Thin Films Division
Room 102A - Session TF+EM+MI+PS-MoA

Thin Films for Advanced Memory Applications and Magnetics

Moderator: Robert Grubbs, Micron Technology

1:40pm **TF+EM+MI+PS-MoA2 ---Multiferroic Integration of Undoped Ferroelectric HfO_2 and Ferrimagnetic $CoFe_2O_4$ Thin films by Radical-Enhanced Atomic Layer Deposition***, J. Chang,* ***Adrian Acosta****, J.P. Chang,* University of California at Los Angeles

Multiferroic materials that exhibit the coexistence and coupling between ferroelectricity and magnetism are of great interest due to their potential for enabling next-generation memories. To overcome the scarcity and weak response of intrinsic multiferroics, composite strategies were proposed to realize robust multiferroic behavior by coupling the properties from constituent ferroelectric and magnetic phases. However, additional challenges for an applicable multiferroic composite are present in the ferroelectric phase since conventional perovskite-based ferroelectrics lack the necessary electrical stability and silicon-compatibility for device integration.

Orthorhombic ferroelectric HfO_2 (FE-HfO_2) based thin films have emerged in the field of microelectronics research owing to its superior compatibility with CMOS technology as well as desirable electrical properties. In this work, multiferroic integration of undoped FE-HfO_2 thin films and ferrimagnetic $CoFe_2O_4$ (CFO) on Si substrates via radical-enhanced atomic layer deposition (RE-ALD) are first demonstrated. For the RE-ALD process, atomic oxygen was utilized in conjunction with TDMAHf and TMHD-based metalorganic precursors for the growth of HfO_2 and CFO respectively. In the composite design, CFO acts as a mechanical constraint to stabilize FE-HfO_2 as well as an active magnetic layer.

Composite ferroelectricity was studied as a function of FE-HfO_2 film thickness as well as post-deposition annealing temperatures. Film crystallinity was investigated through the use of a synchrotron beam source to understand the structural evolution. The induced ferroelectricity was observed to correlate with HfO_2 orthorhombic phase and was maximized when HfO_2 is ~6 nm and after annealing at ~700-800 °C. CFO/FE-HfO_2 composites showed ferroelectric behavior with remnant polarization ~5.5 μC/cm^2 and electrical coercivity ~340-2000 kV/cm, with the potential to be further enhanced via the inclusion of dopants. Comparable magnetism was observed with out-of-plane anisotropy, a saturation magnetization of ~155 emu/cm^3, and a magnetic coercivity ranging from ~1000-3400 Oe. Piezoresponse force microscopy (PFM) verified the strain interaction in the CFO/FE-HfO_2 design. Lastly, a magnetoelectric coupling coefficient of ~5.5×10^{-8} s/m (~55 Oe cm/kV) was obtained from the multiferroic structure with 6-nm thick HfO_2 layer via an *ex situ* poling SQUID magnetometer setup. This work not only highlights the potential of FE-HfO_2 based multiferroic composites in realizing magnetoelectric spintronic devices but also unveils the possibility of utilizing alternative capping layers for achieving multifunctional composite heterostructures.

2:00pm **TF+EM+MI+PS-MoA3 Growth and Characterization of BeO Thin Films Grown by Atomic Layer Deposition using H_2O and O_3 as Oxygen Sources***,* ***Lee Woo Chul****, C. Cheol Jin,* Center for Electronic Materials, Korea Institute of Science and Technology, Korea*; K. Sangtae,* Center for Electronic Materials, Korea Institute of Science and Technology, Korea*; L. Eric S., Y. Jung Hwan,* Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), South Korea*; H. Cheol Seong,* Department of Materials Science and Engineering, and Inter-University Semiconductor Research Center, College of Engineering, Seoul National University, South Korea*; B. Christopher W.,* Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), South Korea*; K. Seong Keun,* Center for Electronic Materials, Korea Institute of Science and Technology, Korea

BeO has a very large band gap (10.6 eV), which is even larger than that of representative large band gap materials; SiO_2 (~9 eV) and Al_2O_3 (~8 eV). BeO thin films reveal high quality of the interface with Si and semiconductors, showing a possibility as a gate dielectric. Furthermore, rocksalt BeO was recently predicted to have a very high dielectric constant (~ 275) and a very large band gap (10.6 eV). However, the fascinating dielectric properties have not been experimentally realized yet because of the instabilty of the rocksalt BeO. Nowdays, atomic layer deposition (ALD) is a common technique for film growth in a semiconductor industry. The ALD process of the BeO thin films is necessary to be developed to implement BeO in the semicoductor industry. Herein, the growth characteristics and properties of BeO thin films grown by ALD are investigated. We demonstrated that ALD chemistries between dimethylberyllium (DMB) and two different oxygen sources, H_2O and O_3, are governed by different reaction mechanisms, resulting in different film properties.

BeO thin films were grown in a traveling-wave type reactor by ALD with DMB and different oxygen sources, such as H_2O and O_3, in the temperature range of 150 to 300 °C. Although H_2O-ALD and O_3-ALD of BeO all showed self-saturation behavior, the growth behavior and film properties are strongly dependant on the oxygen sources. With increasing growth temperatures, the growth per cycle (GPC) of H_2O-ALD of BeO decreases, while that of O_3-ALD of BeO is almost constant. The properties of the BeO films grown in H_2O-ALD are nearly temperature-independent, whereas the BeO films grown in O_3-ALD at low temperatures (< 200 °C) reveal high impurity concentrations and a low film density. These cause lowering of the band gap and dielectric constant of the BeO films grown by O_3-ALD at low temperatures. These findings demonstrate that the O_3-ALD process requires relatively more thermal energy than H_2O-ALD does, to produce high-quality BeO thin films.

2:20pm **TF+EM+MI+PS-MoA4 Atomic Layer Deposition of Magnetic Films and Patterned Features with Tunable Magnetic Properties***, Z. Zhang,* ***John Ekerdt****,* University of Texas at Austin

We report a process to generate carbon-free Co metal films and patterns by first growing films of CoO via atomic layer deposition on various hydroxylated surfaces and then reducing the CoO at low temperatures to Co metal. The CoO ALD process employs (bis(N-tert butyl, N'ethylpropionamidnato) cobalt (II) and water at 180 °C. Similar processes work for Fe and Ni growth. The metal oxides have a lower density than the metal and will spread uniformly over oxide substrates whereas ultra-thin metal films tend to dewet from the oxide and generate discontinuous films. This dewetting is a strong function of temperature and can be mitigated by lowering the temperature of the reduction process or by lowering the energy of the free surface. Temperatures in excess of 420 °C are required to achieve full reduction of 4.5-nm CoO in H_2 (or D_2); films reduced at this temperature are discontinuous. We report the use of atomic deuterium that is generated over a heated tungsten filament and show that we can fully reduce 4.5-nm CoO to Co at 220 °C without the metal film dewetting oxides such as SiO_2, MgO, ZrO_2, and Al_2O_3. Thermal history of the film is critical to tuning the magnetic properties. As ultra-thin films roughen by extended annealing at 200 °C the film coercivity can be manipulated from 90 to 500 Oe. Since the CoO ALD process is initiated on hydroxylated surfaces and can blocked by organic films, we pattern polystyrene using UV crosslinking through a shadow mask or a diblock co-polymer to generate features ranging from microns to tens of nanometers and deposit CoO on the hydroxylated surfaces that are opened in the polystyrene. This presentation will address the interface issues in achieving selective growth and in manipulating the magnetic properties of continuous Co films and shaped features.

2:40pm **TF+EM+MI+PS-MoA5 Tuning of the Magnetic and Electronic Properties of Epitaxial Heusler Compound Heterostructures***,* ***Christopher Palmstrøm****,* University of California, Santa Barbara **INVITED**

Heusler compounds have received a lot of attention because of their large range of properties. Their properties depend on the number of valence electrons per formula unit and have been predicted to be semiconductors, metals, ferromagnets, antiferromagnets, half metals, superconductors and topological insulators. Similar to compound semiconductors, the band structure and lattice parameters of Heusler alloys can also be tuned through alloying but over a much larger range of properties. Magnetic tunnel junctions using Heusler alloys that are predicted to be half metals have shown record tunneling magnetoresistance. Heusler half metals have been predicted to have very low Gilbert damping coefficients. They can also be lattice matched to most compound semiconductors and have been used for spin injecting contacts. Recent theoretical predictions suggest that atomic level Heusler superlattices can result in half metallicity and perpendicular magnetization. This presentation will emphasize the molecular beam epitaxial growth combined with in-situ and ex-situ structural, electronic and magnetic characterization of Heusler heterostructures on III-V semiconductors and MgO single crystal substrates. Tuning of their magnetic and electronic properties through elemental substitution to change the number of valence electrons per

formula unit and atomic level superlattice growth will be discussed. Examples of Heusler heterostructures and controlling of their magnetic and electronic properties include tuning of the spin polarization in $Co_2Mn_{1-x}Fe_xSi$, Heusler contacts for spin injection into GaAs, spin polarization and magnetic anisotropy of Co_2MnAl/Fe_2MnAl atomic scale superlattices, substitution with Fe in CoTiSb with the aim to convert a semiconductor to half metal and interfacial reactions at Co_2MnSi/MgO interfaces. By careful tuning of the half metallic Heusler film composition, Gilbert damping coefficients <0.001 have been observed.

3:40pm **TF+EM+MI+PS-MoA8 Stabilization of Ferroelectric Phase of $Hf_{0.5}Zr_{0.5}O_2$on NbN at 4 K**, ***Michael David Henry***, *S. Smith, R. Lewis,* Sandia National Laboratories*; J. Ihlefeld,* University of Virginia

This work demonstrates cryogenic ferroelectric behavior of atomic layer deposited (ALD) hafnium zirconium oxide (HZO) using reactively sputtered niobium nitride electrodes. With the discovery of ferroelectricity in doped HfO_2, perturbations of the dopants expanded from silicon into mixtures utilizing yttrium and zirconium and with electrodes ranging from platinum to nitrides such as titanium nitride and tantalum nitride. This set of materials have demonstrated stabilizing a crystalline phase permitting both ferroelectric and anti-ferroelectric behaviors to have been observed. With the atomic similarities between Ta and Nb, a natural extension the electrode materials' set to include NbN was explored in this work.

Devices tested at both room temperature (RT) and under cryogenic conditions demonstrated ferroelectric behavior as determined by polarization vs. electric field (P-E) loops. The polarization results show comparable ferroelectric behavior at room temperature and 4 K, however the effect of the dielectric polarization is combined with the remnant polarization (P_r) in this measurement. To separate the two effects, remnant polarization sweeps were performed and plotted only displaying the P_r. A typical measurement on a 170 mm diameter device, was performed starting at 4 K and ending at 150 K. By adding the positive and negative $P_r$with the electric field at 0 MV/cm ($2P_r$), polarization was observed to decrease as the stage was warmed up. A second known behavior of ferroelectrics is the so-called wake-up effect where the ferroelectric phase is understood to be stabilized by oxygen movement as a positive and negative voltage is applied. Here, a 3 V square wave at 1Hz was utilized in 60 second intervals with $P_r$loops performed before and after each wake-up cycling at room temperature. The $2P_r$was seen to come to steady state after approximately 100 seconds. Remnant polarization at the conclusion of 360 seconds is seen to have polarization approximately 10 mC/cm^2, a value comparable to other findings. Polarization values of approximately 10 mC/cm^2suggest that these ferroelectric films could be utilized with superconductors at liquid He temperatures for a new class of superconductor-ferroelectric based devices.

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4:00pm **TF+EM+MI+PS-MoA9 Atomic Layer Deposition of Co/Pt Multilayer films for Perpendicular Magnetic Anisotropy**, ***Devika Choudhury***, *A.U. Mane, C.M. Phatak, A.K. Petford Long, J.W. Elam,* Argonne National Laboratory

"Smaller, Faster and Efficient" are the key words describing the ever increasing need of data-storage industry.[1] This demand has brought about a shift from longitudinal recording in magnetic media to perpendicular recording, where magnetic bits are perpendicular to the plane of the recording media instead of being in the same plane. Significantly higher storage density is obtained as a result of using the perpendicular magnetic recordings utilizing materials demonstrating perpendicular magnetic anisotropy (PMA). Strong PMA is usually observed in ultrathin films of ferromagnetic metals like Co and Fe forming alloys with heavy metals like Pt, Pd, Au and Ta.[2] Of them Co/Pt alloys and multilayer structures are probably the most widely investigated system for understanding the PMA origin and behavior.

The effective anisotropy energy of the multilayer films in the PMA regime depends on various factors like thickness of the individual Co/Pt layers, quality of interfaces and crystallinity of the films.[3] Till date, the commonly used techniques for growth of Co/Pt multilayers have been electron beam evaporation and sputtering. However, for development of higher areal density using three-dimensional media, conformal, uniform and controlled deposition of the thin films is certainly required.

In this work, we utilize atomic layer deposition (ALD) of Co/Pt multilayers to overcome limitations of the other growth processes. ALD provides precise control over the film thickness along with uniform and conformal films thus resulting in distinct sharp interfaces between the individual metal films. Bis(N-t-butyl-N'-ethylpropanimidamidato)cobalt(II) and hydrogen precursors are used for Co ALD while Trimethyl(methylcyclopentadienyl)platinum(IV) and water are used as precursors for Pt deposition. QCM studies confirm self-limiting ALD growth nature of the individual metal films at 300°C. Pt(10nm)/[(Co/Pt)x8](16nm)/Pt(2nm) stacks are grown using alternate cycles of Co and Pt. QCM measurements reveal a short nucleation regime of Pt over Co films. HRTEM imaging and XPS analysis of the multilayer stacks are utilized to study the interfaces of the multilayer films closely. Preliminary SQUID measurements show a change in anisotropy between pure Co and Co/Pt multilayer films. Effects of variation in individual layer thicknesses, deposition temperature, post-deposition annealing temperature etc. remains to be seen.

References:

[1] B. Tudu and A. Tiwari, *Vacuum*, 146, 329 (2017).

[2] V. M. Parakkat, K. R. Ganesh, and P. S. A. Kumara, *AIP Advances*, 6, 056118 (2016).

[3] B. F. Vermeulen, J. Wu, J. Swerts, and S. Couet et al. *Journal of Applied Physics*, 120, 1639031 (2016).

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