

Thin Film

Room: 104 A - Session TF-TuM

ALD for Emerging Applications

Moderator: G.S. Scarel, James Madison University

8:00am **TF-TuM1 Fabrication of Top Gate Graphene Transistor using Physically Transferrable High- κ Nanosheet using Atomic Layer Deposition.** *H. Jung, J. Lee, K. Ko, J. Park, H. Kim*, Yonsei University, Republic of Korea

Graphene, a single layer of hexagonal carbon atom structure with very high mobility (more than 200,000 cm²/Vs at 4.2 K for suspended) draws great attention as a promising material for future nanoelectronics and finally a substitution of silicon. To fabricate devices, especially transistors, gate dielectric is an essential component, which can significantly impact the device performance. Exploring graphene for future devices requires deposition of dielectric materials on graphene. However, deposition of high- κ dielectrics directly onto graphene is difficult task due to the nucleation problem preventing the formation of high quality oxide on graphene because of chemical inertness of graphene surface. Previous reports to deposit high- κ dielectrics on graphene have resulted in significant degradation in electrical properties of graphene. Here, we describe a new strategy to integrate graphene with high quality high- κ dielectrics by transferring high- κ dielectric nanosheet onto graphene. To fabricate a high- κ dielectric nanosheet, we firstly prepared spin-coated water-soluble poly(acrylic acid) (PAA) on Si substrate as a sacrificial layer and high- κ dielectric thin film was deposited on the sacrificial layer using atomic layer deposition (ALD) process. The high- κ dielectric nanosheet was fabricated by soaking the sample in water and removing the sacrificial layer. Dielectric properties of high- κ nanosheet show similar dielectric constant with ALD thin film and lower hysteresis (~ 0 mV) and interface state density (1.7×10^{11} cm⁻²eV⁻¹) than thin film (~ 200 mV, 7.6×10^{11} cm⁻²eV⁻¹). We fabricated and characterized top gate graphene transistors using both directly deposited high- κ thin film on graphene using ALD and high- κ dielectric nanosheet as gate dielectrics. Fabricated graphene device using ALD on graphene did not operate properly. Using high- κ nanosheet as the gate dielectrics, we have demonstrated top gate graphene transistors with field-effect mobility up to 2,000 cm²/Vs and ~ 0 V of Dirac voltage. This method opens a new way to high-performance graphene devices to impact broadly from high frequency high speed circuits to flexible electronics.

8:20am **TF-TuM2 Resistive Switching Devices Based on Ozone assisted ZnO Films by Atomic Layer Deposition.** *R.M. Mundle, A.K. Pradhan*, Norfolk State University

Atomic layer deposition (ALD) is an ideal technique to deposit ultrathin films with high conformality and precise thickness control using water as one its precursors. We demonstrate the growth temperature dependence of film thickness and surface roughness of ZnO films grown by the atomic layer deposition using ozone as oxidizer. The significantly low growth rate of film using O₃ precursor is attributed to the recombinative surface loss of O₃. The variation of the spatial uniformity inferred from the surface roughness of ZnO films and O₃ concentration were explained by a transition from reaction to recombination limited growth. We have fabricated a MOS device consisting of insulating ZnO layer using O₃ source between metallic and semiconducting Al:ZnO layers. The device demonstrated a remarkable resistive switching behavior, indicating the insulating behavior of the ZnO layer due to the electrochemical migration of oxygen vacancies at the interfaces.

8:40am **TF-TuM3 Process Design and Development of ALD for Co(W) Alloy Films as Single Layered Barrier and Liner Material in Future Cu ULSI Interconnects.** *Y. Shimogaki*, The University of Tokyo, Japan
INVITED

The aggressive scaling of ULSI devices requires ultra-narrow Cu interconnect features which have width of 20nm or less and aspect ratio of over 5. Cu diffusion barrier metal (DBM) and adhesion promoting liner layer (APL) should be made on the side wall of these features to protect Low- κ layers from Cu diffusion and enhance the electro-migration life time of Cu lines. As the feature dimension is decreasing, the APL/DBM layers should be less than 3 nm in thickness which may result in poor diffusion barrier performance. We have proposed that Co(W) alloy may be a good alternative to the conventional Ta/TaN as APL/DBM. Co(W) alloy can have a lower resistivity and better barrier property compared to TaN. It can also enhance the adhesion of Cu, better than Ta. Thus Co(W) alloy can work as a single-layered APL/DBM for the future ULSIs.

We have developed novel ALD process using hot-wire assisted technique. Metallocene precursors were effectively reduced by using NH₂ radical generated by hot-wire from NH₃. Conventional ALD process using amidinate precursors was also developed to form Co(W) alloy thin film. The microstructure of the deposited Co(W) alloy films were intensively examined using TEM and the Cu diffusion barrier properties were correlated with the structure. As a summary, the developed ALD process could successfully deposit Co(W) alloy thin film with low resistivity and good barrier properties. The adhesion strength of Cu onto Co(W) alloy will be also discussed.

9:20am **TF-TuM5 Control of Oxygen Vacancies by Plasma Enhanced Atomic Layer Deposition (PEALD) of TiO₂ for Memristors.** *S.-J. Park, J.-P. Lee, J.S. Jang, H. Rhu, H. Yu, B.Y. You, C.S. Kim, K.J. Kim, Y.-J. Cho*, Korea Research Institute of Standards and Science (KRISS), Republic of Korea, *S. Baik*, POSTECH, Republic of Korea, *W. Lee*, Korea Research Institute of Standards and Science (KRISS), Republic of Korea

TiO_x is one of the promising candidates for resistive switching (RS) devices. It has been generally accepted that formation of oxygen deficient Magnéli phase resulting from field-induced migration and ordering of oxygen vacancies (V_O) is mainly responsible for the resistive switching (RS) in TiO_x-based RS devices [1,2]. In this regard, it is worth studying the effect of oxygen vacancy concentration on the RS behaviors of the memristors adopting TiO_x as a switching layer. To this end, Pt/TiO_x/Pt capacitors with different values of x were prepared in this study. It has been well established that stoichiometry of TiO_x was closely related to the oxygen vacancy concentration [3]. TiO_x films were grown by plasma enhanced atomic layer deposition (PEALD) at the substrate temperature of 150 °C. Titanium (IV) tetraisopropoxide (TTIP; Ti[OCH(CH₃)₂]₄) was used as a Ti precursor. High purity oxygen or mixture gas of pure oxygen and nitrogen was adopted as a reactant during the plasma exposure step. By taking advantage of versatile controlling capability of ALD over the film properties, we were able to deliberately control the stoichiometry of TiO_x films by adjusting the flow rate ratio (R_F) of O₂ gas to N₂ + O₂ mixture gas from 0.25 to 1.00.

Microstructure and properties of the resulting films were characterized by Rutherford backscattering spectrometry (RBS), transmission electron microscopy (TEM), X-ray diffraction (XRD), confocal Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and spectroscopic ellipsometry (SE). According to RBS result, x in TiO_x was found to be varied from 1.62 to 1.70 when R_F was altered from 0.25 to 1.00. Phases of PEALD TiO_x films were observed to be amorphous at $R_F = 0.25$, whereas nanocrystalline anatase at $R_F = 1.00$. Raman spectroscopic analysis provided an additional evidence for R_F dependence of the film crystallinity. It turned out from the deconvolution of the O1s XPS peaks that non-lattice oxygen content increases from 15.3 to 20.7% with decreasing the R_F from 1.00 to 0.25, which manifests increases of oxygen vacancies in PEALD TiO₂ film with R_F . It was found from SE analyses that the absorption originated from defect states below bandgap, monotonously increases with decrease of x , i.e., increase of oxygen vacancy. Based on these results, the effect of oxygen vacancy concentration on RS behaviors of TiO_x-based memristors will be discussed in detail in this presentation.

References

- (1) R. Waser, *et al.*, *Adv. Mater.* **21**, 2632 (2009)
- (2) D. H. Kwon, *et al.*, *Nat. Nanotechnol.* **5**, 148 (2010)
- (3) H. Seo, *et al.*, *Nano Lett.* **11**, 751 (2010)

9:40am **TF-TuM6 Area Selective Atomic Layer Deposition of Dielectric Films on Metal/Dielectric Patterns.** *F. Minaye Hashemi, S.F. Bent*, Stanford University

Electronic devices consisting of a variety of different materials continue to undergo rigorous scaling to achieve higher switching speeds. Planar and 3-D structures such as those found in FinFETs and in the transistor backend contain metal/dielectric patterns, for which selective deposition processes may facilitate the fabrication of devices with feature sizes on the order of nanometers. Selective deposition approaches are required that can provide deposition of different materials with a variety of thicknesses while maintaining the selectivity up to higher thickness limits.

Atomic layer deposition (ALD) is a good choice for selective deposition because it is based on self-limiting reactions between gas phase precursors and specific functional groups at the growth surface. This chemical specificity provides a means to achieve selectivity in ALD on a spatially patterned substrate. In previous studies on area selective ALD of dielectrics on a dielectric pattern, deposited thicknesses were on the order of nanometers. The selectivity was generally obtained by passivation of the

surface using self-assembled monolayers (SAM) in the regions where ALD was not desired. However, existing methods for selective ALD likely do not have the robustness needed for deposition of thicker films. Hence, there is a need for new approaches to achieve selective dielectric-on-dielectric growth for film thicknesses of 10 nm or more.

In this work, we probe the thickness limits of area selective deposition of dielectric-on-dielectric by selectively depositing an organic SAM as the blocking layer on metal parts of a metal/dielectric (Cu/SiO₂) pattern. Both alkanethiols and alkylphosphonic acids have been reported to form well packed SAMs on metal surfaces. Here, we apply them to area selective ALD, and examine the blocking properties of octadecylphosphonic acid (ODPA) and octadecanethiol (ODT) SAMs on Cu. We show that both of these SAMs can prevent subsequent deposition of metal oxide dielectric films via ALD. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) confirm no growth of the metal oxide on the ODPA-protected Cu for up to 36 nm of metal oxide deposition, while ellipsometry and XPS results show metal oxide growth on the dielectric regions of the samples, i.e. SiO₂. We also report results on regenerating the ODT SAM protecting layer between ALD cycles and show that this approach is effective in improving the blocking properties of the SAM on Cu. This strategy provides the ability to carry out selective deposition for film thicknesses greater than 30nm, opening up the possibility for new applications in next generation electronic devices.

10:40am **TF-TuM9 Development of an Open-Ended Rotary Reactor for Plasma-Assisted ALD on Particles**, *J. Clancey, J. Yin, L. Baker, A.S. Cavanagh, S.M. George*, University of Colorado, Boulder

The use of atomic layer deposition (ALD) to coat large quantities of particles with conformal thin films is important for many applications. One area that has received recent attention is the efficient deposition of precious catalytic metals such as Pt. The ALD of catalytic metals is particularly challenging because of nucleation difficulties. However, recent studies have shown that plasma-assisted ALD can improve the nucleation and leads to much more conformal metal films after fewer ALD cycles. In this work, a new open-ended rotary ALD reactor design is presented that combines particle agitation in a rotary reactor with a remote inductively coupled plasma (ICP) plasma source. The plasma enters the open end of the rotary reactor with line-of-sight to the particles tumbling in the rotary reactor. A gate valve can separate the ICP plasma source from the open-ended rotary reactor during the metal precursor exposures. This design allows metals to be deposited on the particles without affecting the ICP plasma source. Results will be presented for Al₂O₃ ALD and W ALD on TiO₂ particles. Pt ALD on the TiO₂ particles will also be demonstrated using the W ALD adhesion layer to promote rapid Pt ALD nucleation and conformal film growth. This procedure was described earlier in L. Baker et al., *Appl. Phys. Lett.* **101**, 111601 (2012).

11:00am **TF-TuM10 Metal Ion Photoreduction on ALD Thin Films**, *J.C. Halbur, A. Madan, J.S. Jur*, North Carolina State University

Photoreduction of metal ions onto atomic layer deposited semiconducting surfaces are examined as a means for water reclamation/filtration and development of conductive patterns on polymeric substrates. Specifically, ZnO (via diethyl zinc/H₂O) and TiO₂ (titanium tetrachloride/H₂O) thin films are deposited on polymer film and fabric substrates and evaluated for reducing Ag⁺, Cr⁶⁺, As³⁺, and Au³⁺ from solution into metallic and oxidized coatings. The effect of ALD film thickness and process temperature on the efficiency of UV-light enabled reduction of the metal ions is evaluated. The effect of nucleation behavior of the metal ion reduction is explored and shows dependence on the surface structure and the impurity content in the ALD thin films. For example, reduction on ZnO with a characteristic nanoscale surface roughness shows a distinct nanoflake-like nucleation. On TiO₂, with a much lower surface roughness, island-like nucleation is exhibited. Both nano- and micro-scale islands are shown, likely due to corresponding reduction of Cl impurities from the TiO₂ film as observed by X-ray diffraction. Hard contact masks are applied onto the ALD thin films to explore the efficacy of producing conductive patterned structures directly on the ALD thin films. For applications in water filtration, ZnO ALD functionalization of high surface area fabrics have shown the ability to reduce up to 35% of Cr⁶⁺ and a dependence on the number of ALD cycles is observed. Results for As³⁺ and mixed metal ion solutions are also presented.

11:20am **TF-TuM11 Highly Conductive and Flexible Nylon-6 Nonwoven Fiber Mats Formed using Tungsten Atomic Layer Deposition**, *B. Kalanyan, C.J. Oldham, W.J. Sweet III, G.N. Parsons*, North Carolina State University

Low temperature tungsten atomic layer deposition (ALD) using WF₆ and dilute silane (SiH₄, 2% in Ar) can yield highly conductive coatings on nylon-6 microfiber mats. Coated nonwoven mats are flexible and supple with conductivity of ~1,000 S/cm. We find that an alumina nucleation layer,

reactant exposure, and deposition temperature all influence the rate of W mass uptake on 3D fibers. Transmission electron microscopy (TEM) reveals highly conformal tungsten coatings on nylon fibers with complex 'winged' cross-section. We calibrate tungsten growth rate on nylon-6 by imaging film thickness on high surface area anodic aluminum oxide. Using reactant gas 'hold' sequences during the ALD process, we conclude that reactant species can transport readily to reactive sites throughout the fiber mat, consistent with conformal uniform coverage observed by TEM. The conductivity of 1,000 S/cm for the W-coated nylon is much larger than found in other conductive nonwovens. W-coated nylon mats maintain 90% of their conductivity after being flexed around cylinders with radii as small as 0.3 cm. Metal ALD coatings on nonwovens make possible the solvent-free functionalization of textiles for electronic applications.

11:40am **TF-TuM12 Room-Temperature Atomic Layer Deposition of Platinum**, *A.J.M. Mackus, D. Garcia-Alonso, H.C.M. Knoops, A.A. Bol, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

The material Pt has many applications because of its catalytic activity, chemical stability, and high work function. Several Pt ALD processes have been reported for substrate temperatures in the range 100-300 °C. For certain applications involving temperature-sensitive materials such as polymers, fibers, and biological samples, it is valuable to have processes available for Pt ALD at lower substrate temperatures.

In this work, the temperature window for ALD of low-resistivity Pt has been extended to room temperature by the development of new plasma-assisted ALD processes. During thermal ALD of Pt from MeCpPtMe₃ and O₂ gas, the ligands of the precursor undergo dehydrogenation reactions on the catalytic Pt surface, which leads to a carbonaceous layer that poisons the surface inhibiting further surface reactions.¹ Combustion of this carbonaceous layer during the ALD cycle requires a substrate temperature above 200 °C, or alternatively, the use of strong oxidizing agents such as ozone or oxygen plasma. However, these strong oxidizing agents oxidize the deposited Pt to PtO₂ when the deposition is carried out at low substrate temperatures. The deposition of Pt at low temperatures can be achieved by adding a H₂ gas or H₂ plasma exposure step to the ALD cycle in which the PtO₂ at the surface is reduced to metallic Pt in every cycle.^{2,3}

High-quality, virtually pure films with a resistivity of 18–24 μΩcm were obtained for the three-step ALD processes consisting of MeCpPtMe₃ dosing, O₂ plasma exposure, and H₂ gas or H₂ plasma exposure.³ The reaction mechanism of these processes was investigated by gas-phase Fourier transform infrared spectroscopy (FT-IR). It will be shown that the newly developed processes enable the deposition of Pt on polymer, textile, and paper surfaces. The ability to coat temperature-sensitive substrates significantly broadens the application range of Pt ALD.

1. Mackus et al., *Chem. Mater.* **24**, 1752 (2012)

2. Hämäläinen et al., *Thin Solid Films* **513**, 243 (2013)

3. Mackus et al., *Chem. Mater.*, online early access; DOI: 10.1021/cm400274n

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