ALD Fundamentals
Room Grand Ballroom H-K - Session AF4-MoA
Growth Mechanisms II

Moderators: Viljami Pore, ASM, Mikko Ritala, University of Helsinki

4:00pm **AF4-MoA-11 Monolithic Integration of Single Crystal Perovskites on Semiconductors with ALD*, John Ekerdt,*** University of Texas at Austin **INVITED**

The semiconductor industry faces new challenges in the sub-10 nm era as scaling will no longer dominate performance improvement. New materials provide opportunity to improve performance with minimal architectural overhaul. For example, high-mobility channels of Ge and III-V semiconductors can provide both lower power consumption and faster computing speeds. In certain applications significant advantages are gained by monolithic integration of the oxides directly on the substrates that will host other devices/components. Perovskite oxides offer a wide range of properties from high-k to multiferroic affording the device designer a suite of possibilities and are particularly important due to their common structure and lattice-matching with common semiconductors.

Here, we report the fabrication of monolithically integrated, single crystal, metal-ferroelectric-semiconductor structures. This talk demonstrates the possibilities through the monolithic integration of perovskite oxides on Si(001) for applications in silicon nanophotonic devices and low-power transistors. Barium titanate (BTO) films, and BTO/$La_xSr_{1-x}TiO_3$ ($x \leq 0.15$) perovskite heterostructures are grown on strontium titanate (STO)-buffered Si(001) using atomic layer deposition at 225 °C. Film strain and *c*-axis orientation are manipulated by growth and annealing conditions. Piezoresponse force microscopy (PFM), electrical and electro-optic measurements establish BTO film ferroelectric (FE) behavior at the µm-scale. The $La_xSr_{1-x}TiO_3$ ($x \leq 0.15$) perovskite heterostructures sandwiched between Si(001) and BTO permits examination of a quantum metal between Si and a FE film.

It is possible to grow crystalline perovskites directly on Ge(001) by ALD and we have used this to deposit STO, BTO, $SrHfO_3$, $Sr(HfTi)O_3$, $SrZrO_3$, and $SrSnO_3$ directly on Ge(001). We will also present the growth and properties of theses perovskite layers directly on Ge(001) and will discuss the how the interface chemistry and structure control the interfacial reactions that allow for crystalline film formation during ALD, and how they affect film properties.

4:30pm **AF4-MoA-13 Introducing the Concept of Pulsed Vapor Phase Copper-free Surface Click-chemistry using the ALD Technique*, Iva Saric,*** *R Peter, M Kolympadi Markovic, I Jelovica Badovinac,* University of Rijeka, Croatia*; C Rogero,* Materials Physics Center (CSIC-UPV/EHU), Spain*; M Ilyn,* Donostia International Physics Center (DIPC), Spain*; M Knez,* CIC nanoGUNE, Spain*; G Ambrozic,* University of Rijeka, Croatia

While ALD allows deposition of a broad variety of inorganic materials, MLD typically relies on very few basic organic reactivity concepts and therefore is not yet as versatile as it could or should be. Given the great promise of ALD/MLD, it is highly demanded to extend the choice of available chemistries, providing a greater choice of suitable organic precursors. The idea behind our work is to extend the range of possible surface chemical reactions by introducing click chemistry as an additional option into the organic chemical vapor phase deposition concept. Click chemistry, initially developed for drug delivery, has recently gained increasing attention in surface patterning with important applications in biotechnology and in development of nanomaterials. Here we report for the first time on a model gas phase copper-free azide-alkyne click reaction performed in an ALD instrumentation [1]. The newly developed process is based on an *in-situ* two-step pulsed vapor phase sequence consisting of initial exposure of ZnO to propiolic acid as the first precursor, followed by gas-phase click-chemistry coupling of benzyl azide as the second precursor. The organic phase compositions were analyzed by XPS and FTIR, while the preservation of ZnO surface morphology was investigated by SEM and STEM. When compared to known state-of-the-art *ex-situ* gas phase click reactions [2,3], the ALD/MLD processing conditions ensure reproducibility and improve the time and surface coverage efficiency. The resulting hybrid material exhibits no surface contaminations with physisorbed organic precursors and/or by-products deriving from organic precursor degradation. This study offers great potential toward the development and fabrication of complex functional organic layers on metal oxide surfaces by selective azide-alkyne cycloadditions performed in an ALD/MLD instrument and broadens the variation range of applicable chemistry in MLD. Variation of the functionalities of the organic precursors will allow MLD type of polymer growth based on click chemistry and add degrees of freedom for the design of functional polymeric coatings.

[1] I. Saric, R. Peter, M. Kolympadi Markovic, I. Jelovica Badovinac, C. Rogero, M. Ilyn, M. Knez and G. Ambrozic, *ChemComm*, 2019, DOI: 10.1039/C9CC00367C.

[2] F. Gao, S. Aminane, S. Bai and A. V. Teplyakov, *Chem. Mater.*, 2017, 29, 4063-4071.

[3] M. Konh, C. He, Z. Li, S. Bai, E. Galoppini, L. Gundlach and A. V. Teplyakov, *J. Vac. Sci. Technol. A*, 2018, 36, 041404.

4:45pm **AF4-MoA-14 Surface Enhanced Raman Spectroscopy Studies of Aluminum ALD Precursors for Al_2O_3 Growth*, Michael Foody,*** Illinois Institute of Technology

Trimethylaluminum (TMA) is perhaps the most widely employed and emblematic ALD precursor – mainly for its robust reactivity with hydroxyl surface species and well-behaved ALD growth. Although one would expect other alkyl aluminum compounds to have similar properties, we have found the highly pyrophoric compound triisobutylaluminum (TiBA) does not grow alumina under similar ALD-like conditions. Unlike many other thin-film deposition techniques, ALD is driven by the reactivity at the vapor-substrate interface, and the stark divergence between these chemically similar precursors offers insight into the fundamental principles of ALD.

In this work, we use surface enhanced Raman spectroscopy (SERS) to show the limited reactivity between surface alkyl groups and water. SERS shows when TiBA is exposed to a 3-mercaptopropionic acid surface, only small signals corresponding to Al-C and isobutyl bond modes appear. The small signal corresponding to isobutyl peaks remains even after treatment with water indicating no reactivity between the isobutyl alkyl surface and water. These measurements suggest a mechanism in which proton transfer acts as the limiting step.

This knowledge informed the design of new precursors to test the structural and electronic effects of Al precursors. As a comparison, two additional aluminum precursors were synthesized, and used to grow alumina thin films by ALD. The two new precursors have varying alkyl groups – analogous to TMA and TiBA – as a way to compare the proton transfer reactivity to a methyl group and an isobutyl group at the vapor-substrate interface. Measurements were made using QCM and SERS, and were found to be consistent with our findings of the reactivity profiles of TMA and TiBA. The methyl aluminum complex was found to be a robust precursor for alumina deposition with water, while the isobutyl analogue did not deposit any mass or show films by ellipsometry on silica. All depositions were done under 200C, and SERS measurements were made at 100C, thus demonstrating the relatively low-temperature deposition conditions of these compounds. The SERS measurements presented here are among the first reports using SERS to evaluate ALD systems. They provide powerful insights into deposition mechanism by measuring bond vibrational modes over a much larger range of frequencies than more common methods (FTIR). The measurements (along with QCM) provide a new understanding of the reactivity of alkyl aluminum precursors, which have broader implications for general precursor design.

5:00pm **AF4-MoA-15 Atomic Layer Deposition of Aluminum, Hafnium and Zirconium Oxyfluoride Films with Tunable Stoichiometry*, Neha Mahuli,*** *J Wallas, S George,* University of Colorado - Boulder

The reactivity of metal oxide films with halogen chemistries can be reduced by incorporating fluorine into the metal oxide during film deposition. This study explored the atomic layer deposition (ALD) of various metal oxyfluorides such as aluminum oxyfluoride (AlO_xF_y), hafnium oxyfluoride (HfO_xF_y) and zirconium oxyfluoride (ZrO_xF_y). Techniques were developed to obtain tunable stoichiometry of the metal oxyfluoride films.

The metal oxyfluoride ALD films were deposited at 150°C. H_2O and HF-pyridine were used as the oxygen and fluorine sources. $Al(CH_3)_3$ was used as the Al source and Hf and Zr amidinates precursors were used as the Hf and Zr metal sources. The metal oxyfluorides were deposited using either (1) the halide-exchange method (see Supplemental Figure 1) or (2) the nano-laminate method (see Supplemental Figure 2). Both methods were evaluated using *in situ* quartz crystal microbalance (QCM) measurements and *ex situ* X-ray photoelectron spectroscopy (XPS) analysis.

The halide-exchange method is based on the facile exchange of oxygen by fluorine from HF. HF exposures after deposition of the metal oxide easily replaced oxygen with fluorine. In addition, the fluorine also diffused into the underlying metal oxide film. The oxygen/fluorine exchange and fluorine

diffusion complicates the control of the stoichiometry of the metal oxyfluoride film.

Compositional control was achieved by the halide-exchange mechanism using either metal oxide layers with various thicknesses or different HF pressures. The stoichiometry could also be tuned using the nano-laminate methods with different numbers of metal oxide ALD and metal fluoride ALD cycles. These two methods gave rise to tunable stoichiometry from pristine metal oxide to adjustable oxyfluoride to pristine metal fluoride.

5:15pm **AF4-MoA-16 Fundamental Study on the SiO_2 Growth Mechanism of Electronegativity Difference of Metal-O in the High-*k* Underlayers by PE-ALD Method**, ***Erika Maeda,*** Shibaura Institute of Technology, Japan; *T Nabatame,* National Institute for Materials Science, Japan; *M Hirose,* Shibaura Institute of Technology, Japan; *M Inoue, A Ohi, N Ikeda,* National Institute for Materials Science, Japan; *M Takahashi, K Ito,* Osaka University, Japan; *H Kiyono,* Shibaura Institute of Technology, Japan

To fabricate silicate films such as $HfSiO_x$ and $AlSiO_x$ as gate insulator of GaN power devices, the HfO_2/SiO_2 and Al_2O_3/SiO_2 laminates was initially deposited by atomic layer deposition (ALD) process [1]. Understanding the SiO_2 growth mechanism on HfO_2 and Al_2O_3 layers is an important in terms of the design of the $HfSiO_x$ and $AlSiO_x$ formation. In this study, we systematically investigate the growth rate of SiO_2 film on various high-*k* underlayers (Metal-O) by plasma-enhanced ALD (PEALD) using Tris(dimethylamino)silane (TDMAS) precursor and O_2 plasma gas, and we also discuss about role of the electronegativity difference in Metal-O on the SiO_2 growth mechanism.

At first, 30-nm-thick HfO_2, TiO_2, and Al_2O_3 layers and 5-nm-thick SiO_2 layer on Si substrates were prepared as Metal-O. The thicknesses of the SiO_2 films were varied on Metal-O by changing ALD cycles during PEALD at 300 °C. The thickness of the SiO_2 film was estimated using spectroscopic ellipsometry and Si_{2p} intensities of XPS.

All data of the SiO_2 thickness on HfO_2, TiO_2, Al_2O_3, and SiO_2 layers as a function of ALD cycle satisfied the linear relationship. The growth per cycle (GPC) value of the SiO_2 film was increased in the following order: SiO_2 (0.036 nm/cycle) < Al_2O_3 (0.090) < TiO_2 (0.11) < HfO_2 (0.13). Here, we pay attention to the electronegativity values of the Si, Al, Ti, Hf, and O atoms of Metal-O. Note that the GPC increased as the difference of electronegativity such as Si-O (1.76), Al-O (2.03), Ti-O (2.18), and Hf-O (2.27) in the Metal-O increased [2]. Based of these experimental data, we proposed one idea of the SiO_2 growth mechanism. In the TDAMS precursor supply step during PEALD, the adsorption of TDMAS precursor on the surface of Metal-O must be strongly influenced by the difference of electronegativity. This is because Si atom of the TDMAS precursor is easily attracted to oxygen atoms having a large electron density of Metal-O. Therefore, the adsorbed amount of the TDMAS precursor increases as the electron density of oxygen atoms becomes higher in the following order: Si-O < Al-O < Ti-O < Hf-O. This behavior was observed up to ALD 10 cycles. When the ALD cycle increases more than 10 times, the GPC became the same value (0.036 nm/cycle) as SiO_2 regardless of underlayer materials. This suggests that the adsorption amount of the TDMAS is similar to that of SiO_2 because the 1.2-nm-thick SiO_2 layer covered on the underlayer materials. To understand the SiO_2 growth mechanism, we should pay attention to the difference of electronegativity of Metal-O in underlayer.

[1] T. Nabatame et al., Appl. Phys. Express 12, 011009 (2019).

[2] A. L. Allred et al., J. Inorg. Nucl. Chem., 5, 264 (1958).

5:30pm **AF4-MoA-17 Low Temperature Aluminium Nitride Deposition: Comparing Hydrazine and Ammonia**, ***Aswin L.N. Kondusamy,*** *S Hwang, A Lucero, Z Qin, X Meng,* The University of Texas at Dallas; *D Alvarez, J Spiegelman,* RASIRC; *J Kim,* The University of Texas at Dallas

Aluminium nitride is a wide bandgap material having high thermal conductivity [1]. Depositing thin films of high thermal conductivity such as Aluminium nitride as a capping layer or a passivation layer by a CMOS compatible method is a viable approach to tackle the heat management issue that arises with scaling down of devices. Compatibility demands lower deposition temperature (<300 °C) and improved conformality over high-aspect ratio structures. AlN_x ALD using low reactive NH_3 results in incomplete reaction below 300 °C [2], resulting in carbon and hydrogen impurities and Plasma enhanced ALD (PEALD) frequently exhibits poor conformality. Thermal ALD (t-ALD) with a more reactive nitrogen precursor such as hydrazine is expected to overcome these problems. Newly available ultra-high purity hydrazine sources have been successfully used to deposit metal nitrides at low temperature [3]. In this work we study the low temperature t-ALD growth characteristics of aluminium nitride using hydrazine and trimethylaluminium (TMA) and evaluate the properties of the films. t-ALD results with hydrazine will be compared to films grown by t-ALD with NH_3 and PEALD with NH_3 plasma, all using the same ALD reactor in the same temperature range.

AlN_x films were deposited using a custom-made ALD reactor from 175-350 °C. Hydrazine is supplied from a BRUTE hydrazine source. Growth with hydrazine shows saturation behavior, with growth per cycle (GPC) saturating at hydrazine exposure as low as 0.1 s (~10^4 L). High GPC of 2.8-3.2 Å/cycle is observed at 300 °C with refractive index of 1.890 whereas t-ALD with NH_3 shows lower GPC (1.1 Å/cycle) for similar exposure, which is expected due to superior reactivity of hydrazine. AlN_x growth using hydrazine shows high temperature dependence in the range 175-300 °C. X-ray photoelectron spectroscopy is used to confirm film stoichiometry: films with low carbon (1%) impurities can be achieved. Films deposited below 250 °C get oxidized easily under air due to low film density. A novel densification method is proposed to obtain denser films at these temperatures to overcome this problem. The denser films are expected to have higher thermal conductivity. The detailed experimental results will be presented.

[1] G. A. Slack, R. A. Tanzilli, R. O. Pohl, J. W. Vandersande, J. Phys. Chem. Solids, 48 (1987) 641-647

[2] R. L. Puurunen, M. Lindblad, A. Root, A. O. I. Krause, Phys. Chem. Chem. Phys., 3 (2001) 1093-1102

[3] D. Alvarez, J. Spiegelman, R. Holmes, K. Andachi, M. Raynor, H. Shimizu, ECS Transactions, 77 (2017) 219-225

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