Thin Films Division
Room A122-123 - Session TF-TuA

Emerging Applications for Thin Films

Moderators: Emily McGuinness, Georgia Institute of Technology, Jesse Jur, North Carolina State University

2:20pm **TF-TuA1 Flexible Hybrid Electronics Process Maturation using Printed Inks***, **John D. Williams**,* The Boeing Company **INVITED**

Flexible hybrid electronics (FHE) are at the intersection of additive electronics and printed electronics. This is achieved through the utilization of additive methods on flexible and/or stretchable substrates. FHE leverages the low manufacturing cost of additive manufacturing due to fast processing time and low material waste. There are many applications that benefit from small low-cost sensor arrays and wireless networks, including new data collection devices on both manufacturing floors and aerospace systems to enable big data analytic capabilities.

In 2016, Boeing joined the NextFlex Manufacturing Innovation Institute established by U.S. Department of Defense Manufacturing Technology Program to support industry-wide improvements in the manufacturing readiness level (MRL) of Flexible Hybrid Electronics. Boeing's Radio Frequency Manufacturing and Sensing Technologies (RFMaST) laboratory in Huntsville, AL is working in concert with a dozen companies and university partners on seven different NextFlex efforts to improve manufacturing processes and produce industrially relevant technology demonstrators.

The results to date, document an MRL 6 or higher capability for flexible hybrid electronics technologies. Current and previous work has improved the design interface for the nScrypt additive liquid dispense tool, and pushed the industrial supply chain for thinned Integrated Circuits. Additionally, we have documented repeatable printing processes multilayer passive elements on 2D and 3D surfaces, generated Flexible Antenna Array Technologies (FAAT) for GHz frequency applications, and developed in-situ monitoring approach for FHE print processes. Most recently, Boeing and its partners have shown a demonstrator for the Condition Monitoring Sensor Array (CMSA) project that combines a flexible battery, Bluetooth Low Energy, edge processing, and four sensors onto a single flex circuit. Over the next two years, our team will widen these efforts to include UAV flight applications, composite health monitoring, multilayer flexible PCBs and dozens of other sensing applications.

Coupling these achievements with materials characterization, in-situ process monitoring, and large area digital printing will provide Boeing and the US industrial base with MRL 7 small-scale production capabilities for the next generation of electronic sensors. Today, our company has the manufacturing readiness to vertically implement new FHE products and help establish the supply chain required for utilization in commercial and military products.

3:00pm **TF-TuA3 Large-Area Atmospheric Pressure Spatial ALD for Flexible OLED Display Applications***, C. Frijters, J. Smeltink,* ***Huib Heezen****, P. Poodt,* SALDtech B.V., Netherlands

Atmospheric pressure Spatial ALD (sALD) is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. First industrial applications of Spatial ALD include passivation of c-Si solar cells and roll-to-roll manufacturing of flexible barrier foils. An emerging application for Spatial ALD is flat panel (OLED) displays. Examples include semiconducting and dielectric layers for use in thin-film transistors, and thin-film encapsulation for flexible OLED displays. As today's displays are fabricated using glass panels in the order of several square meters, a remaining challenge is the development of large-area Spatial ALD deposition technology that is able to combine high throughput with uniform performance across very large areas.

We are developing large-area Spatial ALD technology, and as a first step between the lab and the display fab, we have installed a large area Spatial ALD sheet-to-sheet tool which can handle up to 400x325 mm^2 sized substrates. With this tool we are able to deposit uniform films across a deposition width of 400 mm. The whole tool is operated under an atmospheric pressure but inert N_2 environment. The tool can be used to deposit a variety of materials using both thermal and plasma-enhanced Spatial ALD.

We will present the basic deposition performance of the tool in terms of thickness- and compositional uniformity. Large-area thickness non-uniformities of less than 1% are achieved for several oxide materials. Next, we will focus on two display-related applications: thin-film encapsulation of OLED devices, and high mobility InZnO and InGaZnO semiconductors for thin-film transistors. We will explain the requirements, the deposition process and the performance of the deposited films. Finally, the challenges in up-scaling Spatial ALD to plate sizes of 1.5 m and beyond will be discussed.

3:20pm **TF-TuA4 Printed Polymer Heat Sinks for High-Power, Flexible Electronics***, **Katherine Burzynski**,* University of Dayton*; N.R. Glavin, E.M. Heckman,* Air Force Research Laboratory*; C. Muratore,* University of Dayton

Consumers and military personnel alike are demanding ubiquitous electronic devices which require enhanced flexibility and conformality of electronic materials and packaging, while maintaining device performance. Whether it be high-power devices for faster data speeds, such as fifth generation (5G) wireless communication technology or wearable sensors to facilitate the Internet of Things (IoT), the age of flexible, high performance electronic devices has begun. Managing the heat from flexible electronics is a fundamental challenge. Even on rigid substrates with significantly higher thermal conductivity than polymeric and other flexible substrates, the full potential of semiconducting materials is often thermally limited. The flexible gallium nitride (GaN) high electron mobility transistors (HEMTs) employed in this work are conventionally processed devices that can be released from their growth substrate and transferred to a variety of rigid and flexible substrates. Characterization of the GaN device behavior on the as-grown sapphire wafers (prior to transfer) provide a baseline for evaluation of the thermal performance of engineered interfaces and substrates. With conventional substrates, device performance (specifically, the saturation current) is reduced when the device is transferred to polymeric substrates. The thermal dissipation is further restricted due to the addition of an adhesive layer to the substrate. Thermal imaging of devices in operation reveals that the current passing through an as-grown GaN transistor on a sapphire wafer reaches the target operating temperature at approximately five times the power of the same device transferred to a flexible substrate. Printable, thermally conductive nanocomposites integrating 1D, 2D, and 3D forms of carbon in a flexible polymer matrix, as well as metal nanoparticles, were developed to maximize heat transfer from electronic devices. The thermal conductivity of the candidate substrate materials was measured experimentally to have more than a 900 percent increase in thermal conductivity (from 0.2 to 1.7 W/mK), while maintaining desirable mechanical properties. The performance of devices transferred to these novel flexible composite substrates was characterized and used in computational simulations to predict flexible substrate architectures that effectively promote point-to-volume heat transfer to further improve device performance. Additive manufacturing for engineered architectures of the flexible, thermally conductive substrate materials was demonstrated to substantially reduce the thermal limitation of high-power flexible electronics.

4:20pm **TF-TuA7 Selective Deposition by Fast-ALD of Transparent Conductive Metal Oxides for Application in Organic (opto)electronic Devices***, M. Granados, D. Munoz-Rojas,* LMGP, France*; c. fontelaye, G. Nonglaton,* ***Tony Maindron****,* CEA-LETI, France

Future's demands for new TCOs are driven by new developments made toward the realization of displays onto temperature-sensitive plastic substrates, transparent displays, as well as sensor arrays for bio-healthcare applications. With regard to the realization of TCOs, the Atomic Layer Deposition (ALD) technology is well adapted since it allows the realization of high quality materials at low temperatures, together with a digital control of thickness. In the meantime, multicomponent film growth can be reproducible and highly controllable even on large substrates, with the self-limiting reaction of ALD offering great benefits to many materials. The mainstream TCO deposited by ALD today is by far ZnO, as well as its derivatives (ZnO:Al; ZnO:Sn; ZnO: In…). Unfortunately, the ALD of ZnO suffers from two major drawbacks: (i) ALD is a very low throughput technique and (ii) ZnO-based materials are very sensitive to moisture (environmental and during microfabrication processes). Fast-ALD is an alternative new generation high-throughput process that will be approached in this work to make TCO films, to solve issue (i). In the meantime, Area Selective Deposition (ASD) strategies based on the use of vapor-deposited SAMS (Self Assembled Monolayers) will be investigated to selectively deposit the materials. Doing so, this work will leverage the use of intensive photolithography/etching processes of ZnO, to solve issue (ii). A future perspective of this work is to provide innovative fast-ASD deposited TCO-based TFT architectures.

4:40pm **TF-TuA8 Photocatalytic Antibacterial Activity of ALD Thin Films on Fibrous Materials***, **Halil Akyildiz**, S. Diler,* Uludag University, Turkey

Semiconductor metal oxide thin film materials show photocatalytic properties, which can achieve various reactions for a variety of applications such as degradation of organic pollutants. Using similar mechanism, elimination of bacteria is also presented in the literature mostly on planar substrates. Since increase in the photocatalytic performance is expected with increasing surface area, thin films of ZnO and TiO_2 were deposited onto fibrous Nylon 66 surfaces via Atomic layer deposition (ALD) were tested for the elimination of bacteria. Tests were conducted at various thicknesses of ALD films for both types of materials. Formation and morphology of the films were investigated via electron microscope techniques TEM, FTIR, and SEM. Furthermore the structural analysis of the films were conducted via XRD and AFM while optical properties of the films were investigated via UV-Vis and PL spectrophotometers. Photocatalytic activity of the coated fiber materials was investigated by measuring methylene blue degradation. Antibacterial performance of the ALD films on fibers was tested using standard methods ISO 20645 and AATCC 100 against S. Aureus (ATCC 6538) and E. Coli (ATCC 35218) bacteria. As deposited ZnO samples showed better antibacterial performance compared to the TiO_2 films which is attributed the higher crystallinity of ZnO films.

5:00pm **TF-TuA9 A Kinetic and Thermodynamic Study of Aromatic Compounds Interacting with Metal-Organic Framework Thin Films***, J. Shankwitz, D. Speed, D. Sinanan, **Greg Szulczewski**,* University of Alabama

Metal-organic frameworks (MOFs) are a class of highly porous materials that can be synthesized using a variety of inorganic nodes and organic linkers, which enables MOFs for emerging application in gas sensing, gas storage and gas separations. In this talk, we will describe the synthesis of MOF thin films of the UiO-66-X type, where X = H, NH_2 and NO_2 grown on Au-coated Si wafers and Au-coated quartz microbalance crystals using a vapor-assisted conversion method. The thin films were characterized by XPS, XRD, RAIRS and SEM. The thin films were activated by heating under high vacuum and exposed to a saturation pressure of benzene, toluene, ethyl benzene and xylene isomers (BTEX family) while recording the frequency change of the crystal at different temperatures. The Sauerbrey equation was used to convert the frequency change to accumulated mass, followed by calculation of the Henry's constant at each temperature for the BTEX family of compounds. The results show that UiO-66-NO_2 had the highest affinity for all of the aromatic compounds studied. In addition, the kinetics of adsorption have been modeling by a Fickian diffusion process to estimate the diffusion coefficients of the molecules in the MOFs.

5:20pm **TF-TuA10 Carbon's Role in Reducing Alumina's Resistivity Through Catalytic Carbon Nanotube Growth***, **Berg Dodson**, R.C. Davis, R.R. Vanfleet,* Brigham Young University

Alumina is used as a diffusion barrier in the catalytic synthesis of carbon nanotubes (CNTs). Prior to CNT growth, the alumina film is electrically insulating, but becomes conductive following a CNT growth process. Electrical resistance measurements show how this change in conductivity correlates principally with a carbon CVD process. Low resistances are observed even when no iron is present for the CNT growth and when deposited carbon layers are etched off. TEM (and SIMS) data demonstrate that both iron and carbon can diffuse into the alumina layer during processing. Additionally, I will discuss at how predicted doping levels compare to the observed conductivity of the samples.

5:40pm **TF-TuA11 Ferroelectricity in Hafnia-Zirconia based Thin Films: Characterization and Applications***, **Vineetha Mukundan**,* SUNY Polytechnic Institute*; S. Consiglio, D.H. Triyoso, K. Tapily, R.D. Clark, G.J. Leusink,* TEL Technology Center, America, LLC*; J.H. Hazra, K. Beckmann, N.C. Cady, A.C. Diebold,* SUNY Polytechnic Institute, Albany

Hafnia-based materials have tremendous potential to replace perovskites in FeRAM applications due to their unique ferroelectric properties and potential for scalability [1]. Implementation of hafnia-based thin films in FeRAM has recently been demonstrated by Mikalojick *et al* [1]. With hafnia's high coercive field, enhanced endurance and memory window achieved by encapsulation with different electrodes, it is advantageous to also integrate it into a FET device [2]. For use in neuromorphic computing, Jerry *et al.*have employed electric-field controlled partial polarization switching in atomic layer deposited ferroelectric hafnia-zirconia films to demonstrate a FeFET based analog synapse [3]. Ferroelectricity in hafnia doped with Si was recently discovered by Böscke e*t al* [4] and it has been well established that the orthorhombic Pca21 is responsible for its ferroelectric properties. The factors leading to the formation and stabilization of this metastable phase are unclear. Structural modification and stabilization of different metastable states are being investigated by alloying hafnia with ZrO_2, doping with Si and Al, various annealing schemes and different processing schemes including different semiconductor substrates. We study the long range structure of hafnia-zirconia films by grazing incidence in-plane x-ray diffraction (GI-I-XRD) and local structure by extended x-ray absorption fine structure spectroscopy (EXAFS) along with polarization measurements to study their electrical properties. An important part for advancing these ultra-thin films for application as both FeRAM and NCFET devices necessitates studying capacitive stacks in the form of metal-insulator-metal (MIM) and metal-insulator-semiconductor (MIS) [5]. Further, we estimate the percentage content of the different phases including the non-centrosymmetric orthorhombic phases in these stacks varying in composition and thickness. With increasing zirconia content in these stacks, the monoclinic phase decreases and it exhibits anti-ferroelectric property. With increasing thicknesses, it is found that the monoclinic phase increases in content, which should give rise to a decrease in the polarization of these stacks. We observed no change in the structure with annealing after it has been encapsulated by the TiN electrode, even up to 1000°C suggesting the confinement plays an active role in its structural evolution. Additional studies are underway to understand the influence of processing conditions, electrical cycling, annealing temperature, types of electrodes, and substrates on the structure and electrical properties of Hafnia-zirconia based thin films [6].

6:00pm **TF-TuA12 Atomic Layer Deposition-enabled Formation of Laser-Induced Graphene for Charged Membrane Applications***, **David Bergsman**, B.A. Getachew, J.C. Grossman,* Massachusetts Institute of Technology

Membrane-based processes are becoming increasingly popular for water treatment due to their relatively high energy efficiency and low cost compared to other treatment methods. However, the advantages of membranes are mitigated by the need for additional pre-treatment steps that are required to maintain their effective operation. The treatment and prevention of membrane fouling, in particular, constitutes a large fraction of typical membrane operational costs. One potential approach to combat fouling is to design conductive membrane coatings that can prevent the attachment and growth of biofoulants both electrostatically and via electrochemical generation of reactive oxygen species. Despite their potential, these conductive membrane coatings are often expensive, requiring additional chemicals and non-scalable methods to produce, e.g. carbon nanotube mats or other graphitic coatings deposited by vacuum filtration.

In this work, we explore the use of laser-induced graphene (LIG) for the creation of conductive ultrafiltration membranes. Porous polyethersulfone (PES) membranes are first coated in a thin layer of alumina using atomic layer deposition (ALD) before being irradiated with an infrared laser. We show that this alumina film, which can be scalably produced using spacial ALD, can localize LIG formation to the surface of the membrane, preventing the buried, un-lased areas of PES from melting and losing their porosity during the lasing process. This allows the top-most layer of the PES to be a conductive coating that can be used to charge the membrane surface and used to improve membrane performance (e.g. fouling mitigation). The formation of LIG is verified by scanning electron microscopy and Raman spectroscopy. The conductive layer is also shown to possesses relatively high conductivity, which is important for reducing power consumption in devices. Insight into the mechanism behind the improved stability to melting provided by ALD is provided by thermogravimetric analysis, differential scanning calorimetry, and Fourier-transform infrared spectroscopy. The effect of ALD film thickness and the use of sequential infiltration synthesis will also be explored. These insights are used to discuss the potential application of this approach to creating conductive coatings on other polymers using ALD-based approaches.

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