Thin Film
Room: 111 - Session TF+2D+MG+NS-MoA

ALD, CVD, MLD, and PLD on Special Materials
Moderator: Giovanna Scarel, James Madison University, Mark Davidson, University of Florida

2:20pm **TF+2D+MG+NS-MoA1 Optical Enhancement of Polyethylene Teraphthalate Films Modified by Organometallic Vapor Infiltration**, *Halil Akyildiz,* North Carolina State University, *J.G. Simmons,* Redstone Arsenal, *H.O. Everitt,* Duke University, *J.S. Jur*, North Carolina State University

Polyethylene terephthalate is recyclable thermoplastic polymer that has wide application area including packaging, textiles and insulation applications. Due to the ring structures on the backbone of the polymer it shows weak luminescence in the blue spectrum upon UV light absorption by pi electrons. It has previously been shown that vapors of organometallic ALD precursors are able to infiltrate and react with the polymer to form organic inorganic hybrid materials. Infiltration of trimethylaluminum into PET to form polymer-alumina coordination complexes enhanced the photoluminescence and internal quantum efficiency of the material. In this study we present how the polymer morphology (i.e. crystallinity) and the infiltration temperature are able to affect the optical properties of the resulting PET films. Four unique emission bands are observed in pristine PET films; (2) stronger emissions in high crystallinity films attributed to the crystalline regions of the polymer and (2) peaks that show stronger emission in low crystallinity films attributed to the amorphous regions. After the low temperature infiltration (60 °C) emissions attributed to the amorphous regions demonstrate increases intensity, indicating that the infiltration reaction is predominant in the amorphous regions of the polymer. After infiltration at 150 °C, a very high red shift is observed alongside a complete emission spectra changes, suggesting the reactions taking place at high temperatures are different than low temperature processing. This detailed understanding of the photoluminescence behavior of the hybrid films can provide insight for use of these hybrid materials with a bandgap ideal for unique optical applications.

2:40pm **TF+2D+MG+NS-MoA2 Organic and Hybrid Organic-Inorganic Thin Film Deposition by Resonant Infrared, Matrix-Assisted Pulsed Laser Evaporation**, *Adrienne Stiff-Roberts*, Duke University **INVITED**

Over the past fifteen years, matrix-assisted pulsed laser evaporation (MAPLE) has been developed to deposit organic thin films[1-6], inorganic nanoparticles, and hybrid organic-inorganic nanocomposites[4, 7-9]. One variation of the MAPLE technique, resonant infrared matrix-assisted pulsed laser evaporation (RIR-MAPLE), reduces the laser energy (e.g., Er:YAG laser ~2.94µm peak wavelength) in order to minimize polymer degradation. In addition, because the frequency of the IR laser energy is resonant with OH bond vibrational modes in water, a frozen emulsion (comprising a mixture of the guest material dissolved in an organic solvent and water) is used as the target. Therefore, the unique advantage of emulsion-based RIR-MAPLE is that most of the energy from the IR laser is absorbed by water in the frozen emulsion, which evaporates and gently transfers the guest material to the substrate with minimal solvent exposure and degradation.

In the case of hybrid organic-inorganic nanocomposites, inorganic nanoparticles are embedded in a polymer matrix to achieve specific materials properties or functionality; however, nanoparticles that are mixed with a polymer in solution tend to aggregate due to a polarity difference with polymers[10]. In contrast, RIR-MAPLE is fundamentally different from solution processing and reduces nanoparticle phase segregation by eliminating the need to co-dissolve nanoparticles and polymers into a single common solvent; and by depositing the nanoparticles and polymers in a relatively dry state.

We will demonstrate the capability of RIR-MAPLE to deposit continuous nanoparticle films with the same optical properties as nanoparticles in solution and to minimize nanoparticle phase segregation in hybrid films. We will also demonstrate hybrid organic-inorganic thin films deposited by RIR-MAPLE for application to solar cells. This work is supported in part by ONR.

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3:40pm **TF+2D+MG+NS-MoA5 Integrating Ultrathin ALD/ALE Films with 1D and 2D Materials to Enable New Device Structures**, *Virginia Wheeler, N. Nepal,* U.S. Naval Research Laboratory, *A. Nath,* George Mason University, *A.D. Koehler, Z.R. Robinson, J.K. Hite, K.M. Daniels, M.A. Mastro,* U.S. Naval Research Laboratory, *E. Self, P. Pintauro,* Vanderbilt University, *J.D. Caldwell, R.L. Myers-Ward, D.K. Gaskill, C.R. Eddy Jr.*, U.S. Naval Research Laboratory **INVITED**

As device features continue to approach nanoscale dimensions, requisite structures continually grow in complexity often resulting in 3D architectures, nanowires, and/or 2D van der Waals materials. This reduction in size leads to new phenomena, such as quantum confinement effects in electronics or strong localization of light in nanophotonics, which can potentially enable new devices. Realization of novel device structures that exploit these effects requires integration of scalable thin films of various electronic materials onto nanostructures. Atomic layer deposition (ALD) is the preferred method to conformally coat nominally planar as well as complex, high surface area nanostructures with abrupt interfaces, wafer-scale uniformity, and angstrom-scale control of thickness. Additionally, ALD is a low temperature process which allows incorporation with many temperature sensitive nanostructure materials that are not compatible with other deposition techniques. Alternatively, a slightly higher deposition temperature can facilitate atomic layer epitaxy (ALE) of crystalline thin films with all the same beneficial characteristics of ALD. However, the inert nature of 1D and 2D materials often inhibit direct application of ALD/ALE films with desired coverage and uniformity. In this work, we will discuss crucial aspects of ALD/ALE growth, such as surface functionalization and *in situ* nucleation sequences, required to obtain uniform, conformal films on nanostructured substrates.

The essential requirements for integration of ALD/ALE layers with 1D and 2D materials will be evaluated through several case studies including: 1) integration of III-N films on graphene for a hot-electron transistor; 2) coating of carbon fibers for battery and electrode applications; and 3) functional oxide layers on SiC nanopillars to modify their optical response for several potential devices. The substrates in these cases have varying degrees of surface reactivity, so we will address the need for and our current *ex situ* and *in situ* approaches to obtaining sufficient reactivity between the substrate and ALD precursors. Moreover, it was found that ALD parameters (temperature, pulse and purge durations, etc.) impact the effectiveness of uniform, conformal coating of these structures. Other factors, such as sample suspension, are sometime critical to overcoming these limitations while still operating in ALD/ALE windows. Initial devices results will be presented, when appropriate, to demonstrate the feasibility of the integration of ALD thin films in new device structures.

4:20pm **TF+2D+MG+NS-MoA7 Development of the Optical Properties of Silicon Rich Oxide Films Growth by CVD Techniques for Possible Photovoltaic Applications**, *Karim Monfil-Leyva,* Benemérita Universidad Autónoma de Puebla, Mexico, *A.L. Muñoz-Zurita,* Universidad Politécnica Metropolitana de Puebla, Mexico, *E. Ojeda-Durán, A. Benítez, J. Carrillo-López, J.A. Luna-López, R.C. Ambrosio-Lázaro*, Benemérita Universidad Autónoma de Puebla, Mexico

Currently, electronics and semiconductor studies have focused a great effort to overcome the intrinsic disadvantages of bulk-Si to develop optoelectronic devices. In particular, the Silicon Rich Oxide (SRO) has been proposed as a cheap and effective alternative to develop ultraviolet absorbers or silicon-based light emitters. SRO can be deposited by several chemical vapor deposition techniques like Low Pressure Chemical Vapor Deposition (LPCVD) or Hot Filament Chemical Vapor Deposition (HFCVD). Silicon excess in SRO films obtained by LPCVD can be controlled by pressure ratio Ro = N_2O/SiH_4. Meanwhile, silicon excess in SRO films obtained by HFCVD can be controlled by changing the hydrogen flow (H_F).

In this work, we report a study of the optical and structural properties of thin SRO films obtained by LPCVD and HFCVD. Silicon excess was changed by the pressure ratio Ro in the range of 15 and 45 (SRO15 to SRO45) and H_F was changed between 25 and 75 sccm. SRO LPCVD films were annealed at 1100 ºC. Ellipsometry and step measurements were

applied to calculate thickness and the refractive index. Fourier transform infrared (FTIR) measurements were obtained from SRO films to confirm a change on stoichiometry. Absorbance spectra of SRO films showed rocking and bending vibration modes similar to stoichiometric silicon dioxide but an asymmetric stretching mode revealed the non-stoichiometric nature of our semiconductor films. SRO films by LPCVD showed a strong photoluminescence (PL) at room temperature (RT) on two bands, a blue band from 400 to 550 nm or a red band from 575 nm to 875 nm depending on Ro. Blue and red emission bands were related to donor acceptor decays between traps promoted by defects. SRO films by HFCVD also showed a red band from 500 to 1100 nm (depending on the H_F) and this emission was attributed to defects produced by the transport of the precursors. SRO films showed suitable optical properties for possible photovoltaic applications.

5:00pm **TF+2D+MG+NS-MoA9 Radical-Enhanced Atomic Layer Deposition Enabled Multiferroic Composite Synthesis***, C. Pham,* ***Jeffrey Chang****, J.P. Chang*, University of California at Los Angeles

Multiferroic materials, which exhibit controllable magnetic (ferroelectric) behavior via electric (magnetic) field, are of great interest due to their wide spectrum of new device applications such as non-volatile memory devices. Unfortunately, such behavior is extremely rare in natural single-phase systems. Furthermore, the properties of the few single phase multiferroic materials are too insignificant to be integrated into current device designs. Therefore, alternative strategies involving composite materials are proposed to combine the ferroelectricity and magnetism of different materials, achieving multiferroic behavior. By utilizing piezoelectric and magnetostrictive effects in different material phases, a strain-mediated approach shows great promise for applications. In such a strategy, the interface area per volume, as well as the material crystallinity of each constituent, will greatly influence composite properties. The conformal and high quality film growth with atomic layer deposition (ALD) shows great potential for enabling the multiferroic composites described above.

In this work, lead-free ferroelectric/antiferromagnetic $BiFeO_3$ (BFO) and ferrimagnetic $CoFe_2O_4$ (CFO) thin films were grown on $SrTiO_3$ (001) (STO) substrate by radical enhanced ALD (REALD) using metalorganic precursors, $Bi(tmhd)_3$ (tmhd = 2,2,6,6-tetramethylheptane-3,5 dione), $Co(tmhd)_2$, and $Fe(tmhd)_3$. The use of oxygen radicals as an ALD oxidant provides extra process flexibility. Film crystallinities and properties were studied under different conditions. The BFO films showed epitaxial single crystalline growth in a (001) pseudocubic orientation after annealed at 650 °C while the CFO films are polycrystalline due to the lattice mismatch between the film and substrate (~ 1% for BFO and ~7% for CFO). The piezoelectric properties of BFO films were confirmed using PFM while weak ferromagnetic behavior was also observed. Tunable CFO magnetic properties were shown using thickness-related strain relaxation over the range of 5~90 nm.

Synthesis of multiferroic composites was enabled by REALD. When fixing the total thickness at 40nm, 2-2 BFO/CFO nanolaminate composites with an increasing number of sub-layers showed a controllable competition between magnetic and shape anisotropy. 0-3 CFO/PZT composites were enabled by growing conformal CFO ALD films onto mesoporous PZT medium. SEM confirmed the gradual and conformal coating with increasing ALD cycles. It was found that the pore necks limit the incorporation of CFO inside the mesoporous media as it blocks precursor penetration. The volumetric magnetic properties were found to exceed the values found in literature with 0-3 configurations.

5:20pm **TF+2D+MG+NS-MoA10 Plasma Enhanced Deposition of Nanocrystalline Silicon Thin Films from SiF4 by RF-PECVD and MDECR: Key Aspects of Growth Dynamics***, JK. Wang, P. Bulkin, I. Florea, J.L. Maurice,* ***Erik Johnson***, LPICM-CNRS, Ecole Polytechnique, France

For the growth of thin-film hydrogenated silicon by low temperature plasma-enhanced chemical vapor deposition (PECVD), SiF_4 has recently attracted interest as a precursor for numerous reasons, most importantly due the resilient optoelectronic performance of the resulting layers and devices, even when grown in a slightly oxygen-contaminated growth environment. Nevertheless, many questions remain concerning the critical factors determining the quality of hydrogenated microcrystalline silicon (µc-Si:H) thin films grown from this precursor.

To advance knowledge on this subject, we present studies performed on two very different types of PECVD reactor: a standard capacitively coupled RF-PECVD reactor, using a process gas mixture consisting of Ar/SiF4/H2 and at deposition rates up to 4A/s, and a matrix-distributed electron cyclotron resonance (MDECR) PECVD reactor operating at much lower pressures but achieving a higher deposition rate (8 A/s) and using simply an SiF_4/H_2 mixture. In doing so, we reveal key details concerning the growth process. We underline recently obtained results concerning three critical experimental findings about the use of SiF4 as a growth precursor: (1) the importance of temperature for high-deposition rate, low-pressure conditions, (2) the vital role of ion bombardment energy on the quality of growth, and (3) the vastly increased challenge of the nucleation process when using high-density plasma processes. The films generated in these studies have furthermore been studied by cross sectional HR-TEM, revealing more specific details about the changing nature of the films during growth, and the dependence of these dynamics on the maximum ion energy impinging on the surface. These studies - along with residual gas analysis studies and optical emission spectroscopy results – allow us to examine the precise growth mechanism of such films when using an SiF_4/H_2 mixture.

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