ALD Applications
Room Grand Ballroom E-G - Session AA1-TuA
Emerging Applications I

Moderators: Anjana Devi, Ruhr University Bochum, Han-Bo-Ram Lee, Incheon National University

1:30pm **AA1-TuA-1 Atomic Layer Deposition of Indium Gallium Zinc Oxide (IGZO) Semiconductor Thin Films: From Precursor to Thin Film Transistor Application***, **Jin-Seong Park,*** Hanyang University, Republic of Korea**INVITED**

Oxide semiconductor thin film transistors (TFTs) have been extensively researched as a switching device in display industry. Also, the amorphous indium gallium zinc oxide (a-IGZO) have been already adopted for the mass-production of OLED TVs because it showed remarkable performances such as high mobility (>10cm^2/V. sec), low process temperature (<350^{o}C), optical transparency (>3eV) and low-cost fabrication process. Recently, there are a few efforts to fabricate atomic layer deposited (ALD) IGZO thin films and demonstrating their device properties. However, ALD IGZO systems are quite difficult to understand their electrical and chemical properties because each precursor is affected to growth mechanism, crystallinity, and electrical performance.

In this talk, I will show key properties (growth behavior, electrical/chemical properties, and device performances) of indium gallium oxide (IGO) and indium gallium zinc oxide (IGZO) thin films depending on a few In and Ga precursor species. There films are deposited using the concept of “super-cycle” – IGO (n cycle InO$_x$ – m cycle GaO$_x$) and IGZO (n cycle of InO$_x$ – m cycle of GaO$_x$ – k cycle of ZnO). Then, the bottom gate-top contact (inverted staggered structure) thin film transistors were fabricated by ALD processes. The devices with IGO and IGZO active layers are named Device A (IGO TFT using Indium A precursor), Device B (IGZO TFT using indium B precursor), Device C (IGZO TFT using Indium B precursor), Device D (IGZO TFT using indium B’ precursor).

The representative transfer curves and performance parameters are shown in Figure 1 and Table 1. The IGZO device D exhibited boost mobility of 74.4 cm^2/V.sec. but the IGZO device B and C with different Indium precursors showed different mobilities of devices. It may result from a different growth rate and film composition. Thus, it is believed that ALD IGZO TFT will be very promising for the next generation switching transistor beyond the low-temperature poly-silicon (LTPS) thin film.

2:00pm **AA1-TuA-3 ALD Growth of Ultra-thin Co Layers on the Topological Insulator Sb_2Te_3***, **Emanuele Longo,** R Mantovan, R Cecchini,* CNR-IMM Unit of Agrate Brianza, Italy*; M Overbeek,* Wayne State University*; M Longo,* CNR-IMM Unit of Agrate Brianza, Italy*; L Lazzarini,* CNR-IMEM, Italy*; M Fanciulli,* Università degli Studi di Milano-Bicocca, Italy*; C Winter,* Wayne State University*; C Wiemer,* CNR-IMM Unit of Agrate Brianza, Italy

The coupling between ferromagnetic thin films (FMs) and topological insulators (Tis) is nowadays one of the hottest topics in the context of spintronics. The presence of Dirac-like dispersed surface states in the TI, jointly with the presence of a large spin-orbit coupling, is expected to favor a super-efficient (i.e. low-power) FM’s magnetization manipulation through a large *spin orbit torque* (SOT). The role of the interface between Co and TI is fundamental in driving SOT functionalities, making the choice of the deposition technique crucial and itself often responsible of low-quality interfaces formation. The high conformality, excellent low thickness control and its low energetic character make atomic layer deposition (ALD) an appealing technique for spintronic applications. We present here a pure ALD process to grow few nm-thick Co metal films in direct contact with a granular-TI Sb_2Te_3 thin film grown by Metal Organic Chemical Vapor Deposition (MOCVD). The ALD of Co metal films was performed by alternating a saturative pulsing sequence of bis(1,4-di-tert-butyl-1,3-diazadienyl)cobalt (Co(^{tBu2}DAD)$_2$) (4 s), N_2 purge (10 s), *tert*- butylamine ($tBuNH_2$) (0.1 s) and N_2 purge (10 s) at 180°C. In order to compare the Co growth on the Sb_2Te_3 substrate, we performed simultaneous Co depositions on sputtered Pt substrates (conventionally used as a SOT material), maintaining the same number of cycles. We conducted a thorough chemical-structural characterization of the Co/Sb_2Te_3 and Co/Pt heterostructures by employing X-Ray Diffraction (XRD), X-Ray Reflectivity, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The results demonstrated the possibility to synthesize Co thin films from several tens, down to 4 nm, forming uniform and high-quality Co thin films characterized by a stable and sharp interface with the Sb_2Te_3 substrate. Indeed, XRR showed that the thinner Co films replicate the surface roughness of the Sb_2Te_3 buried layer, proving their conformal growth. The growth rate was found to be higher on Sb_2Te_3 than on Pt. XRD evidenced the substrate selectivity of this growth process, showing the structural continuity of the grown Co layer on the underlying substrate. On Pt, the Co grains were found to adapt to the [111] textured substrate by developing a strained cubic structure. On Sb_2Te_3, Co was shown to grow with hexagonal structure, with out-of-plane grains oriented along the [00l] direction, as the rhombohedric Sb_2Te_3 layer. The distinct magnetic ordering of cubic and hexagonal Co polymorphs, with the possibility to selectively grow Co with different magnetic properties, pave the way towards novel applications in spintronics.

2:15pm **AA1-TuA-4 Modifying Interfacial Chemistry of Cellulose-Reinforced Epoxy Resin Composites using Atomic Layer Deposition (ALD)***, **Jamie Wooding**, Y Li, K Kalaitzidou, M Losego,* Georgia Institute of Technology

Automotive and aerospace industries require new lightweight materials that enhance payload and improve efficiency via vehicle weight reduction. Employing composites, such as fiber-reinforced polymer resins, is a common approach to light-weighting these vehicles. In this talk, we will examine the use of ALD to modify the surface chemistry of cellulosic reinforcements to improve the interfacial adhesion in polymer resin composites. Cellulosic reinforcements offer advantages in sustainable materials sourcing, lower density, and lower cost. However, raw cellulosics are hydrophilic and are immiscible with most non-polar thermosetting polymer resins. In this study, a variety of ALD-derived surface modification schemes are discussed as a means to improve resin permeation within the fibrous structure and to establish better adhesion at the cellulose – polymer matrix interface. Specifically, we consider surface modification with the ALD-precursors trimethylaluminum (TMA) and titanium tetrachloride ($TiCl_4$), as well as with vapor-delivered carboxylic acids and silanes. Surface modification is confirmed with XPS studies and contact angle measurements. All are found to make the cellulose prepreg more hydrophobic, but the $TiCl_4$ – H_2O treatment demonstrates the best permeability for the polymer resin. Composites treated with low cycles of $TiCl_4$ – H_2O are found to have a 30% improvement in the modulus of elasticity and a 38% increase in the tensile strength compared to untreated cellulose – resin composites. Furthermore, the $TiCl_4$ – H_2O surface treatment results in a composite tensile strength equal to that of a 3-aminopropyltriethoxysilane, a widely-used surface modifying agent, treatment while avoiding the disadvantages of using wet chemistry. The structural enhancements in the cellulose – resin composite, as demonstrated via wicking studies and scanning electron microscopy (SEM), inform these improvements in mechanical properties.

2:30pm **AA1-TuA-5 Atomic Layer Deposition of Au Nanoparticles on Titania***, **Fatemeh S.M. Hashemi,*** Delft University of Technology, Netherlands*; F Grillo,* ETH Zurich, Switzerland*; V Ravikumar, D Benz, A Shekhar,* Delft University of Technology, Netherlands*; M Griffiths, S Barry,* Carleton University, Canada*; J van Ommen,* Delft University of Technology, Netherlands

Nanoparticles of Au supported on TiO_2 have various applications in photocatalysis, plasmonics and photovoltaics. These supported materials are commonly synthesized using liquid-based techniques such as sol-gel and deposition-precipitation. These methods, while being low-cost, result in high level of impurities and formation of Au particles with inhomogeneous size and composition. Here we present a vapor-based approach via atomic layer deposition (ALD) for controlled deposition of Au nanoparticles on TiO_2. We also use the designed structures for photocatalytic degradation of pollutants.

We perform a low temperature (105 °C) thermal ALD process using Trimethylphosphino-trimethylgold (III) and two oxidizers (ozone and water) in a fluidized bed reactor under atmospheric pressure condition. While plasma-assisted ALD of Au using Trimethylphosphino-trimethylgold (III) has been previously reported (Griffiths et al., Chemistry of Materials 2016), no studies have looked into the thermal deposition process for this precursor. We investigate the effects of Au precursor saturation and oxidizing reactants on controlling the nucleation, particle size distribution and composition of the Au nanoparticles.

Our studies suggest that ozone and water have an opposite effect on Au particle size distribution. While longer ozone pulse time results in the deposition of smaller Au particles, larger particles are formed when water pulse time is increased. TiO_2 nanoparticles have a high surface area of about 50 m^2/g, thus achieving precursor saturation on them requires long precursor dosage times. However, we show that the growth properties can also be controlled in the under-saturation regime. We also investigated the effects of Au loading and particle size on the photocatalytic activity of

Au/TiO_2 nanoparticles. A 3 fold enhancement in the photocatalytic activity of TiO_2 is achieved when Au/TiO_2 nanoparticles are used for degradation of the model pollutants (Acid Blue 9 and Rhodamine B). This all vapor process provides a highly controlled and efficient method for producing Au/TiO_2 particulates that meet the criteria for various applications.

2:45pm **AA1-TuA-6 Multi-layer Protective Coatings on Silver for Protection of Historic Silver Artifacts***, E Breitung,* Metropolitan Museum of Art*; S Creange,* Rijks Museum, Netherlands*; G Pribil,* J.A. Woollam*; A Bertuch,* ***Ritwik Bhatia****,* Veeco-CNT

Historic silver artifacts are usually protected from tarnish by polymer-based coatings such as nitro-cellulose lacquer [1]. These coatings can be problematic because of uneven application, incomplete coverage and yellowing due to age. This has led to investigation of atomic later deposition of oxide layers as a possible alternative to lacquer based protective coating. It is important that the ALD coatings do not change the appearance (color, luminance) of the artifact. This is particularly challenging since historic silver can have bulk compositional variability as well as differences in surface composition [2].

In this work we start with substrates of silver content between 75% - 99.9% with copper as the major impurity. These substrates are characterized by variable angle spectroscopic ellipsometry to obtain their optical properties across the visible spectrum. It is found that (a) optical properties of the silver substrates depend significantly on composition and surface finish, and (b) a thin (2-11nm) interface layer is required to adequately model the ellipsometric data.

The optical model of the substrates obtained by ellipsometry is used to obtain the reflection spectrum and color of the substrates when coated with various ALD films such as SiO2, Al2O3 and TiO2. The modeled color of the coated substrate is compared to an uncoated substrate using the color difference metric (ΔE_{00}) [3]. Consistent with previous findings [4], we show that pure silver (99.99%) can be coated with SiO2 and Al2O3 without a perceptible color difference ($\Delta E_{00} < 1$) for a wide angle of incidence range (AOI = 0-75°). However, for silver alloys (80-95% silver) there is no coating thicker than 10nm that results in $\Delta E_{00} < 1$. [Figure-1]

The need to find a film stack that worked not just for pure silver but for silver alloys led to a multi-objective optimization problem – minimizing ΔE_{00} for silver substrates of different composition and AOI in 0-60°. A multi-layer film stack was found that showed $\Delta E_{00} < 1.25$ for all substrates for AOI=0-70°.

In addition to the optical characterization, modelling and optimization work mentioned above, we will report on the deposition and color measurement of the ALD films stacks on the silver substrates.

References:

[1] Grabow, Nicole et al. Metal 07: Interim meeting of the ICOM-CC Metal WG, Amsterdam, 17-21 September 2007, Amsterdam: Rijksmuseum, 2007, pp. 44-50.

[2] Mass, Jennifer and Matsen, Catherine. Handheld XRF for art and archaeology, Leuven: Leuven University Press, 2012, pp. 215-248.

[3] CIE Improvement to industrial color-difference evaluation. CIE 142-2001 ISBN: 978 3 901906 08 4

[4] Makela M et al. USPTO: 20090004386A1

3:00pm **AA1-TuA-7 Nonlinear Optical Properties of TiO_2-Based ALD Thin Films***,* ***Theodosia Gougousi****, R Kuis, I Basaldua, P Burkins, J Kropp, A Johnson,* University of Maryland, Baltimore County

Nonlinear materials in thin film form are highly desirable for the development of ultrafast all-optical system on-a-chip platforms, optical frequency converters and optical limiting applications. Conventional nonlinear optical (NLO) materials are usually cut from bulk crystals or are liquids that are not suitable for integration with the contemporary semiconductor industry process flow. The third order nonlinear response of ALD TiO_2-based films is investigated using thermally managed Z-scan technique. Some of the as-deposited films exhibit very high nonlinear response which is orders of magnitude higher than conventional nonlinear optical materials such as silica fibers and CS_2. Thermal treatment of the films at 450°C for 3 hours in an oxygen rich atmosphere affects the films' optical properties and results in the loss of the high nonlinear optical response. TiO_2 films deposited by Physical Vapor Deposition (PVD) from a 99.9% TiO_2 target at room temperature are used as control samples and their nonlinear optical response is found below the detection limit of the Z-scan setup. This extraordinary nonlinear optical behavior of the TiO_2 ALD films is linked to the presence of a very small at. % of TiN bonding in the film. We will present detailed characterization of these films by x-ray photoelectron spectroscopy, x-ray diffraction and UV-Vis absorption. The high level of control of the nonlinear index of refraction, n_2, using the deposition process coupled with the ability of ALD to coat non-planar geometries with atomic level precision and the fact that these processes are CMOS compatible have the potential to provide a breakthrough in optical device design and applications.

3:15pm **AA1-TuA-8 Atomic Layer Deposition to Alter the Wetting and Thermal Properties of Lumber***,* ***Shawn Gregory****, C McGettigan, E McGuinness, D Rodin, S Yee, M Losego,* Georgia Institute of Technology

This talk will discuss the use of atomic layer deposition (ALD) to modify the surface chemistry of bulk wood to alter its wettability and thermal conductivity. Wood blocks were ALD treated with three different metal oxide chemistries: $TiCl_4$-H_2O, $Al(CH_3)_3$-H_2O, and $Zn(C_2H_5)_2$-H_2O. All treatments consisted of only 1 ALD cycle. The resulting chemical modification of the wood with TiO_2, Al_2O_3, and ZnO was confirmed with energy dispersive X-ray (EDX) spectroscopy. All ALD chemistries made the wood hydrophobic with contact angles ranging from 90° to 130°. However, upon water submersion, it was found that TiO_2 coated wood had the least water uptake. While untreated wood absorbed up to 70 wt% water, the optimized TiO_2 treatment exhibited only a 10 wt% water uptake after 60 minutes. To understand these differences, we have considered the effective Fickian diffusion kinetics in the high-aspect ratio porosity of the wood structure. Measured pressure changes fit to Fickian diffusion models suggest that $Al(CH_3)_3$, and $Zn(C_2H_5)_2$ follow diffusion limited kinetics while $TiCl_4$ follows reaction limited kinetics. The apparent faster gas diffusion of $TiCl_4$ presumably results in more conformal coverage of the wood's structure. These models also suggest that $TiCl_4$ reacts to a greater extent than either Al or Zn precursor in this study. Because water content contributes significantly to the thermal transport of wood, we also measured thermal conductivity using the hot disc technique. Under dry conditions, untreated and TiO_2 coated wood have approximately the same thermal conductivity (~0.2 $W\cdot m^{-1}K^{-1}$). However, whereas the thermal conductivity of untreated wood increases by 50% in our tested wet environments, the thermal conductivity of $TiCl_4$ treated lumber remains nearly constant.

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