Thin Film
Room: 104 A - Session TF+EM+NS+SS-ThA

Thin Film: Growth and Characterization II
Moderator: C. Vallee, LTM - MINATEC - CEA/LETI, France

2:00pm **TF+EM+NS+SS-ThA1 Comparison of Al_2O_3 Deposited via Prompt Inorganic Condensation vs. Atomic Layer Deposition**, ***S.W. Smith***, *W. Wang, D.J. Matthews, D.A. Keszler, J.F. Conley*, Oregon State University

Due to the purge separated pulsing of precursor and oxidation gases combined with self-limiting surface reactions, atomic layer deposition (ALD) enables the synthesis of dense conformal thin films with atomic scale control. In terms of sustainable manufacturing however, ALD suffers from slow deposition rates, precursor waste, and the requirement of a vacuum system. Solution-based thin-film deposition methods are attractive because they allow for deposition at atmospheric pressure and with shorter processing times. However, traditional solution based approaches often involve organometallic sol-gels with bulky ligands. High temperature post deposition anneals are required to drive off these ligands resulting in a dramatic change in physical dimensions as the films are densified. The resulting films are thus often porous and exhibit poor electrical properties. More recently, a novel solution processing technique known as prompt inorganic condensation (PIC) enables the deposition of dense, smooth, high-quality films through the use of aqueous metal-inorganic precursors.

In this work we compare the electrical and physical properties of Al_2O_3 films produced by ALD and PIC. ALD of Al_2O_3 was performed using trimethyl-aluminum and H_2O at 300°C. PIC of Al_2O_3 was performed using an aqueous aluminum hydroxide nitrate solution at room temperature in atmosphere. Post deposition anneals were performed following PIC to convert the hydroxide to an oxide and densify the films. $Al/Al_2O_3/Si$ MOS capacitors were used for electrical measurements. For 10 nm thick films, 300°C annealed PIC Al_2O_3 shows higher leakage, and lower breakdown strength than ALD Al_2O_3. After a 500°C anneal, the PIC Al_2O_3 shows lower leakage current density at fields >2.5 MV/cm and equivalent breakdown strength to ALD Al_2O_3. Conduction mechanisms will be discussed. Capacitance vs. voltage data showed that PIC films have a lower dielectric constant than ALD films and an anneal temperature dependent flat band voltage shift. X-ray reflectivity indicates that as-deposited PIC films have a low density which increases with increasing anneal temperature to approach that of the ALD films. Finally, X-ray photoelectron spectroscopy and transmission electron microscope data are used to examine the Al_2O_3/Si interfacial region. Differences in interfacial layer formation may explain the reduced leakage current observed in the lower density PIC films. Our results show that PIC is promising method for deposition of thin (~10 nm) Al_2O_3 films on silicon.

2:20pm **TF+EM+NS+SS-ThA2 Static Mode CVD at Low Temperatures: Highly Conformal and Smooth Films in Deep Structures**, *A.N. Cloud, J.L. Mallek, K.A. Arpin, P.V. Braun, G.S. Girolami,* ***J.R. Abelson***, University of Illinois at Urbana Champaign

Chemical vapor deposition can afford smooth and conformal films in high aspect ratio structures in the limit of high precursor pressure and low substrate temperature. Under those conditions, adsorbed precursor molecules cover the growth surface, react to deposit film at useful rates, but also block active sites such that the effective sticking coefficient is reduced. The result – a conformal film in trenches deeper than 30:1 – can be competitive with ALD. This is not surprising, given the underlying kinetic principle, surface site-blocking, is the same.

We report the successful implementation of the most extreme parameters: we perform static CVD in an unpumped glass tube that is pre-filled with precursor up to its vapor pressure and slowly ramped to temperature in a clamshell furnace. The slow heating ramp at maximum possible precursor pressure affords remarkably uniform film nucleation, excellent conformality and surface smoothness. Based on the coating of deep trenches, silica-based synthetic opals, and aerogels, we estimate an effective sticking coefficient < 10^{-5}. Many substrates can be loaded into the tube such that the throughput is good in batch mode. The precursor utilization is excellent (~ 25 %), unlike the case of flowing CVD in which most of the precursor is wasted under conformal growth conditions.

Static CVD is demonstrated for the conformal growth of HfB_2 and elemental Fe films. HfB_2 is an electrically conductive refractory material with high mechanical hardness, excellent tribological properties, and excellent diffusion barrier properties against Cu. The precursor, $Hf(BH_4)_4$, has a remarkably high vapor pressure of 15 Torr at 25°C. This pressure both promotes conformal film growth and provides a large gas density sufficient to deposit 100 nm of film in a single cycle. The precursor is reactive toward O_2 and H_2O and acts as a gas-phase getter for potential contaminants. Thus, despite the rough vacuum apparatus, the films have O and C impurity contents < 1 at. % as evaluated by AES. The film composition is stoichiometric despite the buildup of reaction products. This implies that the growth surface has no net reactivity towards these products.

Fe films are deposited from the precursor $Fe(CO)_5$. Typically CVD Fe films grown from this precursor have faceted surfaces and are not conformal. Here, the film smoothness and conformality is excellent. The O and C impurity contents are ~ 1 at. %.

We will discuss the prospects for coating other materials by static CVD, as well as simple modifications that have the potential to afford thicker films and avoid impurity contamination in cases where the byproduct reactions are not negligible.

2:40pm **TF+EM+NS+SS-ThA3 Growth of Nanocomposite and Epitaxial Nitride and Oxide Thin Films by Magnetron Sputtering for Thermoelectric Applications**, *B. Paul, S. Kerdsongpanya,* ***P. Eklund****, Linkoping University, Sweden **INVITED**

In this invited talk, we first review our recent work on ScN-based thin films for thermoelectrics and correlated theoretical studies. The anomalously high thermoelectric power factor of ScN can be explained in terms of the band structure, with vacancy and impurity states introducing sharp features near the Fermi level yielding a large power factor. We further present results on calcium cobalt oxide thin films grown on $Al_2O_3(0001)$ substrate by co-sputtering from Ca and Co-targets by reactive rf-magnetron sputtering in presence of 1.5 % O_2. As-deposited films were found to be amorphous. Subsequent ex-situ annealing in O_2-atmosphere well crystallized highly c-axis-oriented $Ca_3Co_4O_9$ films were obtained. For higher annealing temperature of 800 °C, the films are found to be single-phase epitaxial $Ca_3Co_4O_9$. X-ray diffraction and pole figure XRD analyses reveal the films are having (001)-orientation. Furthermore, altering the nominal starting composition of the as-deposited films yielded $Ca_3Co_4O_9$-based nanocomposite films with cobalt oxide inclusions, which may act as phonon scatterers for potential reduction of thermal conductivity in a thermoelectric application.

3:40pm **TF+EM+NS+SS-ThA6 Atomic Layer Deposition of $Pb(Zr_xTi_{1-x})O_3$ Thin Films**, ***D. Chien***, *T. Kim, J. Choi, J.P. Chang*, UCLA

Lead zirconate titanate at its morphotropic phase boundary composition, $Pb(Zr_{0.52}Ti_{0.48})O_3$, exhibits strong coupling between electrical and mechanical energies, making it a promising material for piezoelectric MEMS. As MEMS continue to scale down to smaller sizes with more complex topography, the ability to deposit high quality PZT thin film conformally over high aspect ratio 3D structures and surfaces that are not in line-of-sight of deposition sources becomes an enabling factor. Atomic layer deposition (ALD) is a promising method because it is a surface-reaction controlled process based on alternating self-limiting reactions which can obtain superior uniformity and conformality over complex surface structures. Another challenge is to deposit (001) oriented PZT because it has a higher piezoelectric constant than (111) oriented PZT.

In this work, a (100) textured ALD $PbTiO_3$ (PT) seed layer was used to attain (100) oriented PZT on platinized silicon substrates. The PT and PZT thin films were synthesized by depositing alternating layers of PbO, ZrO_2, and TiO_2 using $Pb(TMHD)_2$, $Zr(TMHD)_4$, and $Ti(O^{\cdot}i\text{-}Pr)_2(TMHD)_2$ as metal precursors and H_2O as the oxidant. The growth sequence consisted of a(Pb-O)-b(Ti-O)-c(Pb-O)-d(Zr-O) where a:b:c:d ratio of local cycles and global cycles were regulated to achieve the desired stoichiometry and thickness, respectively. To tailor the composition of PT and PZT by ALD, the incubation time of depositing one constituent oxide on another on KBr crystal disks was quantified by *in-situ* FTIR. The IR absorption spectrums of one metal oxide layer deposited on another were acquired after each ALD cycle until specific stretching vibration mode of the target metal oxide was observed to indicate the required incubation time to initiate the target oxide growth. These results were used to guide the design and synthesis of PT and PZT with precise composition control. The stoichiometry and crystallinity of $PbTiO_3$ and PZT films were confirmed by XPS and XRD, respectively.

To assess the feasibility of ALD P(Z)T films for piezoMEMS application, ALD PZT thin films were deposited on ALD $PbTiO_3$ seed layer and

* **Paul Holloway Award Winner**

fabricated into simple capacitors with platinum as the top electrode. The dielectric and ferroelectric properties of ALD PZT thin films were characterized via CV measurements and PE hysteresis loops, which are sensitive to the composition of PZT. The (100) oriented ALD PZT thin film was poled to attain the desired (001) oriented PZT film, for which the effective transverse piezoelectric coefficient, $e_{31,f}$, was quantified via the wafer flexure method. The conformality of 15nm ALD PZT films were confirmed over 300nmx700nm hollow Si_3N_4 cylinders.

4:20pm **TF+EM+NS+SS-ThA8 Aluminum Nitride Thin Films Deposition, Properties and Applications***, **L. le Brizoual**, J. Camus, K. Ait Aissa, Q. Simon, P.Y. Jouan, M.A. Djouadi,* Univ. de Nantes - CNRS-IMN, France*, Y. Cordier, E. Frayssinet, M. Chmielowska, M. Nemoz, P. Vennéguès, S. Chenot,* CRHEA-CNRS, France*, N. Defrance, M. Lesecq, P. Altuntas, A. Cutivet, A. Agboton, J.C. De Jaeger*, Univ. de Lille - CNRS-IEMN, France **INVITED**

Aluminum nitride (AlN) is a wide bandgap semiconductor and showing intrinsic properties such as high thermal conductivity, high electrical resistivity, good mechanical hardness and efficient piezoelectricity. Due to its intrinsic properties, single-crystalline AlN is a promising III–V semiconductor for applications in high power electronics and optoelectronics such as HEMTs, UV light-emitting diodes and acoustic waves devices. AlN films are grown on a variety of substrates using different deposition methods including chemical vapor deposition techniques and molecular beam epitaxy, laser ablation and reactive sputtering techniques. Among these methods, sputtering techniques permit to obtain *c*-axis oriented AlN films with small surface roughness at relatively low temperatures. Both modes of Magnetron Sputtering are presented: the DC mode and the HiPIMS mode (High Power Impulsed Magnetron Sputtering) for reactive AlN synthesis. HiPIMS for deposition of insulating AlN thin films were used and compare to the DC mode. The processes are optimized for working with Aluminum targets in a reactive atmosphere (Ar-N_2). As the plasma characterization of the ionized species is necessary in order to understand pulsed plasma process, time-resolved investigations were carried out using Optical Emission Spectroscopy and Mass Spectrometry was used for quantifying the ionic and neutral species reaching the substrate and the results are compared to the DC case. The AlN film stress was measured by the substrate curvature technique. The AlNfilm quality was characterized and by X-ray diffraction analysis (XRD), UV Raman spectrometry and Ellipsometry. The first purpose of this contribution consists to compare the structural and microstructural properties of AlN films deposited by DCMS and HiPIMS, in particular, in order to study the influence of the ionic bombardment resulting from the different discharges. Then, from the first deposition optimization study, we developed the epitaxial growth of AlN on a specific buffer layer on Silicon (111) and its electrical characterizations are presented. This AlN epitaxial layer obtained by magnetron sputtering was used to re-growth a thick GaN film in order to obtain HEMT device. This original structure exhibits a low drain current collapse which may be attributed to the enhanced thermal dissipation properties of the structure.

The present study has been supported by the French National Research Agency under grant ANR-2010-EMMA-030 CREATIVEPI.

5:00pm **TF+EM+NS+SS-ThA10 Atomic Layer Deposition of Tungsten Nitride Thin Films — Initial Surface Reactions***, **K. Bernal Ramos**,* The University of Texas at Dallas*, R.K. Kanjolia,* SAFC Hitech*, Y.J. Chabal*, The University of Texas at Dallas

Tungsten nitride (WN_x) films have been reported to form amorphous or amorphous-like phases that are desirable to be used as a diffusion barrier for copper metallization or other contact materials in microelectronics applications. The properties of tungsten nitride, such as high melting temperature, relatively low resistivity and chemical inertness, make it an attractive material for a variety of applications. Its deposition using Atomic Layer Deposition (ALD) is however poorly understood, hindering a wider use.

This work focuses on the ALD of WN_x using a novel tungsten-based ALD precursor, dicarbonyl(methylcyclopentadienyl)nitrosyl tungsten ($MeCpW(CO)_2(NO)$) and hydrazine as its co-reactant. We first examine the reactivity of $MeCpW(CO)_2(NO)$ with OH-terminated oxidized silicon surfaces (O_3Si-OH) in order to better understand and control thin film deposition. In situ infrared (IR) absorption spectroscopy is used to uncover the film growth mechanisms. The spectra indicate that, at a substrate temperature range of 200-300 °C, there is a nucleation period of 5-6 cycles, after which tungsten nitride begins to grow through an expected ligand exchange mechanism, with appearance of N-H vibrational modes at ~3280 and ~1600 cm^{-1} after the hydrazine pulse. X-ray photoelectron spectroscopy (XPS) provides additional information on impurity concentration, such as carbon and oxygen, in addition to confirmation of the growth chemistry. XPS results indicate a low concentration of C impurities in the film bulk.

This study provides insight into the surface chemistry of the precursor's initial reactions necessary to enable future process development and deposition of W-based materials for a wide range of applications.

5:40pm **TF+EM+NS+SS-ThA12 Metal Oxide Growth, Characterization and Spin Precession Measurement in CVD Graphene***, **A. Matsubayashi***, University at Albany-SUNY*, J. Abel,* Intel Corporation*, D. Sinha, J. Lee, V.P. LaBella*, University at Albany-SUNY

Thin metal oxide layers deposited on graphene can be utilized as dielectric barriers between metals and graphene to help isolate a metal contact from the graphene channel. This is important for graphene based spintronic devices as dielectric layers between the ferromagnetic electrode and graphene have been shown to increase the spin relaxation time measured utilizing non-local detection and spin precession measurements. However, simply depositing metal oxide layers such as aluminum oxide on graphene results in non-uniform film lowering the quality of the interface barrier. We will present a systematic study of aluminum oxide layers grown on CVD (chemical vapor deposition) graphene under ultra-high vacuum conditions with and without titanium seed layers. The aluminum oxide layers with the titanium seed layers showed reduced surface roughness. The chemical and structural composition determined by XPS (X-ray photoelectron spectroscopy) will be also presented that shows full oxidation of the aluminum and partial oxidation of the titanium. The results on the spin precession measurements in CVD graphene will be also presented.

Authors Index

Bold page numbers indicate the presenter

— A —

Abel, J.: TF+EM+NS+SS-ThA12, 2
Abelson, J.R.: TF+EM+NS+SS-ThA2, **1**
Agboton, A.: TF+EM+NS+SS-ThA8, 2
Ait Aissa, K.: TF+EM+NS+SS-ThA8, 2
Altuntas, P.: TF+EM+NS+SS-ThA8, 2
Arpin, K.A.: TF+EM+NS+SS-ThA2, 1

— B —

Bernal Ramos, K.: TF+EM+NS+SS-ThA10, **2**
Braun, P.V.: TF+EM+NS+SS-ThA2, 1

— C —

Camus, J.: TF+EM+NS+SS-ThA8, 2
Chabal, Y.J.: TF+EM+NS+SS-ThA10, 2
Chang, J.P.: TF+EM+NS+SS-ThA6, 1
Chenot, S.: TF+EM+NS+SS-ThA8, 2
Chien, D.: TF+EM+NS+SS-ThA6, **1**
Chmielowska, M.: TF+EM+NS+SS-ThA8, 2
Choi, J.: TF+EM+NS+SS-ThA6, 1
Cloud, A.N.: TF+EM+NS+SS-ThA2, 1
Conley, J.F.: TF+EM+NS+SS-ThA1, 1
Cordier, Y.: TF+EM+NS+SS-ThA8, 2
Cutivet, A.: TF+EM+NS+SS-ThA8, 2

— D —

De Jaeger, J.C.: TF+EM+NS+SS-ThA8, 2
Defrance, N.: TF+EM+NS+SS-ThA8, 2
Djouadi, M.A.: TF+EM+NS+SS-ThA8, 2

— E —

Eklund, P.: TF+EM+NS+SS-ThA3, **1**

— F —

Frayssinet, E.: TF+EM+NS+SS-ThA8, 2

— G —

Girolami, G.S.: TF+EM+NS+SS-ThA2, 1

— J —

Jouan, P.Y.: TF+EM+NS+SS-ThA8, 2

— K —

Kanjolia, R.K.: TF+EM+NS+SS-ThA10, 2
Kerdsongpanya, S.: TF+EM+NS+SS-ThA3, 1
Keszler, D.A.: TF+EM+NS+SS-ThA1, 1
Kim, T.: TF+EM+NS+SS-ThA6, 1

— L —

LaBella, V.P.: TF+EM+NS+SS-ThA12, 2
le Brizoual, L.: TF+EM+NS+SS-ThA8, **2**
Lee, J.: TF+EM+NS+SS-ThA12, 2
Lesecq, M.: TF+EM+NS+SS-ThA8, 2

— M —

Mallek, J.L.: TF+EM+NS+SS-ThA2, 1
Matsubayashi, A.: TF+EM+NS+SS-ThA12, **2**
Matthews, D.J.: TF+EM+NS+SS-ThA1, 1

— N —

Nemoz, M.: TF+EM+NS+SS-ThA8, 2

— P —

Paul, B.: TF+EM+NS+SS-ThA3, 1

— S —

Simon, Q.: TF+EM+NS+SS-ThA8, 2
Sinha, D.: TF+EM+NS+SS-ThA12, 2
Smith, S.W.: TF+EM+NS+SS-ThA1, **1**

— V —

Vennéguès, P.: TF+EM+NS+SS-ThA8, 2

— W —

Wang, W.: TF+EM+NS+SS-ThA1, 1