Emerging Materials
Room Regency Ballroom A-C - Session EM1-WeA
Ternary and Quaternary Oxide Materials

Moderator: Bart Macco, Eindhoven University of Technology

1:30pm **EM1-WeA-1 Rhenium(III)-based Ternary Oxides: Novel Materials from Straightforward Synthesis *via* ALD Comprising Uncommon Reaction Pathways***, **Max Gebhard**, S Letourneau, D Mandia, D Choudhury, A Yanguas-Gil, A Mane, A Sattelberger, J Elam,* Argonne National Laboratory

Oxides of rhenium, such as ReO_2 and ReO_3, exhibit high conductivity in the order $\sigma = 10^3 - 10^4\ (\Omega cm)^{-1}$, close to that of metals. This property is of high importance regarding applications with high demands on tailored electrical properties. An example of such an application are microchannel plates (MCPs), which are used as signal amplifiers in advanced detector units for UV-light (space aviation) and photoelectrons (XPS). Also, MCPs play a crucial role in the development of large area photodetectors.[1] MCPs are comprised of a glass capillary array. By applying a material with high secondary electron emission (SEE) yield, an incident electron/photon can create an electron avalanche that eventually increases the signal-to-noise ratio and thereby allows the detection of event starters. Below the SEE layer, a resistive coating must be applied, exhibiting the right range of resistivity to avoid electrons from being drained and to act as electron supplier. This material must be operable at elevated temperatures, *i.e.* it must have a low temperature-coefficient of resistance (TCR) to avoid decreased device performance at higher temperatures. Metal nanoparticles embedded in an Al_2O_3-matrix have been shown to provide the right resistivity for MCP application.[2] However, their TCR values demand for the development of materials with improved properties.

In this context, the development of ternary oxides, comprising ReO_x units with electrical conductivity and other components with dielectric character, provide a good opportunity to overcome the limitations of existing coatings.

Herein, we present two new materials, namely $ReAl_yO_x$ and $ReSi_yO_x$. These materials, where $ReSi_yO_x$ is reported for the first time, have been deposited using ALD and detailed mechanistic studies revealed that during the growth, reductive elimination reactions cause the formation of uncommon but stable Re(III) oxide species. Furthermore, fascinating mechanisms allowing the formation of unsaturated hydrocarbons and hydrogen, were identified during the growth. The processes were explored in great detail employing *in-situ* tools such as QCM, QMS and FTIR. Furthermore, the materials were fully characterized in terms of composition, structure, and electrical properties using XPS, RBS/HFS, XRD, XRR and XAS.

[1] J. Wang, K. Byrum, M. Demarteau, J. Elam, A. Mane, E. May, R. Wagner, D. Walters, L. Xia, J. Xie, and H. Zhao, *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip*. **2015**, 804, 84

[2] J. W. Elam, A. U. Mane, J. A. Libera, J. N. Hryn, O. H. W. Siegmund, J. McPhate, M. J. Wetstein, A. Elagin, M. J. Minot, *et al.*, *ECS Trans*. **2013**, 58 (10), 249

1:45pm **EM1-WeA-2 Growth Bbehavior and Electronic Characterization of $PbZrO_3$ and $PbZr_xTi_{1-x}O_3$ Grown by Atomic Layer Deposition with Several Zr Precursors***, **Nicholas Strnad**,* University of Maryland*; D Potrepka,* U.S. Army Research Laboratory*; A Leff,* General Technical Services, LLC*; J Pulskamp,* U.S. Army Research Laboratory*; R Phaneuf,* University of Maryland*; R Polcawich,* U.S. Army Research Laboratory

Process, structural, chemical, and electrical characterization is presented for $PbZr_xTi_{1-x}O_3$ (PZT) deposited by ALD using different combinations of precursors with thicknesses suitable for piezoelectric microelectromechanical systems (piezo-MEMS). PZT grown by ALD is desired for integration into 3-D MEMS [1] whereby actuators are grown on high aspect-ratio sidewalls, which greatly increases the areal work-density. To determine the viability of ALD PZT for MEMS, the films were integrated into micromachined, released cantilever structures. ALD $PbTiO_3$ (PTO) has been previously grown using lead bis(3-N,N-dimethyl-2-methyl-2-propanoxide) [$Pb(DMAMP)_2$] and tetrakis dimethylamino titanium [TDMAT] as the lead and titanium cation precursors, respectively [2]. Incorporation of tetrakis dimethylamino zirconium [TDMAZ] yielded PZT, but the growth rate of $PbZrO_3$ (PZO) and PZO-rich PZT was suppressed compared to PTO-rich PZT, resulting in a Zr/Ti composition less than the desired morphotropic phase boundary (MPB) composition of 52/48. The PTO-rich ALD PZT (Zr/Ti = 22/78) films were annealed at 700 °C in O_2 to crystallize into the perovskite phase. Micromachined trench structures 45 µm deep were coated with conformal ALD $PbZr_{22}Ti_{78}O_3$ to demonstrate that the process conditions fell within the ALD-window. Transmission electron microscopy images revealed that the ALD PZT films crystallized with grains tens of nanometers in diameter. Rutherford backscattering was used to characterize the chemical composition of the films. In-situ ellipsometry indicated that the as-grown PZT thickness was a linear function of the number of supercycles. For 200 nm-thick ALD $PbZr_{22}Ti_{78}O_3$ films, planar metal-insulator-metal capacitors were created to evaluate the ferroelectric and dielectric properties. The films exhibited an average remnant polarization of 20 $\mu m/cm^2$, a dielectric constant at zero volts of 475, a tuning range of 212-548 from 0 to 450 kV/cm, and a corresponding Tan delta of 0.025 (see supplemental). The ferroelectric properties of the ALD PZT presented here rivals PZT grown at similar compositions and thicknesses by other well-accepted processing methods. Several other zirconium precursors were investigated for inclusion into ALD PZT including zirconium tert-butoxide [$Zr(OtBu)_4$] and tetrakis ethylmethylamino zirconium [TEMAZ]. The incorporation of $Zr(OtBu)_4$ led to improved tunability of the zirconium concentration but also resulted in a lower overall growth rate of PZT.

References

[1] Three dimensional piezoelectric MEMS, US8966993 B2, J.S. Pulskamp and R. G. Polcawich (19 Dec 2012)

[2] N. A. Strnad et al. *J. Vac. Sci. Technol. A* 37(2) Mar/Apr 2019

2:00pm **EM1-WeA-3 Understanding Growth Characteristics of ALD $NiAl_yO_x$: The Role of Ozone***, **Jonathan Baker**, J Schneider, S Bent,* Stanford University

ALD of ternary films has grown in interest as applications requiring the advantages of ALD (including sub-nanometer thickness control, uniformity, compositional control and conformality) have demanded more complex materials. However, depositing ternary materials by ALD is typically more complicated than the binary ALD systems from which the ternary materials are derived. As a result, the growth of a ternary material by ALD often deviates from ideal growth behavior described by the "rule of mixtures." In this work, ALD of $NiAl_yO_x$ was studied using the nickelocene ($NiCp_2$)/O_3 and trimethyl aluminum (TMA)/H_2O precursor systems for nickel oxide and aluminum oxide respectively. Depositions of $NiAl_yO_x$ were performed using the supercycle method, allowing a wide range of compositions to be achieved by altering the cycle ratio of nickel oxide to aluminum oxide ALD cycles. However, composition as a function of cycle ratio was found to be nickel deficient compared to the ideal rule of mixtures. The cause of the observed non-ideality was explored to help elucidate the ALD reaction mechanisms. Characterization of the films revealed that the growth rate of aluminum oxide was significantly enhanced following a $NiCp_2$/O_3 cycle. Modification of the rule of mixtures to account for the enhanced growth rate of Al_2O_3 resulted in a model which fits observed properties well, accounting for both the observed compositions and growth rates. In addition, $NiAl_yO_x$ has shown to be an interesting case study for understanding the deposition of ternary materials of first-row transition metal oxides grown with O_3. Similar to ALD of Fe_2O_3 and MnO_x, which utilize metallocene-derivatives and O_3, NiO ALD requires long precursor and O_3 exposures to achieve fully self-limiting growth. The root cause for this behavior is hypothesized to stem from the use of the strong oxidizer O_3, which may oxidize the metal centers to higher oxidation states or otherwise introduce extra oxygen into the film. For the deposition of $NiAl_yO_x$, low O_3 exposures were used to develop the initial $NiAl_yO_x$ system. To understand the effects of O_3 exposure on the deposition of the ternary ALD film and binary NiO system, growth of $NiAl_yO_x$ as a function of O_3 exposure was explored with an aim to understand the ALD reaction mechanisms at play when using O_3 as an oxidizer. The effect of high O_3 exposures will be discussed.

2:15pm **EM1-WeA-4 Atomic Layer Deposition of $B_xMg_{1-x}O$ Films: Progress Towards Shallow Boron Doping***, **David Mandia**, D Choudhury, M Gebhard,* Argonne National Laboratory*; J Liu,* Northwestern University*; A Yanguas-Gil, A Mane, A Nassiri, J Elam,* Argonne National Laboratory

Preparation of $B_xMg_{1-x}O$ films through an ABC-type ALD program employing bis(cyclopentadienyl) magnesium (II), trimethyl borate ($B(OCH_3)_3$), and water as precursors is presented herein. The thin film properties are extensively characterized by X-ray photoelectron (XPS), diffraction (XRD), and reflectivity (XRR). Moreover, optical properties of the as-grown and post-deposition annealed films are assessed through spectroscopic ellipsometry measurements with a particular focus on the effective optical properties of the B_2O_3 film component, which is an attractive shallow-boron dopant source material. Instead of using the highly toxic diborane (B_2H_6) as a boron doping source, the present work employs ALD to generate MgO-stablized $B_{-2}O_3$. Interestingly, as observed from *in-situ* quartz crystal microbalance (QCM) and Fourier transform infrared (FTIR) analysis, stabilization of B_2O_3 occurs by dosing $Mg(Cp)_2$ after the $B(OCH_3)_3$ pulse which forms Mg-B-O* surface species that undergoes further reaction to B_2O_3 in the succeeding water pulse. Without the $Mg(Cp)_2$ pulse (or MgO "AB" sub-cycle) preferential formation of boric acid ($B(OH)_3$) occurs instead of $B_{-2}O_3$. Post-deposition annealing treatments along with follow-up spectroscopic ellipsometry and high-resolution XPS/depth profiling measurements were performed to characterize the composite films' optical and electronic structural properties, respectively. The thermal ALD synthesis of $B_xMg_{1-x}O$ composite films on silicon in concert with post-deposition annealing is a potentially viable approach towards shallow-boron dopant layer or junction formation through the stable B_2O_3 component and could find use in solid-state electronics applications.

2:30pm **EM1-WeA-5 Enhanced Doping Control of Metal Oxide Thin Films Using a Modified ALD Process***, E Levrau,* IBM TJ Watson Research Center*;* ***Yohei Ogawa,*** ULVAC, Japan*; M Frank, M Hopstaken, E Cartier,* IBM T.J. Watson Research Center*; K Schmidt,* IBM Research - Almaden*; M Hatanaka,* ULVAC, Japan*; J Rozen,* IBM T.J. Watson Research Center

The introduction of controlled amounts of dopants into logic and memory devices has been extensively used in nanoelectronics in order to alter the properties of a material and make it suitable for a specific application. Doping thin films can be complicated because of the difficulty to control thickness and dopant gradient distribution.

Atomic Layer Deposition allows for excellent thickness control and doping is usually achieved by varying the cycle ratio of two metal oxides during deposition, M1O and M2O, in what are called super-cycles. We refer to this method as the standard nanolaminate process [1]. Here, we propose a modified ALD process that allows for finetuning the dopant concentration down to a few atomic % in the metal oxide (MO) thin film. This doping control can happen at thicknesses much thinner than standard nanolaminates thus allowing for a better trade-off between stack functionality and leakage. Doping levels of less than 10cation% are desired, specifically for higher k phases of HfO_2 for ferroelectric devices [2].

In figure 1, a comparison of the minimum deposition thickness required for each method, is given for varying dopant concentrations. This illustrates that the modified ALD process allows for films to be ~6x thinner than the standard nanolaminate process from the studied precursors for Zr-doped HfO_2, while exhibiting less than 5% 1-sigma thickness variation across a 200mm wafer. The process does not involve BEOL thermal budget or partial reactions associated with plasma oxidation and can therefore be very conformal. This makes it compatible with FEOL integration for 3D thin film depositions.

It has been demonstrated that doping can be beneficial for non-volatile memories as it can enhance the endurance and the switching stability of the devices [3]. Here, HfZrO thin films with varying dopant levels of Zr are deposited through the modified ALD method on 200mm substrates. Dopant concentrations are determined by RBS analysis. Film properties are analyzed with spectroscopic ellipsometry and XPS. Thin-film HfO_2-based ferroelectric devices with different dopants will be evaluated.

[2] Fischer D., Kersch A., J. of Appl. Phys., 104(8), 084104 (2008).

[3] Ryu S. W., Cho S., Park J., Kwac J., Kim H., Nishi Y., Appl. Phys. Lett., 105, 072102 (2014).

2:45pm **EM1-WeA-6 As Deposited Epitaxial $LaNiO_3$ and $La(Ni,Cu)O_3$ with Controllable Electric Properties***, **Henrik Hovde Sønsteby,*** University of Oslo / Argonne Natl. Labs, Norway*; O Nilsen, H Fjellvåg,* University of Oslo, Norway

Depositing complex oxides by ALD is a rapidly emerging field, with new materials with excellent properties published every month. $LaNiO_3$ is a perovskite type oxide with metallic behaviour, thought to play a major role in functional multilayer stacks and integrated electronics. Although routes for depositing $LaNiO_3$ has been reported in literature, an annealing step has always been necessary to obtain eptaxial films. In many applications this hinders monolithic device integration, and can cause unwanted strain effects and cracking.

In this presentation we show a facile route for direct epitaxial growth of $LaNiO_3$ by thermal ALD at temperatures as low as 250 °C. The films show excellent conductive properties as deposited, with specific resistivity as low as 10^{-4} Ohm cm. The functional properties of the films are slightly improved upon annealing, reaching specific resitivites in the 10^{-5} Ohm cm order of magnitude. Furthermore, we show that the order of precursor pulses plays a fundamental role in obtaining high quality as deposited epitaxial films.

$LaNiO_3$ is a remarkable member of the $RENiO_3$ series of materials (RE = La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Y, Lu),as it is the only member that remains metallic to 0 K. All other members observe a metal-insulator-transition (MIT) at temperature varying from ~100 K (Pr) to ~600 K (Lu). Controllably tuning the MIT is highly awaited by the community.

In this presentation we also show how substution by Cu on the Ni-site alters the electric properties and MIT temperature of $LaNiO_3$. We show that a full range of compositions is attainable, from $LaCuO_x$ to $LaNiO_3$, and that the electronic properties vary smoothly over this composition range. ALD can be used to obtain a remarkable cation composition control. Furthermore, we hypothesize on the reason behind the varying properties of this material system, and try to explain it by showing how oxygen vacancies are introduced by copper substitution. This may help shed light on the surprising properties of $LaNiO_3$ itself, but more importantly the films can be directly used in applications where a tunable MIT is necessary.

This presentations highlights the use of complex oxide ALD as a real alternative to MBE, with several key advantages such as conformality and low temperature deposition.

3:00pm **EM1-WeA-7 Time Dependence of Pyroelectric Response in Ferroelectric $Hf_{0.58}Zr_{0.42}O_2$ Films***, **Sean Smith,** M Henry, M Rodriguez,* Sandia National Laboratories*; J Ihlefeld,* University of Virginia

HfO_2 based ferroelectrics are a promising family of ferroelectrics stable as thin films. The ferroelectric response in HfO_2 thin films is associated with a metastable orthorhombic phase, typically seen in films < 30 nm thick, stabilized by doping, electrode material, deposition conditions and annealing. Thin HfO_2 based ferroelectrics are attractive for use in memory, energy harvesting, and sensing applications, however the polarization response of the thinnest of these films, <~5 nm, has been reported to be unstable over time. In this work we show that the pyroelectric response of 5 nm $Hf_{0.58}Zr_{0.42}O_2$ with TaN electrodes decreases logarithmically after biasing, decreasing from an initial value of -58 $\mu Cm^{-2}K^{-1}$ to ~-40 $\mu Cm^{-2}K^{-1}$ in the first 24 hours. While films 10 nm and thicker have a pyroelectric response that is constant on the same timescale.

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3:15pm **EM1-WeA-8 Tailoring Nickel Oxide Conductivity by Introducing Transition Metals: From First-principles to Experimental Demonstration***, **Md. Anower Hossain,** T Zhang, D Lambert,* University of New South Wales, Australia*; Y Zakaria,* Hamad Bin Khalifa University, Qatar*; P Burr,* University of New South Wales, Australia*; S Rashkeev, A Abdallah,* Hamad Bin Khalifa University, Qatar*; B Hoex,* University of New South Wales, Australia

Transition metal oxides, such as MoO_3, WO_3, V_2O_5, and NiO have shown potential for application as hole-selective passivating contact for silicon (Si) solar cells. Among them, NiO is a p-type semiconductor which possesses notoriously poor hole-conducting properties. Doping of metal oxides with multivalent metal cations is one of the most effective ways to improve electronic band structure properties of resulting ternary metal oxides because dopants create favorable defect states crucial for charge carrier transport. Therefore, we used first-principles density functional theory (DFT) computations as a predictive tool to identify suitable dopants. The density of states, defect formation energies, and thermodynamic transition levels of various charge states within the band gap of doped NiO were calculated and promising dopants were identified. We synthesized Al-doped NiO ($Al_xNi_{1-x}O$) and Zn-doped NiO ($Zn_xNi_{1-x}O$) films onto 2.0 Ω.cm *p-Si* wafers using atomic layer deposition (ALD). We used a supercycle approach alternating *N* (10, 25, 50) NiO cycles and 1 Al_2O_3 cycle. Cross-sectional transmission electron microscopy and energy dispersive x-ray spectroscopy mapping showed conformal films with the elemental distribution of Ni, O, and Al. X-ray photoelectron spectroscopy (XPS) measurements revealed the presence of Ni^{2+}, Ni^{3+} and Al^{3+} oxidation state in the films. The Al content was found to scale with the number of AlO_x ALD cycles. The density of the Ni^{3+} and Al^{3+} oxidation state increased with the increasing number of AlO_x ALD cycles, confirming the Al incorporation into the host lattice of NiO. However, a significantly higher Al concentration was found in the $Al_xNi_{1-x}O$ film as was expected from the supercycle ratio. This was resulting from a significantly higher growth per cycle of AlO_x compared to NiO. While undoped NiO was found to be resistive, the Al_xNi_{1-x} films showed the contact resistivity of 41.6 - 113 mΩ·cm^2 after annealing in a rapid thermal processing furnace at 200-300 °C under N_2 for 10 minutes. In addition, the $Zn_xNi_{1-x}O$ films deposited by supercycle of NiO and ZnO cycle also showed the Ohmic contact with *p-Si*. The $Zn_xNi_{1-x}O$ films were also thermally stable up to 500 °C with the best contact resistivity of approximately 21.5 $m\Omega\cdot cm^2$. This indicates a significant improvement of contact performance as compared to the undoped NiO counterparts. This work demonstrates that a ternary $Al_xNi_{1-x}O$ and $Zn_xNi_{1-x}O$ films are suitable hole-selective passivation contact for the *p-Si* solar cells.

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