layered BN structure observed in our HR-TEM images that show an interlayer spacing of 0.34nm (Fig S2). The band-gap of ALD grown BN was also estimated to be around 5.1 eV based on the analysis of N 1s XPS loss feature, and the dielectric constant was estimated to be about 3.8 from capacitor measurements. Our results suggest that polycrystalline layered BN can be grown by ALD on Co, SiO_2, HOPG and MoS_2. Further studies will have to be performed to improve the crystalline quality of the films.

We acknowledge partial financial support from the Southwest Academy on Nanoelectronics (SWAN) sponsored by the Nanoelectronic Research Initiative (NRI) and NIST and we thank TMEIC for providing the ozone generator.

Reference

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3:15pm **NS+EM-SuA-8 Fabrication of Functional Complex Nanostructures Based on Novel Atomic Layer Deposition Approach of Boron Nitride*, Wenjun Hao*,** *C Marichy, C Journet, A Brioude,* Univ Lyon, France **INVITED**

Renewal clean energy and environment are two of the most important concerns for the coming decades. Carbon-based nanostructures are leading nanomaterials due to their outstanding properties. Less investigated, hexagonal BN nanostructures such as nanotubes and nanosheets, which can be seen as the structural analogues to their carbon counterparts[1], are very attractive materials with various applications such as energy[2] and environmental domains[3]. Atomic Layer Deposition (ALD) technique is an effective approach for surface modification and fabrication of complex nanostructured materials.[4] However, few ALD processes of BN were reported so far and they are mostly based on ammonia and/or halide precursors and no high crystalline quality was yet achieved[5–8]. Based on Polymer Derived Ceramic (PDC) chemistry[9], a new low temperature ALD

process of BN, that permits access to various h-BN complex nano- and hetero-structures, was developed.

In the present communication, we report for the first time the fabrication of h-BN complex nano- and hetero-structures by a two-step ALD approach using trichloroborazine reacting with hexamethyldisilazane. This two-step process consists first of the growth layer by layer of a preceramic BN films at low temperature, and then to its densification into pure h-BN by annealing process. h-BN thin films were successfully deposited onto various substrates/templates, such as carbon nanotubes, SiO_2 nanoparticles, polycarbonate membrane, sapphire, etc. The obtained h-BN materials were characterized by TEM, SEM, EDS, XPS and Raman. The present low deposition temperature ALD approach provides a versatile ammonia free method to fabricate high quality h-BN nano- and hetero-structures.

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4:00pm **NS+EM-SuA-11 When There is no Bulk: Growth and Structure of Dielectric and Semiconductor Oxide Nanolaminates***,* ***Angel Yanguas-Gil,*** Argonne National Laboratory **INVITED**

Nanolaminates represent the first-order generalization of a conventional ALD process, one in which the traditional ABABAB sequence is replaced by a more general $(AB)_n(CD)_m$ combination of two different processes. In this talk I will focus on the growth, properties, and stability of oxide semiconductor and dielectric laminates. These materials are key for a wide range of applications, including photovoltaics, memory, logic, and power electronic devices. However, in addition to their applied interest, nanolaminates constitute a fantastic model system to explore the structure and properties of sub-nm materials whose structure and coordination environment are different from the bulk. Being intrinsically metastable, the stability of these structures also provides us with a way of probing the mobility of atoms at the nanoscale, an important factor in the long-term reliability of nanomaterials.

Through a combination of in-situ characterization, synchrotron characterization techniques, and simulations we have probed the structure and stability of nanolaminate materials as the thickness of its constituents evolve from a bulk like structure down to isolated clusters in a foreign host, focusing primarily on three different subsystems: Al_2O_3/ZnO, In_2O_3/SnO_2, and MO_2/Al_2O_3, where M=Ti, Hf. Changes in microstructure as determined using X-ray absorption spectroscopy correlate with changes in the chemical and electronic properties of the material. This is the case of the Al_2O_3/ZnO system, for which the departure from a wurzite-like coordination environment in ZnO below 10 ALD cycles correlates with an increase in the etching of the ZnO layer by TMA.

I will also focus on how to control the synthesis of doped and nanolaminate materials to tune the microstructure of amorphous materials. I will show how by adding an in-situ surface functionalization step to the conventional AB ALD cycle we can tune the reactivity and the growth per cycle of a wide range of ALD processes. We can leverage this approach to tune the composition of binary and ternary laminate materials, for instance to control the doping efficiency in transparent conductors or the isotropic mixing of components in as-deposited dielectric laminates. In addition to the modification of the structure of the laminate materials, this technique also allows us to probe the precursor-surface interaction during the first CD cycle of a laminate growth by comparing the growth inhibition observed in the laminate and in each of the individual constituents.

4:30pm **NS+EM-SuA-13 Perfecting Single-Crystal Ternary Perovskite $YAlO_3$ Epitaxial Growth on GaAs(111)A Utilizing Atomic Layer Deposited Sub-Nano-Laminated Y_2O_3/Al_2O_3***,* ***Lawrence Boyu Young****, C Cheng, K Lin, Y Lin, H Wan,* National Taiwan University, Republic of China*; M Li,* National Nano Device Laboratories, Republic of China*; R Cai, S Lo,* Industrial Technology Research Institute, Republic of China*; C Hsu,* National Synchrotron Radiation Research Center, Republic of China*; J Kwo,* National Tsing Hua University, Republic of China*; M Hong,* National Taiwan University, Republic of China

Hetero-epitaxial growth of functional oxides on commercial semiconductor Si and GaAs wafers enables new technological applications, taking advantages of the advanced CMOS ICs and high-speed opto-electronic devices. Moreover, the hetero-growth between distinctly different chemical bonding and lattice constants is scientifically exciting and technologically challenging. In this work, we have perfected single crystal hexagonal perovskite $YAlO_3$ on GaAs(111)A using atomic layer deposited (ALD) sub-nano-laminated (snl) Y_2O_3/Al_2O_3 multi-layers (super-cycles) through post-deposition rapid thermal annealing (RTA) with temperatures above 900°C. We have studied the crystallography of single crystal hexagonal perovskite $YAlO_3$ (YAP) using synchrotron radiation x-ray diffraction (SR-XRD) and scanning transmission electron microscopy (STEM). The epitaxial relationship between $YAlO_3$ and GaAs is $YAlO_3$GaAs, as determined from the XRD radial scan along the in-plane direction. Comparing the YAP crystallinity of snl (super-cycles) and nl Y_2O_3/Al_2O_3 multi-layers, the cross-sectional STEM image for the former (Fig. 1(a)) reveals a more ordered atomic image, smoother crystalline $YAlO_3$/GaAs(111) interface, and continuous crystalline domain over 100-nm along substrate in-plane direction than that for the latter (Fig. 1(b)). Moreover, Pendellösung fringes from the XRD normal scans were observed for the super-cycled samples, much more so than those of nano-laminated samples (Fig. 2), [1] again indicating better crystallinity and smoother interfacial roughness. We have also attained very narrow FWHM of $YAlO_3$(0004) θ-rocking scan ~ 0.026° from the snl samples, compared favorably with 0.27° from the nl samples (Fig. 3). We have studied the surface morphology of the samples using atomic force microscopy (AFM). The smoother surface root mean square roughness of ~ 0.13 nm was observed in the snl super-cycled sample, which is 6 times smaller than that of our previous nl sample, and was close to the surface roughness of GaAs(111)A substrate ~ 0.13 nm as measured using an in-situ scanning tunneling microscope. Finally, the time-evolutions of surface normal radial scans of snl and nl samples were presented. After the 900°C anneal, the formation of $YAlO_3$ was much quicker ~ 2s to reach the saturation thickness than that of our previous sample ~ 60s, indicating that only 1/30 thermal budget was needed to form YAP by using sub-nano-laminated Y_2O_3/Al_2O_3 super-cycles.

[#]LBY, CKC, and KYL have contributed equally to this work.

*CHH, JK, and MH are the corresponding authors.

[1]L. B. Young, et al, J. Vac. Sci. Technol. A 35, 01B123 (2017)

4:45pm **NS+EM-SuA-14 Thermal Coefficient of Resistance (TCR) Measurements for Atomic Layer Deposited Metal-Metal Oxide Nanocomposites***,* ***Anil Mane****, J Avila, Y Zhang, J Elam,* Argonne National Laboratory

Precisely controlled metal-metal oxide nanocomposite layers prepared by atomic layer deposition (ALD) exhibit material properties that can be tuned over a broad range by adjusting the metal content such as band gap, absorption coefficient, resistivity, and electrochemical corrosion resistance. Consequently, these metal-metal oxide nanocomposites are well suited in a variety of applications including resistive layers in microchannel plates (MCPs), protective coatings for lithium ion battery cathodes, charge drain layers for MEMS devices, and selective absorber coatings for concentrated solar power.

For resistive layers in MCPs, the thermal coefficient of resistance (TCR) is a critical materials property because it dictates the range of allowable operating temperatures for devices (e.g. photon, neutron, or particle detectors) that incorporate the MCP for electron amplification. The ability to control the TCR will enable new applications such as cryogenic detectors or detectors that must endure large temperature changes during operation. To address this need, we have synthesized a variety of ALD metal-metal oxide nanocomposite layers by combining different metals (W, Mo, Ta, and Nb) and metal oxides (Al_2O_3, ZrO_2, TiO_2, Ta_2O_5, Nb_2O_5, and HfO_2). We studied the electrical transport properties of these ALD films and focused on their temperature dependence in order to extract the TCR. In all cases, the TCR is negative, so that the resistance drops with increasing

temperature as expected for a semiconducting material. In addition, the magnitude of the TCR increases with the film resistivity, and depends on both the metal and the metal oxide components of the composite (Fig. 1). This presentation will expound on these findings and explain the implications for MCP detectors.

5:00pm **NS+EM-SuA-15 Phase Control of Ga_2O_3 Films Deposited by Atomic Layer Epitaxy***, **Virginia Wheeler**, N Nepal, D Meyer, C Eddy, Jr.,* U.S. Naval Research Laboratory

Ga_2O_3 has attracted significant interest as a promising ultra-wide bandgap material for next generation high-power, high-temperature electronic and UV detector applications. While there are five polymorphs of Ga_2O_3, the β-Ga_2O_3 (monoclinic) is the most stable and thus the most widely studied to-date. By comparison, the ε-Ga_2O_3 phase is slightly less energetically favorable but has a similar bandgap (4.9 eV) and a hexagonal wurtzite crystal structure that results in a polar phase. The calculated polarization strength of ε-Ga_2O_3 is 10 and 3 times larger than that of GaN and AlN, respectively. Like the III-N system, polarization induced charges can lead to higher charge densities and mobilities in two-dimensional electron gases formed at heterojunctions, which would improve the viability of Ga_2O_3 electronic devices. However, experimental data on attaining the ε-Ga_2O_3 phase is extremely limited and homo- or heteroepitaxial films currently demonstrated are of very poor quality. In this work, we use atomic layer epitaxy (ALE) to produce high-quality heteroepitaxial Ga_2O_3 films and demonstrate phase selectivity with a variation in growth temperature, plasma gas chemistry and plasma pressure.

ALE Ga_2O_3 films were deposited on c-plane sapphire substrates in an Ultratech Fiji 200 reactor equipped with a load lock and turbo pump. All films were produced using trimethylgallium and O_2 plasma precursors with pulse/purge times of 0.015s/10s and 10s/10s, respectively. The growth temperature, plasma gas flow, and pressure were varied to determine their impact on resulting film crystallinity and phase composition. Independent of growth conditions, all films were crystalline, high resistivity films with Ga/O ratios between 0.68-0.70 and no indication of C contamination by XPS.

Decreasing chamber pressure an order of magnitude drastically effected the resulting phase, yielding pure β-Ga_2O_3 at high pressure and pure ε-Ga_2O_3 at low pressures. Additionally, at low pressures, as the growth temperature was increased from 300 to 500°C, subsequent films went from mixed phase, to purely ε-Ga_2O_3 at 350°C, to purely β-Ga_2O_3 at 500°C. Alternatively, at 350°C and low pressure, the phase could be altered by a change in O_2 plasma flow. High-quality β-Ga_2O_3 films were produced at 5sccm O_2 that had an RMS roughness of 0.38nm and XRD FWHM of 268 arcsec for a 30nm film. At 40sccm, high-quality ε-Ga_2O_3 films were obtained with an RMS roughness of 0.15nm and XRD FWHM of 250 arcsec for a 30nm film. Thus, using ALE high-quality, phase selective films can be achieved to satisfy application requirements.

5:15pm **NS+EM-SuA-16 High Quality SiN and SiO_2 Films Produced by PEALD with Microwave ECR Plasma Below 200 ºC***, **Jesse Kalliomaki**, V Kilpi,* Picosun Oy, Finland*; T Maline,* Picosun Oy*; H Enami, N Mise,* Hitachi High-Technologies Corp., Japan*; H Hamamura, T Usui,* Hitachi R&D Group

Due to continuous feature size scaling down and change to the 3D structures, currently new process innovations are required more strongly than the previous. Conformal film formation of Si compounds like SiO_2 and SiN is the key technologies and is widely used for double patterning, spacer and liner applications. PEALD at low temperature is one of the suitable solutions for these applications. We reported the superiority of low pressure microwave ECR(M-ECR) plasma for Si substrate nitridation at low temperature [1].

In this study, SiN and SiO_2 film properties were evaluated for demonstrating the advantage of the newly combined tool with the M-ECR plasma and the leading ALD system from Picosun. BDEAS (Bis(Diethylamino)Silane) was used as Si precursor. N_2 and O_2 gas were introduced into M-ECR plasma to form SiN and SiO_2, respectively. Process pressure was set lower than 1Pa. Film density and WER (wet etching rate) were measured by XRR and DHF (0.5%), respectively. Composition of film was analyzed by XPS with Ar sputter.

SiN film density obtained in this study was investigated as a function of deposition temperature and compared with that of the conventional PEALD SiN [2,3] as shown in Fig. 1. The film density slightly increases with rise in deposition temperature and the value is about 2.9 g/cm^3 at low temperature below 200 ºC. This value is much higher than that of the conventional PEALD SiN and nearly equal to that of LPCVD SiN at 850 ºC. WER obtained in this study is extremely low compared to that of the conventional PEALD SiN as shown in Fig. 2. This low WER is advantageous for device fabrication. XPS analyses reveal that residual C in the film is less than 3 %. Longer exposure time of N_2 plasma could reduce the C content and WER. Efficient generation of the radicals and ions by M-ECR plasma at low pressure [4] is supposed to improve the film properties.

SiO_2 film properties deposited at 150 ºC were also investigated. Film density is 2.2 g/cm^3, this value is nearly equal to that of thermal SiO_2. WER is 4.5 nm/min and this value is smaller than that of the conventional LPCVD SiO_2 formed at 750 ºC (6.0 nm/min). O/Si ratio of the film is 2.1 and residual C is less than 1 %.

From these results, PEALD with M-ECR plasma can be one of the most advantageous solutions for next-generation leading edge devices and other novel devices.

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5:30pm **NS+EM-SuA-17 Tertiary Butyl Hydrazine as a Reducing Agent for Low-Temperature Atomic Layer Deposition of Low-Resistivity Copper Thin Films***, **Katja Väyrynen**, K Mizohata, J Räisänen,* University of Helsinki, Finland*; D Peeters, A Devi,* Ruhr-University Bochum, Germany*; M Ritala, M Leskelä,* University of Helsinki, Finland

Copper plays an important role in the development of microelectronics as it is the primary interconnect material. The manufacturing procedure of the Cu interconnects is typically two-fold: first, a Cu seed layer is deposited by PVD followed by a Cu fill process carried out by electrochemical deposition. In order to reduce component sizes, and thus increase device efficiency, thin yet continuous Cu films are desired. This can be accomplished by replacing the existing course of action, or at least the PVD step, with more accurate deposition methods such as ALD. The Cu ALD processes known to date, however, exhibit limited applicability due to issues ranging from agglomeration caused by high temperatures to Zn incorporation and strong substrate sensitivity.

Tertiary butyl hydrazine (TBH) was recently introduced as an ALD reactant for the reduction of silver thin films.[1] Otherwise, the use of hydrazine or its alkyl derivatives in metal ALD has been scarce.[2,3] In this work, Cu thin films were deposited via reduction of $Cu(dmap)_2$ (dmap = dimethylamino-2-propoxide) by TBH. The process was investigated between temperatures of 80 and 140 °C. A saturating growth mechanism was observed with respect to both precursors at 120°C. Both the growth characteristics and the film properties were found to vary depending on the substrate, but deposition was not limited only on certain starting surfaces. The films were identified as crystalline cubic Cu with a minor preference towards (111) orientation. The films were relatively smooth and showed uniform thickness across the 5 x 5 cm^2 substrates. At the lowest, a resistivity of 1.9 μΩcm was measured from a 54 nm film exhibiting a Cu content of 97.2 at.%. Oxygen was identified as the main impurity (1.7 at.%) but it was limited almost entirely to the film surface indicating oxidation upon exposure to air (Figure 1).

The films were deposited in a hot-wall flow-type F-120 ALD reactor (ASM Microchemistry). Thorough film characterization was carried out by energy-dispersive X-ray spectrometry, scanning electron microscopy, X-ray diffraction, four-point probe, and time-of-flight elastic recoil detection analysis.

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