

# Wednesday Morning, November 12, 2014

## Thin Film

Room: 307 - Session TF+MS+PS-WeM

## Applied ALD: Nanoelectronics and Emerging Applications

Moderator: Jesse Jur, North Carolina State University

### 8:00am TF+MS+PS-WeM1 ALD and Beyond CMOS Materials, Robert Wallace, University of Texas at Dallas **INVITED**

Two-dimensional layered materials, such as graphene and transition metal dichalcogenides (TMDs), have been recently proposed for a number of novel device concepts due to their interesting materials properties. For example, the possibility of low surface defect densities due to an anticipated dearth of surface defects and dangling bonds raises the prospect of improved performance for low power tunnel field effect logic devices that switch on and off very rapidly due to the anticipated steep subthreshold slope characteristic. However, for ALD processes, such surfaces present significant challenges for nucleation and growth. This talk will review our recent work on in-situ characterization of 2D materials for such device applications. This research is supported in part by the STARNet Center for Low Energy Systems Technology, sponsored by the Semiconductor Research Corporation (SRC) and DARPA, the SWAN Center sponsored by the SRC Nanoelectronics Research Initiative and NIST, and by an IBM Faculty Award.

### 9:00am TF+MS+PS-WeM4 Combining Gas Phase Aerosol Deposition with Atomic Layer Deposition for Fast Thin Film Deposition: A Case Study of Transparent Conducting ZnO, Elijah Thimsen, Washington University, St. Louis, M. Johnson, A. Wagner, A. Mkhoyan, U.R. Kortshagen, E.S. Aydil, University of Minnesota

Atomic layer deposition (ALD) has emerged as a powerful and scalable technique for a variety of applications where layer-by-layer control over film properties and conformal deposition in tight geometries are needed. One common criticism of ALD is that it is slow and may become uneconomical when thick films and high deposition rates are needed. In fact, deposition rate is often an issue even with physical vapor deposition methods such as sputtering and also chemical vapor deposition. One way to deliver material onto a substrate at high rates is through deposition of nanoparticles. Gas phase aerosol deposition is particularly attractive because rates as high as 100 nm/s are possible even at low temperatures. However, aerosol deposition often yields porous films unsuitable for optoelectronic applications. In this talk, we describe a new two-step strategy for depositing dense thin films at high rates. Our strategy combines the high rates of aerosol deposition with advantages of ALD. In the first step nanoparticles are synthesized in the gas-phase and deposited onto suitable substrates by aerosol deposition. In the second step, the space between the nanoparticles is infilled by ALD. This is a versatile approach since there are many material options for forming both the nanoparticle network and the ALD coating. In the specific example that will be discussed in this talk, the crystalline nanoparticles are synthesized in a nonthermal plasma containing the precursors that lead to nucleation and growth of the desired material. These nanocrystals are deposited on suitable substrates through supersonic expansion and inertial impaction. Using this approach, we demonstrate fast deposition of nanocrystalline ZnO films, an earth-abundant, nontoxic, low cost material that can be used as a transparent conducting oxide (TCO), from a plasma containing Ar, O<sub>2</sub> and diethylzinc. The space between the particles is filled either by Al<sub>2</sub>O<sub>3</sub> or Al-doped ZnO (AZO) to give continuous TCO films. After annealing in H<sub>2</sub> and coating with Al<sub>2</sub>O<sub>3</sub>, the ZnO nanocrystal network becomes conductive with Hall effect electron mobilities as high as 3.0 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Depending on the combination of the nanocrystals, ALD coating, and post processing, we have obtained transparent films with resistivity values as low as 3.8 x 10<sup>-3</sup> Ohm cm. The lowest resistivity films were obtained with undoped ZnO nanoparticles coated with AZO. The resistivity can be improved by doping the nanocrystals, which has proven to be challenging. We will discuss the effects of nanocrystal size, doping of nanocrystals in the gas phase, and film porosity on electrical conductivity.

### 9:20am TF+MS+PS-WeM5 Detecting Order in the Molecular Layer Deposition of Polymer Films by X-Ray Diffraction, David Bergsman, R.W. Johnson, R. Britto, S.F. Bent, Stanford University

The deposition of highly ordered, thin, organic films is of great importance to a variety of fields. The development of biological sensors, organic solar cells, and optical devices relies on the ability to grow thin layers of organic material with various thicknesses, compositions, functionalities, and levels

of crystallinity. One promising method of creating such films is molecular layer deposition (MLD), which uses an alternating sequence of self-saturating reactions by vapor-phase organic precursors at the substrate to grow films in a layer-by-layer fashion. This technique has been demonstrated with a variety of precursor chemistries and has been shown capable of growing films on high aspect ratio features with low surface roughness and high conformality. But despite the growing use of MLD, many questions still remain as to the orientation of the molecular chains within the deposited films and the packing of these chains. Many different factors may contribute to varying degrees of crystallinity during growth, such as chain-chain steric repulsion, Van der Waals forces, chain growth angle, and inter-chain hydrogen bonding. Here, we demonstrate that some MLD chemistries can form nanoscale organic films that exhibit well-ordered packing. Polyurea MLD films with different thicknesses and backbone chemistries were grown in an MLD reactor and then examined with x-ray diffraction (XRD) using synchrotron radiation at the Stanford Synchrotron Radiation Lightsource (SSRL). Spectroscopic ellipsometry was used to observe film thickness, while x-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy monitored for film degradation. XRD results for the polyurea MLD films show peaks at q-values of 1.5/Å, corresponding to a d-spacing around 4.2 Å. Changing the precursor from a more rigid to a more flexible backbone leads to variations in d-spacing and diffraction intensity. Growth on substrates with different surface chemistries and roughness, as well as the effect of heating and re-cooling the films, is also explored. These results suggest that thin organic films with varying levels of packing order can be grown using MLD by tuning the precursor chemistry.

### 9:40am TF+MS+PS-WeM6 Native Oxide Diffusion and Removal During the Atomic Layer Deposition of Ta<sub>2</sub>O<sub>5</sub> on InAs(100) Surfaces, Alex Henegar, T. Gougousi, University of Maryland, Baltimore County

The use of high-κ dielectrics on III-V semiconductors in place of Si/SiO<sub>2</sub> structures in metal oxide semiconductor devices has been perpetually hindered by poor quality native oxides at the substrate/film interface. A promising solution for the removal of these oxides is the atomic layer deposition (ALD) growth technique which has shown the ability to remove native oxides during deposition without additional processing for certain chemistries.<sup>1-4</sup>

In this work, Ta<sub>2</sub>O<sub>5</sub> thin films were deposited on InAs(100) by ALD using pentakis dimethyl amino tantalum (PDMAT) and H<sub>2</sub>O to study the effects of film deposition on the native oxides. 3 and 7 nm films were grown at 150-300 °C on InAs substrates covered with native oxides and substrates chemically etched in NH<sub>4</sub>OH. Analysis of the film deposited on native oxide covered substrates by x-ray photoelectron spectroscopy (XPS) shows arsenic and indium oxides are readily removed during deposition of 3 nm Ta<sub>2</sub>O<sub>5</sub> at 250 and 300 °C, temperatures very close to the optimal ALD temperature for the specific chemistry. At lower temperatures both oxides persist with indium oxides generally being harder to remove.

Depth profiling by argon-ion sputtering data of 7 nm films shows that indium oxides have diffused into the Ta<sub>2</sub>O<sub>5</sub> film. The sharp decrease in oxide signal after the first sputter cycle indicates that the majority of the indium oxide is located near the surface suggesting the migration of indium oxides to the film surface during deposition. Arsenic oxides, however, are detected in smaller amounts and generally speaking remain at the interface. For depositions on etched InAs no arsenic oxides were detected but a small amount of indium oxides remain even at the optimal deposition temperatures. Films grown on etched substrates always contain less indium and arsenic oxides than their equivalents deposited on native oxide surfaces. Mixing of indium oxide in the films may have a significant negative effect on their insulating properties negating any gain from a sharper interface.

<sup>1</sup> P.D. Ye, G.D. Wilk, B. Yang, J. Kwo, S.N.G. Chu, S. Nakahara, H.-J.L. Gossman, J.P. Mannaerts, M. Hong, K.K. Ng, and J. Bude, Appl. Phys. Lett. **83**, 180 (2003).

<sup>2</sup> M.M. Frank, G.D. Wilk, D. Starodub, T. Gustafsson, E. Garfunkel, Y.J. Chabal, J. Grazul, and D.A. Muller, Appl. Phys. Lett. **86**, 152904 (2005).

<sup>3</sup> M.L. Huang, Y.C. Chang, C.H. Chang, Y.J. Lee, P. Chang, J. Kwo, T.B. Wu, and M. Hong, Appl. Phys. Lett. **87**, 252104 (2005).

<sup>4</sup> C.-H. Chang, Y.-K. Chiou, Y.-C. Chang, K.-Y. Lee, T.-D. Lin, T.-B. Wu, M. Hong, and J. Kwo, Appl. Phys. Lett. **89**, 242911 (2006).

### 11:00am TF+MS+PS-WeM10 ALD in High Aspect Ratio Structures and Nanoporous Materials, C. Detavernier, Jolien Dendooven, University of Ghent, Belgium **INVITED**

Atomic layer deposition (ALD) is known to be an excellent technique for the deposition of thin films with uniform thickness over micro- and

nanoscale 3D structures. The superior conformality of ALD is a direct consequence of the self-saturated surface reaction control and makes the technique increasingly useful in the rapidly growing field of nanotechnology. The successful ALD-based processing of nanostructured materials requires however a careful optimization of the growth parameters. In this work, we present an extensive study on the conformality of ALD in high aspect ratio structures and nanoporous materials.

A first experimental approach was based on the use of macroscopic, trench-like structures in combination with low precursor pressures. In this way, the transport of the precursor molecules in the test structures was governed by molecular flow, as in microscopic trenches under standard ALD conditions. This method allowed us to quantify the conformality of the trimethylaluminum (TMA)/H<sub>2</sub>O process as a function of the aspect ratio and the TMA exposure time. Our experimental data indicated that the sticking probability is a determining factor in the conformality of ALD [1]. A better understanding of the effect of this parameter on the conformality was obtained via kinetic modeling and Monte Carlo modeling.

As a second substrate, porous titania thin films with pore sizes in the low mesoporous regime (< 10 nm) were considered in order to get insights on the minimum pore diameter that can be achieved by ALD. Novel in situ characterization techniques were developed to monitor the pore filling by ALD. Synchrotron-based x-ray fluorescence and scattering techniques provided cycle-per-cycle information on the material uptake and densification of the porous film, while ellipsometric porosimetry was used to quantify the pore size reduction. This study nicely demonstrated the ability of ALD to tune the diameter of nanopores down to the molecular level [2].

Finally, we performed ALD of TiO<sub>2</sub> into a 3D ordered silica powder with two types of mesopores [3]. By varying the Ti-precursor exposure time, we investigated the introduction of TiO<sub>2</sub> into the differently sized mesopores. A TEM study revealed the diffusion limited nature of the TiO<sub>2</sub> ALD process, leading to anisotropic penetration profiles in this specific pore structure. We observed a systematic deeper penetration of the deposition front along the main channels compared to the narrower mesopores. These results were corroborated by modeling work.

[1] J. Dendooven et al., *J. Electrochem. Soc.* 156, P63, 2009. [2] J. Dendooven et al., *Chem. Mater.* 24, 1992, 2012. [3] S. P. Sree et al., *Chem. Mater.* 24, 2775, 2012.

11:40am **TF+MS+PS-WeM12 Pyrolysis of Alucone MLD Films to Form Electrically Conducting and Nanodomained Al<sub>2</sub>O<sub>3</sub>/C Composite Films**, *J.J. Travis, J.W. DuMont, Steven George*, University of Colorado, Boulder

Alucone is an aluminum alkoxide polymer grown using molecular layer deposition (MLD) techniques with trimethylaluminum and organic diols or triols as the reactants. Alucone films can be pyrolyzed under inert atmosphere or vacuum to yield electrically conductive Al<sub>2</sub>O<sub>3</sub>/C composite films. This pyrolysis provides a pathway to deposit ultrathin, conformal and conducting Al<sub>2</sub>O<sub>3</sub>/C films on high surface area substrates. Our recent results have shown that the electrical conductance of the Al<sub>2</sub>O<sub>3</sub>/C films is dependent upon the amount of carbon in the film. The initial alucone films are non-conducting. After pyrolysis to 850°C, alucone films grown using glycerol, with three carbons, or hydroquinone, with six carbons, display high electrical conductivity of ~1-3 S/cm. In contrast, pyrolyzed alucone films grown using ethylene glycol, with only two carbons, remain non-conducting. In situ transmission Fourier transform infrared (FTIR) spectroscopy was used to monitor the pyrolysis of the alucone films. The C-H, C-O and C-C vibrational features were lost from the alucone films between 300-450°C. The vibrational spectra also showed prominent carboxylate features at 400-450°C. Carboxylate features are consistent with COO<sup>-</sup> - Al<sup>3+</sup> complexes at the interfaces between the Al<sub>2</sub>O<sub>3</sub> and carbon regions of the composite. High resolution transmission electron microscopy (HRTEM) images are consistent with a highly interfacial nanodomained Al<sub>2</sub>O<sub>3</sub>/C composite. These Al<sub>2</sub>O<sub>3</sub>/C composite films may provide electrical conductivity and oxidation resistance during electrochemical processes on metal and carbon electrodes.

12:00pm **TF+MS+PS-WeM13 Atomic Layer Deposition of Metal Oxides on Ultra-High Aspect Ratio, Vertically Aligned Carbon Nanotube Arrays**, *Kelly Stano, M. Carroll, R.P. Padbury, J.S. Jur, P. Bradford*, North Carolina State University

Atomic layer deposition (ALD) is commonly used to coat high aspect ratio structures, including vertically aligned carbon nanotube arrays (VACNTs). Previous studies, however, have demonstrated precursor diffusion depths of only 60 μm for long exposure times, leading to a “canopy effect” where preferential coating takes place at the top of arrays. In this research we report the first example of conformal Al<sub>2</sub>O<sub>3</sub> ALD on 1.5 mm tall VACNTs with uniform coating distribution from CNT base to tip. Large-scale CNT arrays with free volume aspect ratios ~15,000 were able to be uniformly

coated by manipulating sample orientation and mounting techniques, as confirmed by cross-sectional energy dispersive x-ray spectroscopy. Conformal coating was achieved through modification of CNT surface chemistry via vapor phase techniques including pyrolytic carbon deposition and atmospheric pressure oxygen plasma functionalization. Thermogravimetric analysis revealed that arrays which were functionalized prior to ALD coating were more stable to thermal degradation compared to untreated, ALD coated arrays. Interestingly, CNTs could be easily removed during thermal oxidation to yield arrays of continuous, high surface area, vertically aligned Al<sub>2</sub>O<sub>3</sub> nanotubes. Additionally, functionalized and ALD coated arrays exhibited compressive moduli two times greater than pristine arrays coated for the same number of cycles. Al<sub>2</sub>O<sub>3</sub> coated arrays exhibited hydrophilic wetting behavior as well as foam-like recovery following compressive strain. These processing techniques have been successfully applied to other ALD precursors to yield CNT arrays uniformly coated with ZnO and TiO<sub>2</sub> as well.

# Wednesday Afternoon, November 12, 2014

## Manufacturing Science and Technology

Room: 302 - Session MS+TF-WeA

### Overview: Applications and Manufacturing of Devices on Paper and Textiles

**Moderator:** Liangbing Hu, University of Maryland, College Park, Bridget R. Rogers, Vanderbilt University

2:20pm **MS+TF-WeA1 Challenges and Opportunities in the Production of Cellulose Nanomaterials**, *Junyong Zhu*, USDA Forest Products Lab **INVITED**

Cellulose nanomaterials has attracted great attention in the scientific community due to its unique optical and mechanical properties along with its renewability and abundance. However, the production process is very costly using current technologies, which limited its use to high value products. This created a market mismatch, i.e., a very large amount natural cellulose are available. In this presentation I will outline the challenges in reducing the cost of cellulose nanomaterials. At the same time, I provide some opportunities to reduce the cost. I will specifically outline a few process innovations in our laboratory for both cellulose nanocrystal and cellulose nanofibril productions

3:00pm **MS+TF-WeA3 Engineering Cellulose Nanomaterial Substrates for Flexible Electronics**, *Y. Zhou, C. Fuentes-Hernandez, T. Khan*, Georgia Institute of Technology, *J.-C. Liu, J. Diaz*, Purdue University, *J. Hsu, J. Shim, A. Dindar*, Georgia Institute of Technology, *Robert Moon*, US Forest Service-Forest Products Laboratory, *J. Youngblood*, Purdue University, *B.J. Kippelen*, Georgia Institute of Technology **INVITED**

Fabrication of flexible electronics (e.g. solar cells) on recyclable and biodegradable substrates are attractive for the realization of a sustainable technology, but significant advances are required to make the technologies economically viable and, from a life-cycle perspective, environmentally friendly, and consequently scalable. One of the key areas of research for making this a reality is in the design/engineering of suitable substrate materials that can: mechanically and chemically support the given electronics, have sufficient surface features (low roughness, surface chemistry, etc) to facilitate the process of the electronics, have similar thermal expansion characteristics of the electronics to minimize stress at the substrate-device interface, have the desired optical transmittance for device performance or application of product, and facilitate the recovery of the electronic components during the recycling process, to name a few. Our recent work has focused on the development of cellulose nanocrystals (CNCs) based substrates for such applications. Cellulose nanomaterials (CNM) are emerging high-value nanoparticles extracted from plants that are abundant, renewable, and sustainable. CNCs are rod-like nanoparticles of about 4-10 nm in diameter and 50-400 nm in length and through solvent casting of aqueous suspensions, transparent substrates suitable for electronic devices can be produced. By adjusting the suspension composition, pH, application of shear (control CNC alignment), drying conditions and heat treatment, have been identified as relevant factors affecting the final film/substrate properties.

This talk will provide a general introduction and review of the current state of art in cellulose nanomaterials, their use as substrate materials for flexible electronics, and summarize our work on the measurement of thermo-mechanical properties of CNC-based substrate materials and the development of efficient polymer solar cells fabricated on optically transparent CNC substrates.

4:20pm **MS+TF-WeA7 Circuits on Cellulose: From Transistors to LEDs, from Displays to Microfluidics on Paper**, *Andrew Steckl*, University of Cincinnati **INVITED**

Organic electronics is a rapidly growing field due to a combination of strong performance from improving materials with the low fabrication cost associated with large area printing technology. Recently, the incorporation into organic electronic technology of natural biomaterials that are renewable and biodegradable is being increasingly investigated with the goal of producing "green" electronics that is environment-friendly.

In this presentation, a review is given on the use of cellulose-based paper as a material in a variety of electronic (and related) applications, including transistors, light emitting diodes, displays, microfluidics. Paper is a very attractive material for many device applications: very low cost, available in almost any size, versatile surface finishes, portable and flexible. From an environmental point of view, paper is a renewable resource and is readily

disposable (incineration, biodegradable). Applications of paper-based electronics [1,2] currently being considered or investigated include biochips, sensors, communication circuits, batteries, smart packaging, electronic displays. The potential advantages of paper-based devices are in many cases very compelling. For example, lab-on-chip devices fabricated on paper for bio/medical applications [3] use the capillary properties of paper to operate without the need of external power sources, greatly simplifying the design and reducing the cost. Specific examples of paper-based devices will be discussed, including organic light emitting diodes [4] (OLED) and field effect transistors [5] (OFET) on flexible and transparent paper, medical diagnostic devices utilizing lateral capillary flow on paper.

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2. A. J. Steckl, "Circuits on Cellulose", *IEEE Spectrum* **50** (2) 48, doi:10.1109/MSPEC.2013.6420146 (2013).

3. Rolland, J. P. & Mourey, D. A. "Paper as a novel material platform for devices", *MRS Bulletin* **38**, 299, doi:10.1557/mrs.2013.58 (2013).

4. S. Purandare, E. F. Gomez and A. J. Steckl, "High brightness phosphorescent organic light emitting diodes on transparent and flexible cellulose films", *IOP Nanotechnology*, **25**, 094012, doi 10.1088/0957-4484/25/9/094012 (March 2014).

5. A. Zocco, H. You, J. A. Hagen and A. J. Steckl, "Pentacene organic thin-film transistors on flexible paper and glass substrates", *IOP Nanotechnology*, **25**, 094005, doi 10.1088/0957-4484/25/9/094005 (March 2014).

5:00pm **MS+TF-WeA9 Cellulose Nanostructures for Energy Devices and Flexible Electronics**, *H.L. Zhu, W. Bao, F. Shen, Y. Li, Z. Fang, Liangbing Hu*, University of Maryland, College Park **INVITED**

I will discuss our recent results and the fundamental science of novel transparent paper with tailored optical and mechanical properties, and applications in flexible electronics, origami devices and solar cells. I will also discuss the fundamental advantages of using mesoporous, soft wood fibers for low-cost Na-ion batteries.

5:40pm **MS+TF-WeA11 Designing Functional Paper for Emerging Electronics and Energy Devices**, *Hongli Zhu, L.B. Hu*, University of Maryland, College Park

The natural wood fiber has a hierarchical structure with one regular fiber consisting of numerous smaller fibers, and these small nanofibers can be disintegrated from the microfibril with chemical and mechanical treatment. By integrating electronically conductive material, we apply the low cost and sustainable biomaterial in the electronics and energy storage devices. In the first part, we will introduce a novel transparent paper made of wood fibers that displays both ultrahigh optical transparency (~96%) and ultrahigh haze (~60%), thus delivering an optimal substrate design for solar cell devices. We will also introduce the flexible transparent organic field-effect transistors (OFETs) and organic light emitting diode (OLED) device fabricated on nanopaper. These studies are important for the future development of flexible electronics based on new transparent substrates made from sustainable cellulose instead of plastic. In the second part, we will discuss wood fiber based batteries. The wood fibers are intrinsically porous and soft. Thin film Sn anodes deposited onto wood fibers sustain more than 400 charging/discharging cycles, a new record for Sn anodes in Na-ion batteries. Additionally, dual ion transport pathways within the mesoporous structure of wood cellulose fibers significantly improve the traditionally slow ion transport in Na-ion batteries.

6:00pm **MS+TF-WeA12 Transparent Films of Cellulose Nanocrystals Derived from Waste Cotton T-shirts**, *Nasim Farahbakhsh, J.S. Jur, R.A. Venditti*, North Carolina State University

The hierarchical structure of cellulose materials is a renewable building block for a wide range of novel applications, including electronic devices. In this work we present on the fabrication of the transparent cellulose nanocrystal (CNC) thin films for flexible electronic applications. The CNC platforms were manufactured from waste cotton T-shirts fibers using sulphuric acid at optimum reaction temperature and acid concentration. The derivation of nanocellulose from cotton fibers beneficial due to a high cellulose content (~95%) and high crystalline structure which results in high yield without any intensified purification process. The resultant CNC particles, with an average diameter of 25 nm with average length of 200 nm, are used to produce transparent free-standing films and spun-cast films on silicon. Opportunities related device fabrications are presented.

# Thursday Morning, November 13, 2014

## Manufacturing Science and Technology

Room: 302 - Session MS+PS+TF-ThM

### Processes for Mesoscale Structure on Paper and Textiles

**Moderator:** Jesse Jur, North Carolina State University

8:00am **MS+PS+TF-ThM1 High-Performance Composites Based on Wood Cellulose Nanofibrils**, *Qi Zhou*, KTH Royal Institute of Technology, Sweden **INVITED**

With increasing concerns for the climate and environment, it has been recognized globally that paradigm-shifting research is required to improve the performance of materials based on renewable resources. Attempts to develop very high performance natural cellulosic fibers based composite materials using intact cells from hemp, flax and cotton have failed mainly due to the inherent imperfections of the secondary cell walls of natural fiber cells. These issues have been recently addressed by replacing with cellulose nanofibrils (CNFs), which are three orders of magnitude smaller than the intact fiber cells. The extraction process of CNFs from renewable resource has been extensively investigated in the past decade. A critical challenge in the fabrication of high performance products based on CNFs is to tailor their surface structure and functionality in an efficient and environmentally friendly fashion, thus to accommodate a wider range of applications and sustainability requirements for the next generation of materials. In this talk, I will present our recent work on the fabrication of functional composite materials based on CNFs. In particular, several novel surface modification techniques of CNFs and their effects on nanostructure and material properties of CNFs based composites will be discussed.

8:40am **MS+PS+TF-ThM3 Manufacturing and Applications of Carbon Nanotube Textiles**, *Philip Bradford*, North Carolina State University **INVITED**

Carbon nanotubes (CNTs) are short nanofibers that are usually produced in the form of a black powder. This powder is then incorporated into other materials to produce a wide array of multifunctional products. Processing raw CNTs into materials that look and behave like traditional textiles is a growing area of interest, however the CNTs are often processed in solution and the end products look more like papers than textiles. There are currently only a couple of options for creating fabrics out of CNTs which preserve the high surface area of the individual tubes and retain high porosity. This presentation covers the work of my research group to make this type of fabric from a special type of CNT structure called drawable CNT arrays. These arrays are synthesized in a low pressure chemical vapor deposition process and then utilized for CNT nonwoven fabric formation. My group is also exploring many novel applications for the use of these unique fabrics.

The nonwoven CNT fabrics produced in our lab contain millimeter long CNTs, have a preferential CNT alignment, low CNT bundling and high porosity. These features make them attractive for use in: composites reinforcement, battery electrodes, sensing, filtration and barrier fabrics. Of particular interest to the AVS community may be our recent work with collaborator Dr. Jesse Jur at NC State, to study the atomic layer deposition (ALD) of thin inorganic layers into CNT arrays and fabrics. Through optimization of CNT pretreatment, ALD parameters and sample orientation, we have been able, for the first time, to uniformly coat CNT structures whose characteristic aspect ratios are extremely large. Due to the un-bundled nature of the CNT fabrics we have the ability to uniformly coat CNTs along their entire millimeter length, making for some very unique hybrid CNT structures.

9:20am **MS+PS+TF-ThM5 Carbonized Cellulose Fibers for Low-Cost Energy Storage**, *Fei Shen, L.B. Hu*, University of Maryland, College Park

A low-cost but scalable carbon film was successfully obtained via cellulose fiber carbonization. This cellulose derived film can be also applied as an alternative anode for lithium or sodium ion battery due to its natural mesoporous structure of the starting material which was excellent for ion storage. Furthermore, this new type of carbonized cellulose possesses electrically interconnected three-dimensional framework with advanced dual properties of anode material and current collector, afford to result in a higher energy density by eliminating the extra mass of inactive materials such as binder and carbon black in conventional designs. Electrochemical studies showed the film achieved a high capacity of 800mAh/g for lithium ion battery and a moderate capacity of 200mAh/g for sodium ion battery at C/10.

9:40am **MS+PS+TF-ThM6 Traditional, 20<sup>th</sup>, and 21<sup>st</sup> Century Strengthening Techniques for Cultural Heritage Papers Weakened by Cellulose Depolymerization**, *L. Pei, M. McGath, John Baty*, Johns Hopkins University

Cellulose depolymerization leading to paper brittleness can occur throughout the sheet, or be localized to where a corrosive substance is present. Uniform brittleness is associated with mass-produced, inexpensive, and acidic papers. Rendering millions of books and unbound papers useless, paper brittleness impairs scholarly communication and destroys historic and artistic works. Localized brittleness is most commonly associated with corrosive pigments and inks, including iron gall ink. It visually alters and can also physically destroy paper-based works. In the absence of techniques to restore the cellulose polymer to its initial condition, diverse techniques have been developed to strengthen paper. Traditional conservation techniques vary from conceptually simple ones, such as backing the sheet with a reinforcing layer, to complex ones, such as splitting the sheet into two plies to adhere a reinforcing sheet in-between. 20<sup>th</sup> century techniques include the widespread lamination of documents with a cellulose acetate film, the present condition of which we have studied and discuss along with its successor, the encapsulation of papers within a polyester film envelope to which the sheet is only electrostatically attracted. Both of these techniques involve the addition of a visible film, altering the look and feel of the artifact. Therefore, we are studying chemical vapor deposition (CVD) using Parylene to deposit a thin, conformal, barely perceptible coating to add strength to brittle papers. We conclude that, here as elsewhere, scientific research can improve traditional conservation techniques by making additional tools available to the conservator; that both cellulose acetate lamination and polyester film encapsulation have achieved a greater preservation benefit than they are credited for; and that CVD is a useful tool for both single-item as well as batch treatments to preserve cultural heritage papers weakened by cellulose depolymerization.

11:00am **MS+PS+TF-ThM10 Visualizing the Interface in Strained Cellulosic Nanocomposites**, *Chelsea Davis, J. Woodcock, A.M. Forster, M. Zammarano, I. Sacui, N. Chen, S.J. Stranick, J.W. Gilman*, National Institute of Standards and Technology (NIST)

In fundamental composite theory, the nature of the interface is often the key parameter which determines the strength of the resulting composite structure. While it is possible to observe interfacial failure and characterize the areal coverage of the matrix on the surface of the reinforcement phase in conventional composite materials, directly quantifying interfacial strength and contact area in a nanocomposite becomes far more difficult. A novel solution developed at NIST has been to utilize Förster resonance energy transfer (FRET) imaging<sup>[1,2]</sup> by preferentially labeling the interface within a nanocomposite system, allowing direct imaging of the interface with an optical microscope.<sup>[3]</sup> Zammarano et al. have shown that the incorporation of a FRET dye pair onto the surface of a cellulosic nanoreinforcement phase (dye 1) and within a polymer matrix (dye 2) allows visualization of the nanoscopic interphase region as the two dyes transfer energy on the same scale as the interphase depth (1 nm-100 nm).<sup>[3,4]</sup>

Building upon this FRET-based interfacial characterization technique, our goal is to develop a globally nondestructive measurement system that allows the quantitative characterization of key interfacial properties; first, the wetting and surface contact formed between the nanocellulose and an epoxy matrix and second, the deformation of the interface on the nanoscale upon application of small mechanical strains. We are constructing a suite of mechanical strain tools to enable *in situ* mechanical interrogation with simultaneous FRET imaging. The development of the first of these tools, uniaxial tensile test will allow a preliminary observation of small strain effects on the interphase region regarding the fluorescent response of the FRET dye pair. As a first proof of concept, it has been shown that FRET can be used to observe nanoscopic interfacial fracture and to determine local (microscopic) stress concentration zones before macroscopic failure of the nanocomposite is observed.

This *in situ* FRET/mechanical deformation approach allows the use of an optical microscope to probe nanoscale features in a powerful way, enabling characterization of nanomaterials which will complement measurements made by electron microscopy and standard mechanical property testing methods.

Topic Area: Novel nanocomposites, Multi-technique characterization of nanostructured materials

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[2] E. a Jares-Erijman, T. M. Jovin, *Nat. Biotechnol.***2003**, 21, 1387.

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11:20am **MS+PS+TF-ThM11 SERS-based Chemical and Biological Analytics on Inkjet-fabricated Paper Devices**, *Ian White*, University of Maryland

SERS-based chemical and biological analytics on inkjet-fabricated paper devices

Abstract. As a bio/chemical sensing technique, surface enhanced Raman spectroscopy (SERS) offers sensitivity comparable to that of fluorescence detection while providing highly specific information about the analyte. The high sensitivity of SERS detection results from the localized plasmons generated at the surface of noble metal nanostructures upon excitation by resonant electric fields at optical frequencies. Although single molecule identification with SERS was demonstrated over a decade ago, today a need exists to develop practical solutions for point-of-sample and point-of-care SERS systems. Recently, we demonstrated the fabrication of SERS substrates by inkjet printing silver and gold nanostructures onto paper and other similar membranes. Using a low-cost commercial inkjet printer, we deposited silver nanoparticles with micro-scale precision to form SERS-active biosensors. Using these devices, we have been able to achieve detection limits comparable to conventional nanofabricated substrates. Furthermore, we have leveraged the fluidic properties of paper to enhance the performance of the SERS devices while also enabling unprecedented ease of use, which is critical for extending chemical and biological analytics from central labs out into the field.

In this presentation we will review the capabilities of inkjet-fabricated paper SERS devices as chemical and biological sensors. We will introduce the fabrication of paper-based fluidic SERS devices using inkjet printing, and we will review results for chemical detection with paper SERS devices, including the use of the paper substrates as swabs and dipsticks for pesticide detection, as well as chromatography SERS on PVDF membranes for the detection of melamine in infant formula. We will then present the results of the fluidic paper SERS devices for biomolecule detection, including paper SERS dipsticks that leverage the chromatographic separation properties of paper to distinguish the outcome of multiplexed TaqMan PCR from a single reaction. In particular, we have utilized this technique to detect the presence of two drug resistance biomarkers for methicillin-resistant *S. Aureus* (MRSA).

11:40am **MS+PS+TF-ThM12 NSF Scalable Nanomanufacturing (SNM) Program**, *Khershed P. Cooper* **INVITED**

Abstract: Nanomanufacturing involves the fabrication of nano-scale building-blocks (nanomaterials, nanostructures), their assembly into higher-order structures such as nanodevices and nanosystems, and the integration of these into larger scale structures and systems such that both heterogeneity and complexity are possible with manipulation and control at nano-scale. In 2010, following a review of the NNI, PCAST recommended greater emphasis be put on commercialization of nanotechnologies by doubling Federal Government investment in nanomanufacturing R&D. In 2011, the inter-Agency NNI Signature Initiative (NSI) in Sustainable Nanomanufacturing was announced. In response to the NSI, the NSF Scalable Nanomanufacturing (SNM) Program was launched. SNM's emphasis is on research to overcome the key scientific and technological barriers that prevent the production of useful nanomaterials, nanostructures, devices and systems at an industrially relevant scale, reliably, and at low cost and within environmental, health and safety guidelines. The SNM program's objective is to address challenges presented at the various stages of the nanomanufacturing value chain of nano-scale building-blocks to nano-enabled products. It sponsors fundamental scientific research in well-defined technical areas that are strongly justified as approaches to overcome critical barriers to scale-up and integration. It seeks discovery of scalable processes and methods for large-area or continuous manufacturing at the nano-scale. It encourages the study of design principles for production systems leading to nanomanufacturing platforms, identification of metrology, instrumentation, and standards, and development of methodologies needed for process control and assessing quality and yield. SNM encourages an inter-disciplinary approach, industry collaboration and integration of research and education. SNM projects are studying a variety of building-blocks—CNT, graphene, membranes, BCPs, DNA, nanowires, nanofibers, QDs, etc., a variety of top-down and bottom-up processes—thermal, vapor-based, solution-based, lithography, patterning, bio-inspired, etc., targeting applications across the board—energy, environmental, electronics, sensors, structural, etc. Many projects are investigating roll-to-roll processing systems, some are studying in-line metrology and quality control. Moving ahead, SNM seeks to explore new research opportunities in processing (hierarchical nanomanufacturing, cyber-enabled nanomanufacturing, etc.), in materials (graphene, MoS<sub>2</sub>, etc.), in devices (plasmonics, ultrafine vias, etc.), and in manufacturing platforms (3D printing, bio-enabled assembly, etc.). SNM encourages an inter-disciplinary approach involving the disciplines of engineering, physical sciences and

mathematics. The ultimate goal is to create a knowledge base for the reliable production of nano-enabled systems and products.

# Thursday Afternoon, November 13, 2014

## Manufacturing Science and Technology

Room: 302 - Session MS+PS+TF-ThA

## Functionalization of Paper and Textiles & Their Applications

**Moderator:** Jack Rowe, North Carolina State University, Bridget R. Rogers, Vanderbilt University

2:20pm **MS+PS+TF-ThA1 Vapor-Phase Infiltration of Cellulose and Cotton**, *Mato Knez, K. Gregorczyk, M. Garcia, I. Azpitarte*, CIC nanoGUNE, Spain, *D. Pickup, C. Rogero*, Centro de Fisica de Materiales (CSIC-UPV-EHU), Spain **INVITED**

There is a significant interest in using inexpensive biological materials as substrates and scaffolds for emerging applications due to their natural occurrence. Of particular importance is the use of paper based materials and substrates for potential applications in energy storage, catalysis, solar cells, etc. Atomic layer deposition (ALD) has been proven to be the technique of choice to modify paper and other cellulose based materials due to its low reaction temperatures, extreme thickness control, and conformality. Furthermore, vapor phase infiltration techniques, which are a recent modification to ALD, have allowed infiltration of metal-organic precursors into a variety of organic materials including spider silk, porphyrins, and polytetrafluoroethylene (PTFE), leading to a more detailed understanding of the reaction between these organic substrates and the metal-organic precursors, as-well-as surprising changes in bulk properties. Understanding the chemical interactions between precursors and substrates are crucial in order to approach applications. We modified cellulose and cotton with common ALD precursors and monitored the chemical changes after the reaction a semi-*in-situ* XPS experiments. Our findings show that the precursors induce small, but important changes to the biopolymer upon chemical interaction and that the precursors indeed react different to each other. The experiments also compare well to the final results of standard *ex-situ* XPS. Changes in the bulk mechanical properties of the substrates were studied through use of tensile testing. The ultimate tensile strength (UTS), Young's modulus (YM), and toughness are shown to be a non-linear function of both the precursor used and the number exposure cycles.

3:00pm **MS+PS+TF-ThA3 Patterned Photoreduction of Metal Atoms on Polymeric Substrates for Flexible Electronic Applications**, *Halil Akyildiz, J.C. Halbur*, North Carolina State University, *A.T. Roberts*, Redstone Arsenal, *H.O. Everitt*, Duke University, *J.S. Jur*, North Carolina State University

Flexible electronics are of interest for displays, sensors, and health monitoring systems. Polymeric substrates, being flexible, easy to manufacture and inexpensive, are wanted for such applications. However, polymers, aside from good properties usually require alteration of electronic and optical properties. Sequential vapor infiltration (SVI) is a technique that modifies polymer properties by formation of hybrid materials via infiltration of organometallic precursors into bulk polymers. In this work we present how SVI tailors the optical properties of polyethylene terephthalate (PET) fibers by infiltration of trimethylaluminum (TMA) precursors to form PET-Alumina hybrid structures. Photoluminescence (PL) spectroscopy showed an order of magnitude increase in photoluminescence as compared to the pristine PET fibers which is attributed to the increased interactions between polymer chains by formation of alumina polymer coordination complexes. Furthermore metal ions out of a metal salt solution were reduced onto the modified substrates by photo catalytic effect. Patterned silver lines on PET fabric were successfully achieved by selective excitation of the fabric using a laser source showing promising results for integration of electronic devices.

3:20pm **MS+PS+TF-ThA4 Multifunctional Fabrics via Tungsten ALD on Kevlar**, *Sarah Atanasov, B. Kalanyan, G.N. Parsons*, North Carolina State University

Multifunctional materials combine two or more distinct capabilities into a single article unit. Kevlar is a high strength fiber used for personal protection and other mechanically demanding applications. Adding conductivity to Kevlar creates a new multifunctional protective/electronic material for electromagnetic shielding, communications, and erosion resistant, anti-static fabrics and cables for space and automotive technologies. For this study, we coated Kevlar fibers and woven mats with ALD tungsten, using  $WF_6$  and dilute silane ( $SiH_4$ , 2% Ar) at 220°C. Kevlar's thermal stability makes it a very amenable polymer for ALD coating at relatively high temperatures. Before W ALD, we deposited a  $TiO_2/Al_2O_3$  bilayer by ALD onto the Kevlar, at various temperatures (50-

220°C). The  $Al_2O_3$  layer promotes W nucleation. The  $TiO_2$  layer is important because previous mechanical analysis indicates that the TMA precursor degrades the Kevlar polymer backbone, whereas  $TiO_2$  ALD using  $TiCl_4$  and  $H_2O$  was less damaging. XPS analysis confirms the presence of  $TiO_2$ ,  $Al_2O_3$  and W on the fibers after each coating step. After W ALD, the yarns and mats are highly conductive (~3000 S/cm) and remain flexible. Tensile testing shows that upon coating with 20 ALD cycles, the strength of the Kevlar decreases from 3.32 GPa to 3.02 GPa. The ability to create highly conductive Kevlar with mechanical strength within 90% of the original mechanical performance could open new areas of application for large area low temperature ALD processing.

4:00pm **MS+PS+TF-ThA6 Direct and Self-Assembly of Nanocellulose Cleaved from Fiber Cell Walls and Integration in Device Manufacture**, *Orlando Rojas*, North Carolina State University **INVITED**

We introduce our work related to the application of surface and colloid science in the development of cellulose nanomaterials. These efforts take advantage of the process by which nature assembles fibers in a highly hierarchical structure encompassing a wide range of sizes, from the nano to the meter scales. A number of materials cleaved from the cell wall have been the subject of intensive research, including, nanofibrillar cellulose and cellulose nanocrystals, i.e., defect-free, rod-like crystalline residues after acid hydrolysis of cellulose fibers. Interest in nanocellulose originates from its appealing intrinsic properties: nanoscale dimensions, high surface area, unique morphology, low density, chirality and mechanical strength. Directing their assembly back to different hierarchical structures is a quest that can yield useful results in many revolutionary applications. As such, we will discuss the use of non-specific forces to create ultrathin films of nanocellulose at the air-solid interface for applications in nanocoatings, sensors, etc. Assemblies at other interfaces will be introduced as means to produce Pickering emulsions. Methods common in biophysics and employed to control the packing density of nanocellulose at the air-liquid and air-solid interfaces will be presented. A convective assembly setup assisted by shear and electric fields will be discussed as a suitable method to produce highly ordered structures. Concepts related to piezoelectric cellulose nanocrystal films, organic-inorganic hybrid materials with magnetic and other properties. Overall, the prospects of such novel materials will be explained in light of the unique properties of cellulose and its nanostructured assemblies.

5:20pm **MS+PS+TF-ThA10 Van der Waals Materials on Nanostructured Paper -- Aqueous Gating and Sensing Application**, *Wenzong Bao, Z. Fang, J. Wan, L.B. Hu*, University of Maryland, College Park

We report the first aqueous transistors on a bilayer-structured paper with a nanoscale smoother surface. Such transistors have a planar structure with source, drain and gate electrodes on the same surface of paper, and the mesoporous paper is used as an electrolyte container. Such transistors are enabled by a bilayer-structured all-cellulose paper with nano-fibrillated cellulose on the top surface that leads to an excellent surface smoothness, while the rest of micro-sized cellulose fibers can absorb electrolyte effectively. Based on 2D Van der Waals materials such as graphene and  $MoS_2$ , we demonstrate high-performance transistors with large on-off ratio. Our devices also show excellent bending flexibility. Such planar transistors with absorbed electrolyte gating can be used as sensors integrated with other components towards paper microfluidic systems.

5:40pm **MS+PS+TF-ThA11 Mechanistic Understanding of Anomalous Scaling Law of Mechanical Properties of Nano-Cellulose Paper**, *S. Zhu, Z. Jia, Y. Li, Z. Fang, S. Parvinian, N.J. Weadock, O. Vaaland, Y.C. Chen, L.B. Hu, Teng Li*, University of Maryland, College Park

The quest of both strength and toughness is perpetual in advanced material design; unfortunately, these two mechanical properties are generally mutually exclusive. A general and feasible mechanism to address the conflict of strength vs. toughness still remains elusive. Here we demonstrate an anomalous but highly desirable scaling law of the mechanical properties of cellulose nanopaper: both its strength and toughness increase simultaneously (40 & 130 times, respectively) as the size of the constituent cellulose fibers decreases (from a diameter of 27 microns to 10 nm). Our theoretical mechanics modeling and molecular dynamics simulations reveal the underlying mechanistic understanding of such an anomalous scaling law. These stimulating results suggest a fundamental bottom-up strategy generally applicable for other material building blocks, and thus hold the promising potential toward a new scaling law: the smaller, the stronger AND the tougher. There are abundant opportunities to utilize the fundamental bottom-up strategy to design a novel class of functional materials that are both strong and tough.



# Thursday Evening Poster Sessions

## Manufacturing Science and Technology

Room: Hall D - Session MS-ThP

### Manufacturing Science and Technology Poster Session

**MS-ThP1 Development of Dispersed C<sub>60</sub>-Molecules/Al Composite Materials Using Nanocrystalline Al Powder Synthesized by Pulsed Wire Evaporation Method, Daiki Muto, A. Matsumuro,** Aichi Institute of Technology, Japan

Carbon dioxide reduction is global environmental issues are urgent for all over worlds. As one of the problem solving methods, it is necessary to develop innovative higher specific strength materials. From this viewpoint, we focused on synthesis of new C<sub>60</sub>/Al composites materials.

In this study, C<sub>60</sub>/Al composite materials were prepared by a usual press sintering method. We must prevent from aggregation of C<sub>60</sub> powders in composite materials because the aggregation parts would surely cause a loss of strength of the materials. In order to distribute C<sub>60</sub> molecules around Al powders, ultrasonic vibration was applied with isopropyl alcohol as a solvent for 1 h when both powders were mixed before sintering composite materials. The powder for press sintering was prepared to dry in a furnace at about 340 K for 10 minutes. The average diameter of Al powders and the crystal grain size were about 100 nm measured by SEM and several tens of nm estimated by X-ray diffraction method, respectively. The composite materials with uniform dispersion of C<sub>60</sub> were fabricated by press sintering process under the condition of the applied pressure of 1 GPa and the temperature of 723K for 4 hour in Ar gas atmosphere. We investigated the optimal condition of the composite materials as changing composition rates from 0 to 5.0 wt.%C<sub>60</sub>.

In our results, we could not find remarkable aggregated parts of C<sub>60</sub> powders mixing powders up to 1.0 wt.%C<sub>60</sub> powders by SEM observations, and the microstructures must be considered to dispersion of C<sub>60</sub> molecules around Al powders. All specimens sintered were looked like uniform bulk materials. The densities of composite materials decreased according to the increase in the composition rate of C<sub>60</sub>, and decreased from  $2.7 \times 10^3$  kg/m<sup>3</sup> of Al to  $2.36 \times 10^3$  kg/m<sup>3</sup> of 1.0 wt.%C<sub>60</sub>. X-ray diffraction method showed only Al crystalline structure for all composite materials and FT-IR analysis clarified the existence of C<sub>60</sub> molecules in composite materials. Vickers hardness of Al material showed drastic increase up to 300 Hv in comparison with about 60 Hv of commercial Al materials due to nanocrystallization effect. The composite material with 1.0 wt.%C<sub>60</sub> showed the maximum value of 340 Hv. The specific strength of 1.0wt.%C<sub>60</sub> was increased up to 5.4 times comparing with those of industrially Al materials. This maximum specific strength of this study clarified surprisingly enhancement of over 3 times in comparison with that of commercial Mg alloys. Therefore, dispersed C<sub>60</sub>-molecules/Al-matrix composite materials with nanocrystalline powder give us dreams of development for innovative high specific strength materials.

**MS-ThP2 Reliability Improvement in Metal Hard-mask based Cu/Ultra Low-K Interconnects by Damage Reduction, MingDa Hsieh,** United Microelectronics Corporation, Taiwan, Republic of China

Among the several factors of the circuit reliability degradation, Low-k damage is one of the major factors. The purpose of this paper is to improve reliability by reducing the damage during etching. Low-k damage has been quantified by analysis of measured k value, Relief etch, Thermal Desorption Spectroscopy (TDS) and Leakage Current. Based on all the results, we can infer that Low dissociation Ash and low power PET reduces low-k damage and improves VRDB.

**MS-ThP4 Electrical Contact Resistance Characteristics of 28nm HK/MG Gate-Last Process with Advanced Manufacture Technology, Ching-Pin Hsu, C.L. Lu, Y.C. Lin, F.Y. Chang, K.Y. Liao, C.L. Chen,** United Microelectronics Corporation, Taiwan, Republic of China, L. Chen, C. Huang, C. Chen, Tokyo Electron Taiwan, Republic of China, J. Tsai, Y. Hsiao, A. Wang, Hermes Epitex, Taiwan, Republic of China

The High-k Metal Gate (HK/MG) Contact Rc is an extremely key factor to dominate the HK/MG MOS transistor device performance. Therefore the HK/MG Contact Rc stability and controllability become relatively important. However, the influence of HK/MG Contact Rc stability would come from the Contact etching process especially. This paper presents HK/MG Contact Rc performance evaluation to achieve the goal of mass production with the control of process flow time, and with several difference treatment methods of Dry and Wet process.

**MS-ThP5 Double Patterning Critical Open of Dual Damascene Approach for 14nm Node Beyond, ShihChun Tsai,** United Microelectronics Corporation, Taiwan, Republic of China

Double patterning lithography (DPL)

technologies have become a must for 32nm

nodes below. Currently have 2 approaches for DPL:

Self-aligned double patterning(SADP) and litho

etch litho etch(LELE).In this paper, we focus on

LELE induce issue, and present an etching solution

to solve this critical VIA open issue.

**MS-ThP6 Vertical Poly Dimethylsiloxane (PDMS) Fluidic Channel Fabrication by Rapid Prototyping, Yu-Hsin Lin, P.L. Chen,** NARL, Taiwan, Republic of China, Y.S. Lin, Hungkuang University Hungkuang University, Y.H. Tang, C.C. Yang, M.H. Shiao, C.N. Hsiao, NARL, Taiwan, Republic of China

This paper describes a rapid fabrication process in vertical poly dimethylsiloxane (PDMS) fluidic device for bio-applications by Rapid Prototyping (RP). Rapid Prototyping is fast, easy and mask-less process to build the 3-dimension structures. The process allows for the stacking of many PDMS channel layers to realize vertical fluidic device. In this paper, the vertical PDMS fluidic device is consisted two PDMS fluidic channel layer included top fluidic channel layer and bottom fluidic channel layer. The fluidic channel structures is manufactured by Rapid Prototyping then glued on a glass substrate with UV curing as a master. The Teflon-like film is coated on the surface of master. The PDMS is cast against the master producing molded channel layer. After curing process, the PDMS replica is easily peeled off from the master. The top and bottom fluidic channel layers are aligned and bonded together by oxygen treatment to form vertical fluidic device. The performance of vertical fluidic device prepared using this rapid prototyping technique has been demonstrated by fabricating a miniaturized bio-application system.

**MS-ThP7 Fabrication of Deeply Striped Pattern Structures by ICP-RIE Technique on the Lithium Niobate Substrate, Chun-Ming Chang, M.-J. Huang, J.Y. Su, N.N. Chu, C.N. Hsiao, M.H. Shiao,** ITRC, NARL Taiwan, Republic of China

In this study, striped pattern structures with linewidth of 5 μm and 10 μm on lithium niobate (LiNbO<sub>3</sub>) substrate were fabricated by the inductively coupled plasma reactive ion etching (ICP-RIE) technique for the waveguide applications. Pure nickel (Ni) thin film of 300 nm in thickness used as the etching mask and was deposited by sputtering technique on the LiNbO<sub>3</sub> substrate with a 20 nm adhesion layer of nickel-chrome (Ni-Cr) alloy with a composition ratio of 80/ 20. The LiNbO<sub>3</sub> substrates with the Ni etching mask was etched in the boron trichloride (BCl<sub>3</sub>)/ Argon (Ar) mixed etching gas which flow ratio was controlled at 30/ 5 SCCM and the working pressures controlled at 30 mTorr, 40 mTorr, 50 mTorr, and 60 mTorr, respectively. The ICP powers were controlled from 100 W to 600 W and the RF powers were controlled from 100 W to 500 W during 45 minutes of each ICP-RIE process.

From the experimental results, it can be found that the DC bias (-V) decreases with the working pressure, and increases with the ICP powers and the RF powers. Under suitable ICP-RIE etching parameters, the structure with 6 μm in depth and the sidewall angle of 80° was successfully prepared on the surface of LiNbO<sub>3</sub> substrate, which the etch selectivity ratio was 10 and the etching rate was 70 nm/ min.

**MS-ThP9 Fabrication of Micro ring Resonators for Nonlinear Optics Applications using Silicon Nitride Film Deposited at Room Temperature Overcoming the Stress Limitation, Adriano Ricardo do Nascimento Jr., L.T. Tiago Manera, J.A. Alexandre Diniz, A.R. R. Silva, M.V. Vinicius Puydinger dos Santos,** University of Campinas, Brazil, A.C. Cerqueira S. Jr., National Institute of Telecommunications, Brazil, L.A. A. M. Barea, N.C. C. Frateschi, University of Campinas, Brazil

Silicon nitride (Si<sub>x</sub>N<sub>y</sub>) films deposited by low-pressure electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-CVD) at room temperature are proposed for nonlinear optics applications in the telecommunications C-band. Due to the high silicon nitride nonlinearity, these films recently have also been used for nonlinear optics [1]. For nonlinear applications such as the generation of frequency combs, the waveguide needs a zero dispersion point in the middle of C-band, requesting large waveguide area. Unfortunately, these thick Si<sub>x</sub>N<sub>y</sub> films (>400 nm) have high stress and suffer from catastrophic cracking, which



reduces the device efficiency [2]. Using numerical simulations it was demonstrated that for refractive index ( $\eta$ ) values greater than 2, the area of the waveguide with zero dispersion point at  $\lambda = 1.55 \mu\text{m}$  is greatly reduced.

By varying deposition parameters, such as gas pressure (4-6 mTorr) and Si/N ratio (0.62-1.25),  $\text{Si}_x\text{N}_y$  films with high deposition rate and high refractive index was obtained. In many cases, for larger pressure values a considerable increase in the deposition rate is observed, and for lower  $\text{N}_2$  flow was observed a large increase of  $\eta$  (due to high concentration of Si). However, increasing the gas pressure, a reduction of  $\eta$  due the incorporation of hydrogen in the film was also observed.

A Si-rich silicon nitride layer with 730 nm of thickness, refractive index of 2, high deposition rate, low hydrogen concentration and roughness average of 0.52 nm was deposited above a Si/SiO<sub>2</sub> wafer during 100 minutes using ECR-CVD and applied for fabrication of nonlinear microring resonators. Due to the low temperature deposition, no thermal stress was observed in the  $\text{Si}_x\text{N}_y$  film, allowing a large thickness (obtained with only one deposition process). The main advantage of higher Si concentration in this film is the higher values of  $\eta$  and the absence of losses caused by two-photon absorption, responsible for the introduction of additional losses in silicon based waveguides [3].

After experimental measurements, microring resonators having a radius of 60  $\mu\text{m}$ , presented an equidistant Free Spectral Range and a Q-factor of  $4 \times 10^3$  was achieved, showing the high efficiency of the device. Finally, using the deposition process at low temperature and controlling the process parameters such as pressure and gas ratios, a remarkable free thermal stress silicon nitride film was obtained, overcoming the stress limitation of thick silicon nitride films.

[1] J. S. Levy *et al.*, Nat. Photonics, vol. 4, no. 1, pp. 37–40, 2009.

[2] K. Luke *et al.*, Opt. Express 21, 22829-22833, 2013.

[3] H. K. Tsang *et al.*, Appl. Phys. Lett., vol. 80, no. 3, p. 416, 2002.

# Friday Morning, November 14, 2014

## 2D Materials Focus Topic

Room: 310 - Session 2D+EM+MS+NS-FrM

## 2D Materials: Device Physics and Applications

Moderator: Daniel Gunlycke, Naval Research Laboratory

8:20am 2D+EM+MS+NS-FrM1 1, 2, 3... **Ripples, Gaps and Transport in Few-layer Graphene Membranes**, *ChunNing(Jeanie) Lau*, University of California, Riverside **INVITED**

Graphene, a two - dimensional single atomic layer of carbon, has recently emerged as a new model system for condensed matter physics, as well as a promising candidate for electronic materials. Though single layer graphene is gapless, bilayer and trilayer graphene have tunable band gaps that may be induced by out-of-plane electric fields or arise from collective excitation of electrons. Here I will present our results on mechanical manipulation and transport measurements in bilayer and trilayer graphene devices with mobility as high as 400,000 cm<sup>2</sup>/Vs. We demonstrate ripple formation due to thermally or mechanically induced strain, the presence of an intrinsic gapped state in bilayer and trilayer graphene at the charge neutrality point and evidence for quantum phase transition. Our results underscore the fascinating physics in these 2D membranes, and have implications for band gap engineering for graphene electronics and optoelectronic applications.

9:00am 2D+EM+MS+NS-FrM3 **Photoinduced Doping in Heterostructures of Graphene and Boron Nitride**, *Jairo Velasco Jr., L. Ju*, UC Berkeley, *E. Huang*, Stanford University, *S. Kahn*, *C. Nosiola*, *H.-Z. Tsai*, UC Berkeley, *W. Yang*, Beijing National Laboratory for Condensed Matter Physics, Republic of China, *T. Taniguchi*, *K. Wantanabe*, National Institute for Materials Science (NIMS), Japan, *Y. Zhang*, Fudan University, Republic of China, *G. Zhang*, Beijing National Laboratory for Condensed Matter Physics, Republic of China, *M.F. Crommie*, *A. Zettl*, *F. Wang*, UC Berkeley

Van der Waals heterostructures (VDH) provide an exciting new platform for materials engineering, where a variety of layered materials with different electrical, optical and mechanical responses can be stacked together to enable new physics and novel functionalities. Here we report an emerging optoelectronic phenomenon (i.e. photo-induced modulation doping) in the graphene-boron nitride VDH (G/BN heterostructure). We find it enables flexible and repeatable writing and erasing of charge doping in graphene with visible light. We demonstrate that the photo-induced modulation doping maintains the remarkable carrier mobility of the G/BN heterostructure, and it can be used to generate spatially varying doping profiles like *pn* junctions. Our work contributes towards understanding light-matter interactions in VDHs, and innovates a simple technique for creating inhomogeneous doping in high mobility graphene devices. This opens the door for new scientific studies and applications.

9:20am 2D+EM+MS+NS-FrM4 **Two-dimensional Resistance Map of Graphene p-n Junction in the Quantum Hall Regime**, *Nikolai N. Klimov*, *S. Le*, *C.A. Richter*, National Institute of Standards and Technology (NIST), *J. Yan*, University of Massachusetts, Amherst, *E. Comfort*, *J.U. Lee*, SUNY-University of Albany, *D.B. Newell*, National Institute of Standards and Technology (NIST)

Graphene, a two dimensional (2D) electronic system with a unique band structure, is a promising material for future electronic devices, especially for electrical metrology [1]. Currently, devices based upon GaAs heterostructures 2D electron gases (GaAs-2DEG) are used to realize a single quantum resistance standard value of  $(\frac{1}{2})h/e^2 = 12,906.4035 \Omega$  with metrological accuracy. It is important to realize resistance values over a wider resistance scale to expand the technical relevance of quantum resistance standards.

In the past, attempts have been made by using parallel or series GaAs-2DEG Hall bars to achieve multiple or fractional resistance values of  $h/e^2$ . However, the difficulties of fabricating ideal contacts and metal interconnects between the Hall bars severely limit the yield of properly operating devices. Graphene, with its ability to create both electron and hole 2D gases on a single Hall bar device without metal interconnects, is an ideal platform to overcome this difficulty [2].

We have fabricated a graphene FET p-n junction device in a Hall bar geometry and experimentally characterized it at large magnetic fields to determine the range of quantized resistance values that can be obtained. The device features two doped polysilicon split gates that are buried in a SiO<sub>2</sub> substrate within 100 nm-150 nm from the surface of graphene. The fabrication process achieves an atomically smooth dielectric surface, which is needed to preserve the intrinsic band structure of graphene. Independent

voltage control on these gates allows separate tuning of both type and concentration of charge carriers in the two parts of graphene conducting channel. In addition, a very narrow 150 nm gap between split gates gives a very sharp junction. Measurement of the sample's resistance at different gate values and measurement configurations in the quantum Hall regime allows us to fully characterize the device and to obtain multiples or fractions of the resistance value  $h/e^2$ . We will show that our experimental results can be explained by the Landauer-Büttiker edge-state transport model with the assumption of a partial mixing at the p-n interface. Potential application of graphene p-n junction devices for resistance standards with a wide range of resistance values other than  $h/2e^2$  will be discussed.

References:

[1] A. Tzalenchuk, *et al.*, Nature Nanotech., 5, 186 (2010)

[2] M. Woszczyzna, *et al.*, APL, 99, 022112 (2011)

9:40am 2D+EM+MS+NS-FrM5 **Electrical Breakdown and Current Carrying Ability of Multilayer MoS<sub>2</sub> Transistors**, *Philip Feng*, *R. Yang*, *Z. Wang*, Case Western Reserve University

We report the first study of electrical breakdown of multilayer molybdenum disulfide (MoS<sub>2</sub>) transistors through precision electrical measurements and simulation that shows the effect of varying the device size and conductivities on the breakdown limit. We demonstrate that the multilayer devices have better current carrying capabilities compared to thin layer devices. We also study the effect of varying MoS<sub>2</sub> thickness upon electron mobility in the channel.

MoS<sub>2</sub> has recently emerged as a new two-dimensional (2D) semiconducting crystal with attractive properties, such as the absence of dangling bonds, high thermal stability, and having a thickness-dependent bandgap [#\_edn1]. While prototype single- and few-layer MoS<sub>2</sub> FETs and circuits have been demonstrated, in practice multilayer (up to 10s of nanometers) devices may be more desirable for certain applications: they can have higher carrier mobility and density of states under the same dielectric environment, greater mechanical strength, higher current limit and better manufacturability [#\_edn2] [#\_edn3]. While the breakdown of single layer MoS<sub>2</sub> transistors has been demonstrated [#\_edn4], breakdown of multilayer devices has not been studied.

In this work, we study the electrical breakdown of devices with different thicknesses through experimental demonstration and simulation with finite element method (FEM). We observe that the breakdown process happens gradually with multiple voltage sweeping cycles, and thicker devices generally show higher breakdown current, which is also demonstrated in the simulation. The highest breakdown current in the measurement is 1.2mA, which is one of the highest current reported results so far for MoS<sub>2</sub> transistors. Simulation also shows that with higher conductivity channel, the breakdown current and breakdown current density both increase. The high field transport characteristics of multilayer MoS<sub>2</sub> transistors demonstrate that the devices could drive high loads in circuits and could be used for circuits that require high power or current. The thickness dependence of mobility shows that the device performance can be further improved by carefully tuning the device parameters.

[i] [#\_ednref1] Q. H. Wang, *et al.*, *Nat. Nanotechnol.* **7**, 699 (2012).

[ii] [#\_ednref2] D. Jariwala, *et al.*, *ACS Nano* **8**, 1102 (2014).

[iii] [#\_ednref3] R. Ganatra, Q. Zhang, *ACS Nano* (2014), DOI: 10.1021/nn405938z.

[iv] [#\_ednref4] D. Lembke, A. Kis, *ACS Nano* **6**, 10070 (2012).

10:00am 2D+EM+MS+NS-FrM6 **Lithography-free Fabrication of Graphene Devices**, *Nick Thissen*, *R.H.J. Vervuurt*, Eindhoven University of Technology, Netherlands, *J.J.L. Mulders*, FEI Electron Optics, Netherlands, *J.W. Weber*, *A.J.M. Mackus*, *W.M.M. Kessels*, *A.A. Bol*, Eindhoven University of Technology, Netherlands

Graphene device fabrication on large-area graphene typically involves several patterning steps using electron beam or optical lithography, followed by graphene etching and metallization for application of metallic contacts. However, the resist films and lift-off chemicals used in lithography introduce compatibility issues, such as the difficulty of removing the resist from the graphene. This resist residue has a negative influence on the thermal and electrical properties of the graphene and interferes with functionalization of the graphene. This motivates the development of a 'bottom-up', direct-write, lithography-free fabrication method.

In this work, a lithography-free fabrication method for graphene-based devices was developed. As a first step, the method involves direct

patterning of large-area graphene by focused ion beam (FIB) in order to isolate graphene from the bulk. The patterning of the graphene is performed in a DualBeam (SEM / FIB) system, in which a 30 kV FIB is used to locally remove graphene from the substrate. An *in situ* Raman microscope allows for direct observation of the graphene quality before and after FIB processing, from which it was determined that a low Ga-ion dose of 10 C/m<sup>2</sup> is sufficient for complete graphene removal. By optimizing the pattern design, the ion beam current and the background pressure in the DualBeam system, unintentional damage of the graphene by scattered ions is almost completely prevented.

After FIB patterning, as a second step a direct-write atomic layer deposition (ALD) technique is applied in the same system to locally deposit contacts to the isolated graphene. In the direct-write ALD technique, the patterning capability of electron beam induced deposition (EBID) is combined with the material quality of ALD. A thin seed layer consisting of small Pt grains in amorphous carbon is deposited on the graphene by EBID in the desired contact pattern. Subsequently, a selective ALD process purifies the seed layers and builds them into high-quality Pt contacts. This combined approach yields virtually 100% pure Pt (resistivity of 12 μΩcm) with a lateral resolution of 10 nm<sup>11</sup>. This chemical approach to contact deposition is expected to yield lower contact resistances compared to conventional physical deposition techniques.

By combining patterning and direct contact deposition in the same system, graphene devices were fabricated from large-area graphene without the use of lithography. First results from sub-optimal devices demonstrate field-effect mobilities approaching 500 cm<sup>2</sup>/Vs and contact resistances as low as (40 ± 30) Ω.

[1] A.J.M. Mackus et al., *Nanoscale* **4**, 4477 (2012)

#### 10:40am 2D+EM+MS+NS-FrM8 Electronic Transport in Transition Metal Dichalcogenides, Joerg Appenzeller, Purdue University INVITED

Since the discovery of graphene for electronic applications, there has been a substantial worldwide effort to explore other layered materials. Transition metal dichalcogenides (TMDs) like MoS<sub>2</sub>, MoSe<sub>2</sub>, or WSe<sub>2</sub>, to just name a few, not only offer the desired ultra-thin body structure that translates into superior electrostatics as desirable for nanoelectronics applications, but also exhibit a sizable band gap. While to date the ideal application space for these materials has not been identified, it is obvious that only through a detailed understanding of the underlying transport in these layered materials intrinsic properties that lend themselves to particular applications can be uncovered.

In my presentation I will first discuss the benefits of an ultra-thin body structure for scaled tunneling FET applications including tunneling devices. Contacts play a particularly crucial role in this context and can easily mask the intrinsic performance of TMDs as will be discussed based on experimental Schottky barrier tunneling data obtained from MoS<sub>2</sub>, MoSe<sub>2</sub> and WSe<sub>2</sub> field-effect transistors. A careful analysis of all these material systems reveals details about Schottky barrier heights for electron and hole injection as well as the band gap. These findings are then put into the context of channel length scaling and layer thickness dependence of three-terminal TMD devices based on MoS<sub>2</sub> transistors. Last, experimental data on the band-to-band tunneling in partially gated WSe<sub>2</sub> device structures will be discussed and projections about the potential usefulness of TMDs for tunneling device applications will be made.

#### 11:20am 2D+EM+MS+NS-FrM10 Controlled Synthesis and Fuel Cell Application of Carbon Nanowalls, Hiroki Kondo, S. Imai, K. Ishikawa, M. Sekine, M. Hori, Nagoya University, Japan, M. Hiramatsu, Meiji University, Japan

Carbon nanowalls (CNWs) are one of carbon nanomaterials and contain stacks of graphene sheets vertically standing on a substrate. Each wall with the top edge is continuous crystallographically through bending or branching and composed of nanographite domains. Recently, we have developed the formation method of the ultra-high-density over 10<sup>13</sup> cm<sup>-2</sup> Pt nanoparticles on the whole surface area of the CNWs with a diameter of 2-3 nm employing metal-organic chemical fluid deposition (MOCFD) method in supercritical fluid (SCF). They are promising as a catalytic electrodes for a polymer electrolyte fuel cell because of its high-specific-surface-area and high aspect ratio. On the other hand, while it is known that Pt nanoparticles are poisoned by CO below 100°C, it is reported that Pt-Au nanoparticles are excellent candidate for a low-temperature anode electrocatalyst. In this study, supporting processes of Pt-Au nanoparticles on the CNWs using the SCF-MOCFD method and their catalytic properties were investigated.

We used the SCF-MOCFD system to support Pt and Au nanoparticles on the CNWs. Firstly, Pt nanoparticles were supported using 1wt% (CH<sub>3</sub>C<sub>3</sub>H<sub>4</sub>)(CH<sub>3</sub>)<sub>3</sub>Pt solution (2 ml). Then, Au nanoparticles were subsequently supported using (CH<sub>3</sub>)<sub>2</sub>Au(CH<sub>3</sub>COCHCOCH<sub>3</sub>) solution (1 ml). Both precursors were diluted by n-hexane [CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>].

According to the SEM images of the CNWs after the supporting processes of only Pt nanoparticles and, both Pt and Au ones, the nanoparticles are supported on the entire surface area of each CNWs in the both cases. It is also found that the diameter and its distribution of the nanoparticles decrease after the second Au supporting process, while its density increases. This means that the relatively large Pt nanoparticles are effectively removed and small Au nanoparticles are simultaneously supported at the second supporting process. On the other hand, we evaluated cyclic voltammetry (CV) characteristics using CNWs with different-density Pt nanoparticles, in which density of 3.0×10<sup>12</sup> cm<sup>-2</sup> and diameter of 1.1 nm obtained for 10 min supporting and, density of 8.3×10<sup>12</sup> and diameter of 1.5 nm obtained for 30 min supporting. Peaks related to adsorption and desorption of hydrogen were found in both cases. With increasing the supporting time, the specific surface area of Pt evaluated from the CV about twofold increased. However, according to the TEM images, the ratio of surface area of Pt nanoparticles are about fivefold. It is deduced that some parts of Pt nanoparticles are inactive. Therefore, there results indicate that not the crystallinity control of CNWs are essential to improve the catalytic performance.

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