Thursday Morning, November 10, 2016

Thin Film
Room 105A - Session TF2-ThM
Area-selective Deposition and Sequential Infiltration Synthesis

Moderator: Giovanna Scarel, James Madison University

8:00am **TF2-ThM1 Area Selective Deposition from an Aqueous Fog***, N. Murari, R.H. Mansergh, Y. Huang, D.A. Keszler, **John F. Conley, Jr.,*** Oregon State University

As ULSI technology continues to scale towards the sub-10 nm regime, lithographic patterning and registration to existing features have become increasingly difficult, expensive, and time consuming. Direct patterning or area selective deposition of materials only on desired areas of a substrate has been proposed as a way to overcome these lithographic challenges. Recently, several groups have demonstrated area selective atomic layer deposition (ALD) through approaches such as area deactivation - the use of polymers and self-assembled monolayers (SAMs) to inhibit ALD nucleation. While this work shows promise, alternatives to elevated temperature, vacuum based deposition techniques are desired by the microelectronics, photovoltaics, and display industries. Solution based deposition techniques offer a lower cost, more sustainable approach. Traditional spin-coating, however, is primarily limited to planar substrates and lacks the ability to form uniform films over large surface areas. A number of mist based deposition techniques have attempted to address the limitations of spin coating, but typically suffer from one or more disadvantages such as the requirement of high volatility precursors, uneven mist distribution, complex vapor transport, and/or poor control of film uniformity. A new aerosol based technique overcomes these problems by employing a novel atomizer consisting of two opposing jets located within the deposition chamber. Head-on collision of the opposing jets shears the precursor droplets into a fine mist / fog, allowing the use of low volatility precursors. The uniform generation of mist is scalable for deposition on arbitrarily large substrate areas. In this work we use this method to demonstrate area selective deposition from an aqueous fog at room temperature and pressure.

Aerosol deposition was conducted on a BENEQ ACS 200-101at room temperature and pressure using precursor fog of aqueous based aluminum phosphate inorganic clusters. An octyltrichlorosilane (OTS-8) based SAM with a hydrophobic tail group is used as a growth inhibitor. OTS-8 is patterned on a hydrophilic Si wafer surface. Selective deposition of oxide thin films from an aqueous precursor aerosol fog is achieved with growth occurring only in the hydrophilic regions and not on the areas covered by OTS-8. Smooth films with sharp boundaries are deposited with average surface roughness of less than 1 nm RMS. Deposition selectivity is investigated as a function of pattern size, shape, and half pitch. Overall, room temperature area selective aerosol deposition is shown to be a potentially promising sustainable alternative to AS-ALD for large area electronics.

8:20am **TF2-ThM2 "Patterned-by-Printing" ZnO Vertical TFTs***, **Carolyn Ellinger**, S.F. Nelson,* Eastman Kodak Company

"Patterned-by-printing" uses selective area deposition (SAD) as an alternative approach to printed electronics: an inhibiting polymer ink is printed and the active materials are deposited via spatial atomic layer deposition (SALD). We have previously illustrated the use of this methodology to make planar ZnO thin-film transistors (TFTs) with equivalent device performance to TFTs fabricated from the same materials but patterned by conventional photolithographic means. We have further shown how patterned-by-printing enables freedom in circuit design due to the orthogonal nature of the patterning process, demonstrating facile fabrication of circuits with architectures that can be difficult to obtain using subtractive processing methods.

This talk will address fully patterned-by-printing vertical thin-film transistors (VTFTs), fabricated without any vacuum metallization steps. Using our standard toolset of SALD, inkjet printing and cleaning, we have explored the unique advantages offered by a patterned-by-printing approach for vertical TFT and circuit architectures. In addition to controlling the inhibitor pattern on the substrate by the print pattern, surface structures can be used to control the spatial location of the inhibitor ink via capillary forces. These vertical transistors have liberal design rules and low print resolution requirements as a result of self-aligned source and drain contacts. Starting with a gate structure having a re-entrant profile on the edge, conformal Al_2O_3 gate dielectric and ZnO semiconductor are patterned at low resolution using a printed inhibitor ink and SALD. The same inhibitor ink is printed at the same low resolution so that it is drawn into the reentrant profile, defining the semiconductor channel between SALD-deposited AZO source/drain contacts. The VTFTs have considerably shorter channel lengths than directly obtainable by the printed resolution, and correspondingly higher device performance from a simple additive patterning process. Furthermore, since each step is the same as used for our planar TFTs, circuits having mixed transistor architectures can be used to optimize performance. Individual device characteristics as well as circuit performance will be discussed.

8:40am **TF2-ThM3 Area-selective Atomic Layer Deposition of Metal and Magnetic Films***, **John Ekerdt**, H. Nallan, Z. Zhang, S. Chopra,* University of Texas at Austin **INVITED**

In this work, we demonstrate the selective atomic layer deposition of Co onto MgO/Si and HfO_2/Si substrates. Magnetic materials such as Ni and Co are used in a wide variety of devices ranging from microelectronics to RF technology to energy. Recently, Co films have been explored as the magnetic material for a magnetic tunnel junction structure of an STT-RAM heterostack. Previous efforts to deposit Co metals using ALD precursors bis(N-tert butyl, N'ethylpropionamidnato) cobalt (II) and H_2 have suffered from carbon and nitrogen incorporation into the film. Furthermore, etching ferromagnetic films typically relies on plasma processes that can generate side products and are detrimental to device performance.

Here we offer an alternative to this deposition and patterning approach through a sequence of area-selective atomic layer deposition (A-SALD) followed by an oxide reduction. A-SALD is a process by which the energy of a surface can be manipulated such that there is preferential wetting and nucleation of ALD precursors only in desired regions. It is shown that CoO ALD is successfully blocked on MgO or HfO_2 surfaces that have been treated with a self-assembled monolayer such as n-octadecyltrichlorosilane or a diblock polymer such as poly(trimethyl)silystyrene/polystyrene. Once patterned, these organic blocking layers are used to prevent CoO deposition in particular areas of the substrate. The CoO deposition is performed at a temperature of ~180° using cobalt bis(diisopropylacetamidinate) and water as co-reactants. Following deposition, it is shown that the CoO can be reduced to form Co metal using a reducing gas such as H_2 or CO at elevated temperature and/or by capping the CoO film with an oxygen-scavening layer of Al that reacts to Al_2O_3. With this approach, we are able to deposit Co metal in only desired regions of the substrate. X-ray photoelectron spectroscopy is used to determine the oxidation state of cobalt and film stoichiometry. Film crystallinity and structure of the films are analyzed with X-ray diffraction and reflection high-energy electron diffraction. Using a scanning superconducting quantum interference device, we explore how the magnetic properties of the Co films can be manipulated using different CoO thickness and capping metals.

9:20am **TF2-ThM5 Selective Area Epitaxy of Magnesium Oxide Thin Films on Gallium Nitride Surfaces***, **Mark Losego**,* Georgia Institute of Technology*; J-P. Maria,* North Carolina State University*; E.A. Paisley,* Sandia National Laboratories

Selective area growth of thin films reduces the number of steps in microfabrication processing and enables novel device structures. Here we report for the first time selective area epitaxy of an oxide material on a GaN surface. Chlorination of the GaN surface via wet chemical processing is found effective to disrupt Mg adsorption and selectively prevent molecular beam epitaxy (MBE) growth of MgO. MgO films grown on neighboring, non-chlorinated surfaces are epitaxial with a (111) MgO || (0001) GaN crystallographic relationship. In-situ XPS studies reveal that a surface monolayer of adsorbed chlorine acts to prevent MgO deposition. Better than 3 micron lateral resolution for the selective area growth of MgO on GaN is demonstrated. This talk will present our current understanding of this selective growth process and detail our studies of the surface chemistry mechanisms.

9:40am **TF2-ThM6 Sequential Infiltration Synthesis (SIS) and its Applications in Nanofabrication***, **Qing Peng**,* University of Alabama

Chemical assembly of materials with atomic/molecular precision is the key to enable new generation technologies. Such sophisticated controllability relies on the understanding of fundamental mechanisms during atomic/molecular assembly processes. In this presentation, I will present the applications of sequential infiltration synthesis (SIS) in nano materials fabrication. The SIS method is based on the coupled diffusion and substrate site-limited reaction process. It shows great promise in the modification of the properties of polymers, and in the scalable and controllable manufacture of nanomaterials. The underlying mechanisms involved in the SIS process will be discussed along with its applications in the advanced lithography, nanostructure engineering and catalyst fabrication.

11:00am **TF2-ThM10 Understanding Growth of Infiltrated ZnO an Atomic Step at a Time**, ***Leonidas Ocola**, D.J. Gosztola, A. Yanguas-Gil,* Argonne National Laboratory; *A. Connolly,* Vassar College

We have investigated a variation of atomic layer deposition (ALD), called sequential infiltration synthesis (SiS), as an alternate method to incorporate ZnO and other oxides inside polymethylmethacrylate (PMMA) and other polymers. The precursors used to synthesize ZnO in PMMA are water (H2O) and Diethylzinc (DEZ). SiS of ZnO in PMMA was accomplished by infiltrating (H2O:DEZ) cycles at 95 °C for periods of up to 4 min per cycle. Energy dispersive spectroscopy (EDS) results show that we synthesize ZnO up to 300 nm inside a PMMA film.

A key feature of an ALD process is the ability to add an atomic layer at a time. This characteristic allows for a detailed study of the formation of ZnO in the polymer matrix after each atomic step is formed. We followed each growth step of ZnO in PMMA using ex-situ photoluminescence (PL), Raman spectroscopy and x-ray photoemission spectroscopy (XPS). These studies show clear differences between mono, dimer and trimer Zn atom configurations. Mono Zn atoms (O-Zn and O-Zn-O) are formed with a single DEZ precursor pulse and one or two H2O pulses and exhibit pure UV emission with no evidence of oxygen vacancy states (V_O). Dimer Zn atoms (O-Zn-O-Zn and O-Zn-O-Zn-O) are formed with two pulses of DEZ and two or three pulses of H2O. They do not form yet a continuous film as shown with Raman spectroscopy. Dimers do show strong PL emission from V_O states In addition, XPS data show no evidence of ZnO wurtzite bonding. After 3 precursor cycles we observe first evidence of film formation inside the polymer matrix with Raman spectroscopy and wurtzite formation with XPS. The evolution of ZnO properties studied with PL, Raman and XPS from these initial stages up to 12 cycles of SiS ZnO will be presented. Such detailed study allows insight to growth mechanisms of ZnO in a non-traditional environment, which may lead to novel applications of ZnO as sensors or detectors.

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11:20am **TF2-ThM11 Investigation of Vapor Phase Infiltration Kinetics: Infusing Metalorganic Vapors in Polymer Thin Films**, ***Collen Leng***[*], *M.D. Losego,* Georgia Institute of Technology

Polymers can be chemically modified via infiltration and reaction with gaseous metalorganic precursors to create new hybrid organic-inorganic materials with novel electrical, chemical, and/or physical properties. These new materials can have applications as chemical barriers, filtration media, or photolithographic hard masks. Here, the focus is to have a better knowledge of the diffusion and reaction kinetics during this vapor phase infiltration process with the goal of understanding how both polymer structure and processing conditions can maximize the depth of inorganic infiltration. In this study, we use the model system of poly(methyl methacrylate) (PMMA) films exposed to trimethylaluminum (TMA) gaseous precursors. Spectroscopic ellipsometry is used to track infiltration by film swelling and changes in refractive index. At a process temperature of 60°C, films are found to initially swell in thickness with the square root of time, suggesting that kinetics are dominated by Fickian-like diffusion behavior. A maximum film swelling of 60% is measured at any exposure time exceeding 1000 minutes. Using these swelling curves as a proxy for infiltration amount, we calculate effective diffusion coefficients for TMA in PMMA at 60° C to be on the order of 10^{-15} cm^2/s, with faster diffusion in PMMA films of lower molecular weight. At higher temperatures (160° C), swelling is less significant, but refractive indices of infiltrated films increase by 2% to 3%. We interpret the decrease in swelling as a result of faster chain relaxation when processing above the glass transition temperature of the polymer. To determine whether polymer films infiltrated and swollen below T_g can also undergo similar polymer relaxation behaviors, a systematic study of post-annealing was carried out at 150° C. In these instances, the amount of swelling decreases by approximately half and refractive index increases but to a lesser degree than those from the initial high process temperatures. The results of this study will be put in context with other ongoing research in the field to help build a phenomenological model that can be used to better design vapor phase processing schemes to form organic-inorganic hybrid materials.

11:40am **TF2-ThM12 Pyrolysis of Organic-Inorganic Hybrid Materials Formed by Sequential Organometallic Vapor Infiltration**, ***Halil Akyildiz**,* Uludag University, Turkey; *P.D. Bradford, J.S. Jur,* North Carolina State University

Organic inorganic hybrid materials are of interest for wide variety of applications including flexible electronics and catalysis. This work explores the use of a sequential vapor infiltration (SVI) process by which organometallic ALD precursors are infiltrated into the bulk polymer materials and react with the available functional sites to form a network of organic-inorganic hybrid materials. In this study, thermal degradation characteristics of the SVI hybrid materials are studied with thermogravimetric analysis (TGA) under inert atmosphere. Higher thermal stability of the fibers of SVI hybrid materials is observed compared to the pristine PET fibers and different degradation steps in TGA are defined. Furthermore, increased thermal stability of hybrid materials is demonstrated by pyrolysis of SVI treated nylon-6 and polyester fiber mats at 900°C with high heating rates (up to 200°C/min). It is shown by SEM imaging that fabrics with SVI treatment retain their fibrous structure and high surface area, whereas pristine fabric samples are either completely degraded. Raman spectroscopy analysis of these carbon fibers confirms the graphitic and disordered carbon structures formation.

12:00pm **TF2-ThM13 Carbon Nanofibers Derived from a Cellulosic Polymer Enabled by Vapor Infiltration of Diethyl Zinc for Carbon Based Supercapacitors**, ***Wenyi Xie**, O.J. Rojas, S. Khan, G.N. Parsons,* North Carolina State University

Common thermoplastic polymers, such as polyvinyl alcohol and cellulose derivatives are viable precursors to prepare carbon materials for supercapacitor electrodes. These polymers can be readily processed to prepare high external surface area nanofibers. However, thermoplastic polymers undergo melting transition upon heating, therefore result in loss of initial morphology and low carbon yield. In this study, vapor infiltration of diethyl zinc is applied to modify cellulose based nanofibers as the carbon precursor. Our goal is to investigate the effect of inorganic modification on the morphology, surface area and pore volume, as well as the supercapacitor performance of the carbon product from the modified cellulose based nanofibers.

Vapor infiltration of diethyl zinc (DEZ), was performed using a home-built viscous-flow hot-wall tube reactor. One cycle of the vapor infiltration chemistry consisted of a short dose of DEZ (1 s), followed by a DEZ-hold step (60 s) to enable the reactant to diffuse into the nanofibers, and then followed by a N_2 purge step (40 s) to remove excess reactant and byproducts. *Scanning electron microscopy* (SEM) revealed that the fiber structure of cellulose-based nanofibers could be preserved with at least ~ 8.0 wt % of Zn. Nitrogen sorption measurements at 77 K showed that the surface area and pore volume could be tuned by the DEZ infiltration process. Two-electrode symmetric capacitors were fabricated using the carbon materials from the DEZ modified cellulose based nanofibers. Cyclic voltammetry measurements were performed using 1 M KOH as the electrolyte to determine the specific capacitance. The carbon materials obtained from the DEZ modified cellulose based nanofibers showed a specific capacitance in range of ~25 to 50 F/g.

In this work, vapor infiltration of DEZ has enabled the preparation of carbon nanofibers from cellulose based nanofibers. By varying the loading of Zn, the surface area and pore volume of the resulting carbon nanofibers can be tuned to enhance the supercapacitor performance. Therefore, we believe that inorganic modification by vapor infiltration of DEZ is promising for modifying thermoplastic polymers to produce high performance nanostructured carbon materials for supercapacitors

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[*] **TFD James Harper Award Finalist**

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