

# Monday Morning, October 29, 2012

## Nanomanufacturing Science and Technology Focus

### Topic

Room: 16 - Session NM+AS+MS-MoM

## Metrology and Environmental Issues in Nanomanufacturing

Moderator: N.A. Burnham, Worcester Polytechnic

Institute, L.J. Gamble, University of Washington

8:20am **NM+AS+MS-MoM1 Nanomanufacturing – Beyond Silicon, J.A. Liddle**, National Institute of Standards and Technology **INVITED**

The fabrication of integrated circuits in silicon is the preeminent nanomanufacturing technology, and it occupies a very special niche in terms of functionality and value provided per unit area. As a consequence, it is economically viable to use very expensive fabrication processes to generate the required nanostructures. In addition, the degree of control over the manufacturing process that is required necessitates the use of complex and expensive metrology systems. In contrast the vast majority of other nanotechnology products cannot support the cost of comparably sophisticated manufacturing methods or the associated metrology schemes. In this talk I will give examples of how the complexity of the final product and its value dictate what type of nanomanufacturing approach is viable. In particular, I will describe the need for new metrology techniques that can provide nanoscale information, but do so at rates consistent with the high-volume manufacturing of low-cost products.

9:00am **NM+AS+MS-MoM3 Use of Mueller Matrix – Spectroscopic Ellipsometry for Scatterometry based Measurement of Critical Dimensions during Semiconductor Manufacturing, G.R. Muthinti, A.C. Diebold**, University at Albany-SUNY, B. Peterson, Nanometrics Inc.

Scatterometry is one of the most useful metrology methods for the characterization and control of critical dimensions (CD) during nanoelectronic manufacturing. Most Scatterometry is based on Spectroscopic Ellipsometry (SE) and Normal Incidence Reflectometry (NI) measurement and the simulation of the measured spectra through the Rigorous Coupled Wave Approximation. Evolution of better optical hardware and faster computing capabilities led to the development of Mueller Matrix (MM) based Scatterometry (MMS). Typically, spectroscopic ellipsometry based Scatterometry uses Y the D measured at each wavelength. In this presentation we discuss dimensional metrology using full Mueller Matrix (16 element) Scatterometry in the wavelength range of 245nm-1000nm measured using a dual rotating compensator spectroscopic ellipsometer. Unlike SE and NI, MM data provides complete information about the optical reflection and transmission of polarized light through a sample. The advantage of MMSE over traditional SE Scatterometry is its ability to measure samples that have anisotropic optical properties and depolarize light. We demonstrate this using a series of structures fabricated by e-beam lithography.

9:20am **NM+AS+MS-MoM4 Atomic Layer Deposition Monitored and Characterized by Joint In Situ Real-Time Spectroscopic Ellipsometry and Direct Surface Analysis, M. Junige, M. Geidel, M. Knaut, M. Albert, J.W. Bartha**, Technische Universität Dresden, Germany

Atomic layer deposition (ALD) is a special kind of chemical vapor deposition, which pulses at least two chemical reactants into a vacuum reactor alternately and separated by purging steps. ALD has emerged as a powerful technique for the conformal and uniform coating of complex three-dimensional structures, even on large-sized substrates. Accordingly, ALD has a high potential for application throughout the entire field of nanotechnology.[1]

Since ALD alters the physical and chemical properties of a surface during a material's deposition, these changes are observable by direct surface analysis techniques like photoelectron spectroscopy (PES) or scanning probe microscopy (SPM) and also by spectroscopic ellipsometry (SE). As previously described in the References [2] - [4], we acquired ellipsometric spectra *in situ* and in real-time and thus monitored the ALD processes at exactly the place and the time of a sample's modification. In addition, we conducted PES as well as SPM measurements without breaking a high vacuum after the ALD. This revealed, among others, the chemical composition as well as the roughness of a coated surface without alteration in air and so enabled the generation of appropriate optical models, which translate the ellipsometric spectra into rather descriptive quantities like a film thickness or a surface roughness.

In the present work, we will demonstrate the capability of joint *in-situ* real-time SE and direct surface analysis based on the ALD of two exemplary materials: tantalum nitride and ruthenium. In the linear homogeneous film growth regime of both the ALD processes, the film thickness increment per cycle (also growth per cycle, GPC) was quantified and studied for varying process parameter sets. The initial ALD growth of TaN showed all the three possible growth modes according to Puurunen [5] depending on the starting substrate material. In the case of Ru, the ALD growth initiation indicated a substrate-inhibited island growth mode irrespective of the starting substrate.

[1] G. N. Parsons, S. M. George, and M. Knez, in *MRS Bulletin* **36**, 865 (2011).

[2] M. Junige, M. Geidel, M. Knaut, M. Albert, J. W. Bartha, in *IEEE 2011 Semiconductor Conference Dresden* (Dresden, 2011). – DOI: 10.1109/SCD.2011.6068739

[3] M. Knaut, M. Junige, M. Albert, J. W. Bartha, *J. Vac. Sci. Technol. A* **30**, 01A151 (2012).

[4] M. Geidel, M. Junige, M. Albert, J. W. Bartha: In-situ analysis on the initial growth of ultra-tin ruthenium films with atomic layer deposition, *Microelectron. Eng.* (manuscript submitted).

[5] R. L. Puurunen, *J. Appl. Phys.* **97**, 121301 (2005).

10:40am **NM+AS+MS-MoM8 Transformation of Engineered Nanomaterials in the Environment: Effects of Size, Shape and Morphology on Nanomaterial Toxicity, S. Obare**, Western Michigan University **INVITED**

Engineered nanomaterials (ENMs) are known to possess unique size and shape dependent chemical and physical properties. As a result of their properties, ENMs have been effective in several important applications including catalysis, sensor design, photonics, electronics, medicine, and the environmental remediation of toxic pollutants. Such properties and applications have led to an increase in the manufacture of ENMs and a rise in their presence in consumer products. The increase of ENMs in consumer products presents several opportunities and challenges, and necessitates a proactive study of their health and safety. An important and essential criterion toward a systematic study of the environmental safety of ENMs is the need to control their size, shape and morphology, and to produce them in high quantities. Synthetic procedures that produce gram-scale, well defined and monodisperse metallic nanoparticles with controlled size and shape, is not trivial and requires careful control of reaction conditions. This presentation will demonstrate our ability to develop new organic ligands that when used as stabilizers for metal nanoparticles, provide the ability to gain control of the particle size in one-step synthetic procedures. Monodisperse metallic nanoparticles were synthesized and characterized using spectroscopic, microscopic and x-ray techniques. The chemical composition, surface reactivity, solubility, and aggregation tendency of ENMs were studied under various environmental conditions. We will also discuss how ENMs interact with various components in the environment with an emphasis of their interaction with Gram-negative and Gram-positive bacteria. The results provide insights on the need for green manufacturing strategies of ENMs, their use and safe disposal practices.

11:20am **NM+AS+MS-MoM10 An Integrated Approach Toward Understanding the Environmental Fate, Transport, Toxicity and Occupational Health Hazards of Nanomaterials, V. Grassian**, University of Iowa **INVITED**

Nanoparticles, the primary building blocks of many nanomaterials, may become suspended in air or get into water systems, e.g. drinking water systems, ground water systems, estuaries and lakes etc. Therefore, manufactured nanoparticles can become a component of the air we breathe or the water we drink. One important issue in understanding the environmental fate, transport, toxicity and occupational health hazards of nanoparticles is in characterizing the nature and state of nanoparticles in air, water or in vivo. For the nanoparticles of interest in these studies, metals and metal oxides, it can be asked: (i) will metal oxide and metal nanoparticles be present in air or water as isolated particles or in the form of aggregates? (ii) will metal oxide and metal nanoparticles dissolve in aqueous solution or in vivo? and (iii) under what conditions will metal oxide and metal nanoparticles aggregate or dissolve? As the size regime will be very different depending on the state of the nanoparticles, as dissolved ions, isolated nanoparticles or nanoparticle aggregates, these questions are important to address as it impacts the size regime that needs to be considered or modeled in for example environmental transport or lung deposition models. Furthermore, the effect on biological systems including nanoparticle-biological interactions and toxicity will depend on the state of nanoparticles. In the studies discussed here, macroscopic and molecular-based probes that includes quantitative solution phase adsorption

measurements, molecular based probes, light scattering and zeta-potential measurements to investigate the behavior of nanoparticles in aqueous suspensions. We have focused on several different metal and metal oxide nanoparticles including Fe, Ag, Zn, Cu, Ce and Ti. Some of our newest results which focus on aggregation and dissolution, including detailed size-dependent studies, in the presence and absence of organic acids will be discussed. This research is beneficial as it significantly contributes to the growing database as to the potential environmental and health implications of nanoscience and nanotechnology and how nanomaterials will behave in the environment and impact human health.

# Monday Afternoon, October 29, 2012

## Nanomanufacturing Science and Technology Focus

### Topic

Room: 16 - Session NM+NS+MS+EM-MoA

### ALD and Scalable Processes for Nanomanufacturing

Moderator: T.S. Mayer, Penn State University

2:00pm **NM+NS+MS+EM-MoA1 From R&D Towards Industrial Atomic Layer Deposition: Challenges in Scaling up, M. Putkonen, Beneq Oy, Finland**

More and more ALD-enabled applications are emerging. Most of the ALD processes and applications are first demonstrated by small scale experiments. In optimal cases, the innovations lead to material-application combinations which have solid commercial interest. In the subsequent verification and pilot production phase, there is need for increased throughput and reduced costs also for the ALD processed materials.

There are two main features of ALD, that should be optimized when industrial scale production is being considered. Firstly, in large-area coating processes, more attention should be paid to the properties of the precursors. For large-area coatings, large doses of precursors are delivered to the substrates, preferably in very short pulses in order to keep the total cycle time as short as possible. This often requires either DLI-type sources or increased vapor pressure (i.e. increased thermal stability of metal precursors). In addition, although the ALD chemistry should be surface controlled and not dependent on the substrate surface area, deposition rates and film uniformities are habitually dependent on the tool configuration.

Secondly, ALD has so far been largely confined to laboratories due to non-availability of efficient, larger scale, high-throughput ALD systems. Whereas sputtering and CVD have been mainstream coating tools for decades, ALD has only recently started to gain acceptance as a mainstream industrial coating method. For example, ALD is widely seen as the desired manufacturing technology for producing high-quality functional layers for solar cells and packaging materials, but ALD is commonly considered too slow for high throughput manufacturing. However, large-area batch ALD tools, such as the Beneq P800, can operate up to 10 m<sup>2</sup> batch sizes and still maintain ALD cycle times in the range of 3-5 s. Currently, industrial ALD is diffusing into various industrial thin film areas where single wafer, batch or roll-to-roll ALD is the preferred coating method.

In this presentation, we discuss the different requirements for single wafer, conventional batch, cross-flow batch as well as spatial ALD deposition processes and tools for large throughput applications. In addition to conventional Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> processes, SiO<sub>2</sub> processes are used as examples when scaling up chemistry from single wafer to batch ALD. In addition, process transfer from an R&D scale Beneq TFS 200R rotating drum reactor to the true roll-to-roll Beneq WCS 500, developed for OLED encapsulation applications, is discussed in detail. Results of the studies using this system are presented including temperature dependence of growth rate, RI and WVTR measurements.

2:20pm **NM+NS+MS+EM-MoA2 Enabling ALD for Semiconductor Manufacturing, D. Chu, Applied Materials Inc. INVITED**

Atomic layer deposition (ALD) is being extensively studied for semiconductor applications because of its precise, atomic level thickness control for very thin films; ALD is extremely conformal and the overall thermal budget is lower than its CVD alternatives. However, ALD is inherently slow which makes it cost prohibitive.

Adoption of ALD processes into manufacturing requires consideration of multiple factors. At Applied Materials, we focus on three main areas to enable ALD for volume manufacturing.

1. Atomic level engineering to create differentiated solutions that boost device performance.
2. Tool architecture and methods to allow integration of multiple films without vacuum break. This is particularly of importance when films scale to Angstrom level, stability of the film becomes an issue. Extendable tool architectures allow integration of other films such as capping layers and pre-post treatments to address this issue
3. Accelerate adoption of standalone ALD films by improving manufacturability and productivity while maintaining single wafer performance

Example applications and challenges for each area will be discussed in this paper.

3:00pm **NM+NS+MS+EM-MoA4 Migration to ALD Techniques in the Semiconductor Industry: Pattern Effects, Microloading and Film Thickness Variability in Dielectric Thin Films Deposition, M.P. Belyansky, IBM Semiconductor R&D Center**

The continuation of scaling in the microelectronics industry is having a profound effect on thin film deposition techniques and processes. One of the consequences of the scaling is a decrease in average film thickness to accommodate the shrinking device dimensions which amplifies the problem of film thickness variability. Most of the CVD deposition techniques and tooling are reaching the limit of reliable thickness control of very thin films. At the same time, circuit designs are becoming more complex, which leads to significant pattern density variation on macro scale. Therefore CVD technology is facing a tremendous challenge in controlling film thickness and properties across variable pattern density which has been one of the major reasons that facilitated the transition to ALD-like deposition techniques and processes in the industry.

The paper discusses the microloading effect (dependence of thin film deposition rate on pattern density) as well as other manifestations of pattern effects in the semiconductor manufacturing. The data shows the effect of microloading on the variation of as deposited film thickness across features of different size as well as for identical features with different pattern density in the surrounding areas. The microloading performance of CVD and ALD silicon oxide and silicon nitride dielectric thin films is covered as well as methods aimed at quantifying and improving thin film variability. The effects of major process parameters, precursor chemistry and tool design on the thin films microloading performance are delineated. Thin films step coverage over a nano scale feature and pitch to pitch film thickness dependence for CVD and ALD dielectric processes are also discussed.

3:40pm **NM+NS+MS+EM-MoA6 Interface Analysis of PEALD TaCN Deposited on HfO<sub>2</sub> using Parallel Angle Resolved X-ray Photoelectron Spectroscopy for sub-20nm Gate Last CMOS Transistors, F. Pierrat, ST Microelectronics, France, V. Beugin, R. Gassilloud, P. Michallon, CEA Grenoble, France, L. Dussault, B. Pelissier, LTM - MINATEC - CEA/LETI, France, C. Leroux, CEA Grenoble, France, P. Caubet, ST Microelectronics, France, C. Vallée, LTM - MINATEC - CEA/LETI, France**

Sub-20 nm high-k/metal CMOS devices require about 2 nm thin metal gate electrode with adapted work function (WF) and chemical inertness regarding the high-k dielectric sub-layer. TaCN material deposited by Plasma Enhanced Atomic Layer Deposition (PE-ALD) has been investigated as a possible gate electrode candidate [1-2]. Depending on the carbon content TaCN can presents a *p-type* behavior with a WF from 4.5 to 4.7eV [3]. Besides plasma used for deposition may have an impact on the under-layer dielectric such as an increase of the EOT [4]. A deviation from bulk material characteristics of the metal gate WF is induced by the intimate bond linking environment at high-k/TaCN interface, but these chemical mechanisms are still unclear. Thus, in this work, interface of TaCN and HfO<sub>2</sub> dielectric is carefully analyzed by X-Ray Photoelectron Spectrometry (XPS), using Ta4f, Hf4f, O1s, C1s, N1s and Si2p core levels, and obtained bonding environments are correlated to work function extracted from MOS capacitors.

Thanks to chemical stability of SiO<sub>2</sub> [5], bonding environments of TaCN/SiO<sub>2</sub> and HfO<sub>2</sub>/SiO<sub>2</sub> stacks were chosen as reference for XPS analysis. Then, by comparing TaCN deposited on HfO<sub>2</sub> spectra with these references, the evolution of the chemical environments can be determined, thus a mechanism of interaction between the two materials is proposed. Furthermore, it appeared that, when deposited on HfO<sub>2</sub>, TaCN oxidation is higher than on SiO<sub>2</sub>, which is attributed to the higher capacity of HfO<sub>2</sub> to have O deficiency [6].

In addition, TaCN/HfO<sub>2</sub>/SiO<sub>2</sub> stack was measured using Parallel Angle Resolved XPS (PARXPS) in order to build a depth composition profile. This profile confirms the modifications of chemical environment such as oxidation of the electrode close to high-k/metal interface, it also shows N penetration in HfO<sub>2</sub>, which could be induced by plasma densification.

Finally, electrical results from MOS capacitors with TaCN/HfO<sub>2</sub>/SiO<sub>2</sub> stacks and TiN/W plug have shown an evolution of the *p-like* metal flat band voltage (V<sub>fb</sub>) with plasma conditions. The modifications of chemical bonding environment observed at the high-k/metal interface can give insight on this deviation of V<sub>fb</sub> with plasma.

[1] W. S. Hwang, D. Chan, B. Jin Cho, IEEE Transactions on Electron Devices, 55, (2008)

[2] H. Zhu and R. Ramprasad, Journal of Applied Physics 109, 083719 (2011)

- [3] H. N. Alshareef, et al., *Electrochemical and Solid-State Letters*, 11, H182 (2008)
- [4] H. C. Shin and C. Hu, *Semiconductor Science Technologic*, 11, 463, (1996)
- [5] M. Zier, et al., *Applied Surface Science* 252, 234 (2005)
- [6] G. D. Wilk, R. M. Wallace and J. M. Anthony, *Journal of Applied Physics* 89, 5243 (2001)

**4:20pm NM+NS+MS+EM-MoA8 Atmospheric Pressure Atomic Layer Deposition of Al<sub>2</sub>O<sub>3</sub> using Trimethylaluminum and Ozone, M.B. Mousa, D.H. Kim, C.J. Oldham, G.N. Parsons, North Carolina State University**

Atomic layer deposition (ALD) is used for nanoscale coatings with high uniformity and precise thickness control. Currently, most commercial ALD processes operate in batch mode. Expanding to ambient pressure can increase throughput and facilitate its integration for applications such as smart textiles, flexible electronics and synthetic polymer coatings. We find that under certain flow conditions in the trimethylaluminum (TMA)/water ALD process for Al<sub>2</sub>O<sub>3</sub>, increasing the reactor pressure from ~ 2 Torr to 760 Torr can produce excess film growth per cycle.

For this work, we studied ALD of Al<sub>2</sub>O<sub>3</sub> using TMA/O<sub>3</sub> and compared growth at ~ 2 Torr to that at 760 Torr in a flow tube reactor. We measured film thickness by ellipsometry and surface morphology by AFM. Also, we plan to monitor in-situ growth using a quartz crystal microbalance (QCM). At 2 Torr, by changing the ozone and TMA exposure times, we saw clear ALD saturation at ~ 0.45 Å/cycle at 170°C. A shorter purging time after the ozone exposure tends to increase the growth per cycle. Deposition at higher pressure results in growth rates between ~0.3 and 0.6 Å/cycle at 205°C, with lower growth rates obtained under higher gas flow rate conditions. For both the water and O<sub>3</sub> processes at 760 Torr, a low gas flow rate of 0.5 standard liters per minute (slm) in our flow-tube reactor leads to a high growth rates of ~3 Å/cycle (for water) and 0.6 Å/cycle (for O<sub>3</sub>). For the water process at 760 Torr, increasing the flow rate to 10 slm somewhat decreases the growth per cycle to ~1.35 Å /cycle. However, for the O<sub>3</sub> processes at 760 Torr, we need only a relatively small increase to 1.5 slm to achieve growth of 0.3 Å/cycle. This could be due to enhanced ozone desorption kinetics compared to the rate of water desorption under the conditions used. Also interestingly, we find for the water process that films deposited at high pressure have higher surface roughness than films deposited at low pressure. These results will help to identify the key parameters for new continuous atmospheric pressure ALD reactors designs.

**4:40pm NM+NS+MS+EM-MoA9 An Industrial Solution for Surface Passivation of c-Si using AlO<sub>x</sub> Film Deposited by In-line Atmosphere Chemical Vapor Deposition, K. Jiang, Gebr. Schmid GmbH + Co, Germany, K.O. Davis, University of Central Florida, C. Demberger, H. Zunft, H. Haverkamp, Gebr. Schmid GmbH + Co, Germany, W.V. Schoenfeld, University of Central Florida, D. Habermann, Gebr. Schmid GmbH + Co, Germany**

Among the different dielectric passivation layers for crystalline silicon (c-Si) solar cells, AlO<sub>x</sub> has recently received a great attention due to its excellent chemical and field effect passivation performance for p-type c-Si surface. It offers great promise as a rearside passivation material for passivated emitter and rear cell (PERC) designs. However, up to this point in time, most of the development has been based on laboratory scale deposition systems and methods. Common approaches for synthesizing these passivation layers are thermal or plasma-assisted atomic layer deposition (ALD), whose deposition rates are typically too low (< 10 nm/min) to be compatible with high-volume manufacturing. Other deposition methods like PECVD or spatial separated ALD enable an increase in deposition rate by one order of magnitude (i.e. 100 nm/min). An industrially-compatible deposition technique with low processing cost, easy-handling, compact size, and high throughput that still retains comparable passivation performance to ALD films remains a challenging task.

Using an in-line atmosphere chemical vapor deposition (APCVD) tool, we have synthesized amorphous AlO<sub>x</sub> films from precursors of trimethylaluminum and O<sub>2</sub>, yielding a maximal deposition rate of up to 150 nm/min per wafer. Deposition rate is determined by the film thickness divided by wafer transportation time through the CVD injector. Both top view and the cross-sectional SEM images present an intact AlO<sub>x</sub>/Si interface. A smooth surface is shown without any outgassing (blistering) after deposition and a subsequent firing step. The as-deposited layers exhibit an over stoichiometric O/Al ratio of 1.65~1.75 due to the incorporation of an OH group inside the layer. For both high and low doped p-type c-Si wafers deposited with APCVD AlO<sub>x</sub>, excellent surface passivation is achieved with a maximum effective surface recombination velocities ( $S_{\text{eff,max}}$ ) of 8 cm/s following by a firing step. These findings are attributed to the buildup of a large negative charge ( $Q_f \approx -3 \times 10^{12} \text{ cm}^{-2}$ ) and low interface defect density ( $D_{\text{it}} \approx 4 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ ) following the firing

process. It is believed that the incorporated OH group plays an essential role during the firing step. During the annealing/firing step, a certain degree of dehydration takes place (i.e. Al sites bonded OH termination start to bond via an O bridge), which may involve an octahedral to tetrahedral coordination change. This could facilitate the negative charge formation and release of atomic H for passivating the Si dangling bonds at the AlO<sub>x</sub>/Si interface.

This data implies a high application potential of APCVD AlO<sub>x</sub> for low cost industrial solar cell applications.

**5:00pm NM+NS+MS+EM-MoA10 Solution Based Processing of Floating Gate Memory using Additive-Driven Self-Assembly and Nanoimprint Lithography, J. Watkins, University of Massachusetts**

**INVITED**

Polymer and polymer-inorganic hybrid materials organized at the nanoscale are at the heart of many devices that can be created on flexible substrates for applications in energy generation and storage, microelectronics, optoelectronics, communications and sensors. The challenge is to produce these materials using process platforms and materials sets that are environmentally and economically sustainable and can be scaled for cost-effective, high value-added manufacturing. Here we describe a resource efficient, additive approach based on roll-to-roll coating of self-assembled hybrid materials. Specifically we report that nanostructured templates with periodic spherical, cylindrical, and lamellar morphologies exhibiting sub-10 nm domains can be easily obtained through the blending of commercially available disordered polymer surfactants with commodity homopolymers that selectively associate with one segment of the surfactant. We further demonstrate that order in the surfactant systems and in block copolymer templates can be induced by nanoparticle additives that undergo multi-point hydrogen bonding with one of the segments of the polymer template. These additives, which include metal and semiconducting nanoparticles, fullerenes, and other active components, impart functionality to the device. The strong interactions further enable particle loadings of more than 40% in the target phase, resolving a crucial constraint for many applications. These systems can be scaled in our newly constructed R2R processing facility, which includes a custom micrograture coater for hybrid materials that is equipped for in-line substrate planarization and a precision R2R UV-assisted nanoimprint lithography (NIL) tool.

We illustrate the capabilities of these approaches by the fabrication of floating gate field effect transistor memory devices. For this application, the charge trapping layer is comprised of well-ordered polymer/gold NP composites prepared via additive-driven self-assembly; the addition of gold nanoparticles that selectively hydrogen bond with pyridine in poly(styrene-*b*-2-vinyl pyridine) copolymers yields well-ordered hybrid materials at gold nanoparticle loadings of more than 40 wt.%. The charge trapping layer is sandwiched between a dielectric layer and a poly(3-hexylthiophene) semiconductor layer. We can achieve facile control of the memory windows by changing the density of gold nanoparticles. The devices show high carrier mobility (> 0.1 cm<sup>2</sup>/Vs), controllable memory windows (0~50V), high *on/off* ratio (>10<sup>5</sup>) between memory states and long retention times. Strategies for patterning of the device using NIL will be discussed.

# Tuesday Morning, October 30, 2012

## Nanomanufacturing Science and Technology Focus

### Topic

Room: 16 - Session NM+MS-TuM

### All Invited Session: Challenges of Nanomanufacturing from an Industrial Perspective

**Moderator:** S. Butler, Texas Instruments, B.R. Rogers, Vanderbilt University

#### 8:00am NM+MS-TuM1 Challenges of Nanomanufacturing from an Industrial Perspective. A. Sekiguchi, Tokyo Electron Limited **INVITED**

In the semiconductor industry, we have been able to benefit from cost reductions associated with physical scaling of memory and logic devices for decades. By reducing the physical dimensions of our devices from generation to generation, we have been able to drive bit cost of memory and processing power cost of our logic devices with ease. Today however, challenges associated with atomic scale manufacturing and control are daunting, to say the least. Dimensional controls are in the single nm range, six sigma, for lateral scales, and in the sub-Angstrom range for critical film thicknesses. The talk will describe the device level challenges that we face in this era of nano-scale manufacturing, explore options that we have in terms of patterning at 1x nm node and below, and discuss process options that will be needed in the next generation of devices.

#### 9:00am NM+MS-TuM4 PRINT® Nanomanufacturing Technology-Precisely Engineered Particles for Life Science Applications, M. Hunter, Liquidia Technologies, INC. **INVITED**

Nanomedicine, an offshoot of nanotechnology, refers to highly specific medical intervention at the molecular scale for treating and curing disease or repairing damaged tissues, such as bone, muscle, or nerves. At this size scale – about 500 nanometers or less –biological molecules and structures operate inside living cells. The pharmaceutical industry continues to evaluate the potential of these new technologies to alleviate the burden of rising research costs, improve the speed and efficiency of the discovery process, and create high-value new generation therapeutics. While nanotechnology is widely seen as having huge potential, the pharmaceutical industry remains skeptical that success at the bench scale can successfully be translated into high volume products.

Liquidia's PRINT® technology (Particle Replication in Non-Wetting Templates) is one example of a breakthrough in micro- and nanoparticle manufacturing that allows complete control over particle size, shape and chemical composition. Since its inception, Liquidia has been addressing nanoparticle manufacturing scale-up by adapting the PRINT particle fabrication process to merge the high-volume production methodologies of roll-to-roll processing and the high precision fabrication methods of the microelectronics industry. Using PRINT technology, Liquidia has the ability to rapidly scale up cGMP manufacturing of particles with unprecedented control over the composition and geometry. This creates the unique ability to manufacture high volumes of complex micro- and nanostructured objects in a number of particle geometries and a variety of materials in a cost paradigm that is very attractive. Using manufacturing methodologies developed and proven in other industries including the printing, film and medical device industries, Liquidia plans to scale its particle manufacturing capabilities to supply commercial quantities for a variety of industries, including diagnostics, vaccines and therapeutics.

#### 10:40am NM+MS-TuM9 High Productivity Combinatorial R&D Technologies for Cost-Effective Nanomanufacturing, D. Lazovsky, C. Hunter, Intermolecular, Inc. **INVITED**

Nanomanufacturing is inherently more challenging than the production of micron-scale and larger device structures, as interface effects increasingly dominate device performance for nano-scale devices. Theoretical understanding of such effects lags the results of practice, so empirical experimentation is necessary to simultaneously co-optimize multiple critical elements. Such co-optimization using traditional research and development (R&D) methods is typically inefficient, slow and expensive.

Cost-effective nanomanufacturing starts with the development of an optimized device structure, which depends upon our ability to learn about material interactions. For example, while a basic photovoltaic (PV) cell can be made with just 4 layers (n- and p-regions, two contacts), thin-film PV cells designed for optimum efficiency today use additional 10-50nm thick layers to modify band-gaps, optimize light reflection, and extract maximum current.

Even if an optimized nanodevice structure has been identified, it cannot be trivially transferred to high-volume manufacturing (HVM). Different tooling alters process conditions, which generally results in non-optimal final device performance as well as manufacturing yield losses. As an example, while the champion Cu(In,Ga)Se<sub>2</sub> (CIGS) cell from a lab has reached >20% conversion efficiency, the best reported from HVM lines today is only ~14%.

Once a nanomanufacturing line is running, experiments are needed to enhance device performance and improve line yield. However, it is inefficient to do R&D using the production line since the experiments must compete with manufacturing runs, and the HVM tools are generally not ideal for experiments. With inefficiency in R&D learning cycles, improving yield is slow and expensive.

A more efficient approach uses a high productivity combinatorial (HPC™) platform—such as that developed by Intermolecular—to dramatically accelerate R&D by 10-100x relative to traditional methods. With unique combinatorial process tools, throughput-matched characterization, and an informatics analysis and data management system, in less than a year we developed a world-class 17.7% active-area efficiency CIGS PV cell using a two-step sulfur-free process flow.

Intermolecular's HPC platform is purpose-built for the R&D of semiconductor and clean-energy products, and is used in Collaborative Development Programs (CDPs) with a growing number of customers. For example, leading-edge semiconductor memory chips today use dielectrics and metal electrode layers that are only 1-10 nm thick, and HPC technology has accelerated R&D learning-cycles and time-to-market for our customers producing such memory chips.

# Friday Morning, November 2, 2012

## Graphene and Related Materials Focus Topic Room: 13 - Session GR+EM+ET+MS+NS-FrM

### Graphene Device Physics and Applications

**Moderator:** A. Turchanin, University of Bielefeld, Germany

#### 8:20am GR+EM+ET+MS+NS-FrM1 Heterointegration of Graphene with Nano and Molecular Scale Structures for High Performance Devices, X. Duan, University of California, Los Angeles **INVITED**

Nanoscale integration of dissimilar materials with distinct compositions, structures and properties has the potential to create a new generation of integrated systems with unique functions and/or unprecedented performance to break the boundaries of traditional technologies. In this talk, I will focus my discussion on the heterointegration of graphene with a variety of nano and molecular scale structures of designed architectures to open up exciting opportunities for nanoscale device engineering. In particular, I will discuss our recent effort in integrating graphene with a self-aligned nanowire gate to create the highest speed graphene transistors, integrating graphene with plasmonic nanostructures to create multi-color high speed photodetectors, integrating graphene with nanoscale templates for the creation of graphene nanostructures, and integrating graphene with various  $\pi$ -conjugating molecular systems for band gap engineering and molecular sensing.

#### 9:00am GR+EM+ET+MS+NS-FrM3 Graphene RF: From Fundamentals to Opportunities, J.S. Moon, H.-C. Seo, M. Antcliffe, S. Lin, A. Schmitz, D. Le, C. McGuire, D. Zehnder, HRL Laboratories LLC, L.O. Nyakiti, V.D. Wheeler, R.L. Myers-Ward, C.R. Eddy, Jr., D.K. Gaskill, P.M. Campbell, Naval Research Laboratory, K.-M. Lee, P. Asbeck, UC San Diego **INVITED**

Graphene is a topic of very active research from basic science to potential applications. Various RF circuit applications are under evaluation, which include low-noise amplifiers, frequency multipliers, mixers and high-speed radiometers. Potential integration of graphene on Silicon substrates with CMOS compatibility would also benefit future RF systems. The future success of the RF circuit applications depends on vertical and lateral scaling of graphene MOSFETs to minimize parasitics and improve gate modulation efficiency in the channel. In this presentation, we highlight recent progress in graphene materials and devices. For example, with hydrogen intercalation, a graphene wafer showed an electron mobility of 2500 cm<sup>2</sup>/Vs at 6.8 x 10<sup>12</sup>/cm<sup>2</sup> carrier density, and sheet resistance of 230 ohm/square. The Ti-based ohmic contact resistance is below 100 ohm\* $\mu$ m and hysteresis in HfO<sub>2</sub>/Graphene MOSFET transfer curves are no longer concerns in RF applications. We will show graphene MOSFETs in mixer and detector applications with performances comparable to and better than the current state-of-the-art technologies. Also, we will present recent progress in graphene heterostructure based diodes with on/off ratio greater than 10<sup>6</sup>. In summary, while graphene is relatively new material, it shows a strong potential to become disruptive in RF applications.

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The views, opinions, and/or findings contained in this article/presentation are those of the author/presenter and should not be interpreted as representing the official views or policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the Department of Defense.

[1] J. S. Moon and D. K. Gaskill, IEEE Trans. Microwave Theory and Techniques, p. 2702, 2011

#### 9:40am GR+EM+ET+MS+NS-FrM5 Graphene and Dielectric Integration: A Sticky Situation?, V.D. Wheeler, N.Y. Garces, L.O. Nyakiti, R.L. Myers-Ward, D.J. Meyer, U.S. Naval Research Laboratory, A. Nath, George Mason University, C.R. Eddy, Jr., D.K. Gaskill, U.S. Naval Research Laboratory **INVITED**

Scalable high- $\kappa$  dielectric integration is needed to realize graphene-based THz transistors. Yet, the inert nature of graphene inhibits direct application of high-quality uniform atomic layer deposition (ALD) dielectrics. While several methods have rendered the surface more susceptible to ALD[1], they often degrade mobility and/or shift the Dirac voltage due to charges within the gate stack. Recently, we developed a dry chemical functionalization approach using XeF<sub>2</sub> that results in conformal, thin high- $\kappa$  ALD oxide films with a 10-25% improvement in graphene mobility[2], high dielectric constants (HfO<sub>2</sub>=18.5, Al<sub>2</sub>O<sub>3</sub>=8.9), and small Dirac voltage shifts (HfO<sub>2</sub>=2V, Al<sub>2</sub>O<sub>3</sub>=0.1V), indicating the effectiveness of F functionalization.

We will present in-depth details of our fluorination process, discuss its advantages and limitations with respect to other methods used to enhance ALD reactivity with graphene, and provide future directions for this field of study.

Fluorination of EG surfaces was performed in a Xactix X3 XeF<sub>2</sub> etcher operating in pulse mode. Results show that 15 nm pinhole-free Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> films are obtained with an optimized XeF<sub>2</sub> surface treatment prior to ALD consisting of six, 20s pulses (XeF<sub>2</sub>=1 torr, N<sub>2</sub>=35 torr). This optimal treatment resulted in ~6% fluorine surface coverage, as semi-ionic C-F bonds (F1s ~687eV) only, which provided additional ALD reaction sites needed to obtain uniform oxide films. This unique semi-ionic nature of the C-F bond allows the graphene lattice to maintain planarity and minimize degradation to transport properties.

Theoretical studies suggest that the semi-ionic nature of the C-F bond is related to the graphene electron sheet carrier density ( $n_e$ ), requiring at least 10<sup>13</sup> cm<sup>-2</sup> to form[3]. To test this, EG samples with similar thickness but varying  $n_e$  (2x10<sup>12</sup>-1.3x10<sup>13</sup> cm<sup>-2</sup>) were fluorinated simultaneously using the optimal conditions above. Samples with  $n_e > 1 \times 10^{13}$  cm<sup>-2</sup> had only semi-ionic C-F bonding, but those with  $n_e < 1 \times 10^{13}$  cm<sup>-2</sup> had both covalent and semi-ionic bonding – verifying the theoretical calculations. The amount of covalent bonding increased as  $n_e$  decreased, and an increased pinhole density was seen in subsequent Al<sub>2</sub>O<sub>3</sub> films. This implies that the underlying EG properties can impact the effectiveness of this fluorination method. Yet, by adjusting the pulse conditions one can tailor this method to still obtain uniform ALD oxides on low carrier density and even p-type EG. To this end, results of our XeF<sub>2</sub> approach on p-type H<sub>2</sub> intercalated EG samples will be shown.

1. Garces, et al. *JVST B* **30**(3) 03D104 (2012)
2. Wheeler, et al. *Carbon* **50** 2307 (2012)
3. Sofo, et al. *Phys Rev B* **83**(8) 081411(R) (2011)

#### 10:20am GR+EM+ET+MS+NS-FrM7 Achieving Scaled Dielectrics on Graphene Using Atomic Layer Deposition, S. Jandhyala, G. Mordi, R.M. Wallace, J. Kim, University of Texas at Dallas

In order to realize high-performance graphene-based field-effect-devices, local gating of graphene channel is one of the foremost requirements [1]. Therefore, deposition of high-quality, scalable dielectrics on graphene is required. The ability to precisely control thickness and conformally deposit materials makes atomic layer deposition (ALD) an ideal technique for achieving such dielectrics [2]. However, ALD is a surface-reaction limited process [2] and graphene, being sp<sup>2</sup> bonded, has no *out-of-plane* covalent functional groups [3] and this can cause difficulties in initiating the ALD reaction [4]. In previous studies we have shown that using a reversibly physisorbed ozone (O<sub>3</sub>) functionalization approach, we can deposit high quality ALD oxides (such as Al<sub>2</sub>O<sub>3</sub>) on graphene with thicknesses below 5 nm [5]. Further understanding regarding the interaction of O<sub>3</sub> and metal precursors with graphene is required for successfully applying the ozone process to deposit different oxides.

In this study, we will use *in-situ* electrical measurements of graphene devices inside an ALD chamber as a characterization technique in order to understand the adhesion mechanisms of oxidants (such as O<sub>3</sub> and H<sub>2</sub>O) and metal precursors (such as trimethylaluminum-TMA, titanium tetrachloride-TiCl<sub>4</sub>) on graphene surfaces. The characterization scheme used is packaged back-gated graphene-FETs which can detect the molecules adsorbed on the graphene surface. We will compare exfoliated graphene and chemical vapor deposited (CVD) graphene (which tends to have a higher number of defect sites). Using such *real-time* electrical measurements, the observed charge scattering mechanisms and the effect on mobility and doping due to the interaction of these molecules with graphene will be presented.

### Acknowledgement

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- [3] A. H. Castro Neto, et al., *Rev. Mod. Phys.* **81** (1), pp. 109-162 (2009)
- [4] L. Liao, X. Duan, *Mat. Sci. Eng. R* **70** (3-6), pp. 354-370, (2010)
- [5] S. Jandhyala, et al., *ACS Nano*, **6** (3), pp. 2722-2730 (2012)

10:40am **GR+EM+ET+MS+NS-FrM8 Atomically-Smooth MgO Films Grown on Epitaxial Graphene by Pulsed Laser Deposition.** *S.C. Stuart, A.A. Sandin*, North Carolina State University, *O. Nayfeh, M.D. Dubey*, Army Research Laboratory, *J.E. Rowe, D.B. Dougherty*, North Carolina State University, *M.D. Ulrich*, Army Research Office

The growth of high quality insulating films on graphene is a crucial materials science task for the development of graphene-based spintronics because graphene is a potentially revolutionary material for electronic and spintronic applications. For efficient spin-injection, graphene is expected to suffer from the well known “conductivity mismatch” problem at metal-semiconductor spin electrode interfaces. The standard approach to mitigating this problem has been to grow thin, insulating tunnel barriers between the graphene and the magnetic metallic electrode to provide a spin-dependent resistance via the tunneling magnetoresistance effect. It has been demonstrated by several experiments that direct spin injection from a magnetic electrode to graphene is possible but using aluminum oxide or MgO tunnel barriers to assist injection in graphene spin-valve devices is more efficient if suitable oxide-graphene interfaces can be formed. To address this problem we have used pulsed laser deposition (PLD) to grow thin (1-1000 nm) magnesium oxide films directly on epitaxial graphene on SiC(0001). We observe very smooth film morphologies (typical rms roughness of ~0.4 nm) that are nearly independent of film thickness and conform to the substrate surface which had ~0.2 nm rms roughness. Surface roughness is less than 0.5 nm for thicknesses up to 1000 nm and is independent of deposition laser pulse energy within the range 300-700 mJ/pulse at rates of 1-50 Hz. X-ray diffraction shows predominant (111) and (100) orientations, indicating the possibility of doping the graphene by the polar (111) interface. Raman spectroscopy indicates that the graphene is not measurably damaged by magnesium oxide growth. This work shows that PLD is a good technique to produce graphene-oxide interfaces without pre-deposition of an adhesion layer. The films are free of defects or pinholes (that can be observed by atomic force microscopy) and can be grown at arbitrary thicknesses without increasing the roughness or damaging the graphene. The details and kinetics of the deposition process will be described with comparisons being made to other dielectric-on-graphene deposition approaches.

11:00am **GR+EM+ET+MS+NS-FrM9 Facile, Controllable Graphene-based P-N Junctions Using Self-Assembled Monolayers.** *J. Baltazar, H. Sojoudi, J. Kowalik, L. Tolbert, S. Graham, C.L. Henderson*, Georgia Institute of Technology

In this study we investigate the use of a self-assembled monolayer (SAM) to create a p-n junction in graphene films. Previous techniques rely on charge transfer from adsorbants or electrostatic gate/potentials. Here we demonstrate that, by successfully modifying the SiO<sub>2</sub> surface with an aminopropyltriethoxysilane (APTES) layer, and using intrinsically p-doped transferred CVD graphene films, a well-defined junction can be achieved. Field-effect transistors and p-n junction regions are fabricated prior to graphene film transfer, in order to preserve the pristine properties of the graphene. The I-V characteristic curve indicates the presence of two thermally-controllable neutrality points. This method allows a facile, controllable and low temperature fabrication of graphene p-n junctions.

11:20am **GR+EM+ET+MS+NS-FrM10 Impact of Cleaning Procedures on the Performance of Graphene-Based Field Effect Transistors.** *M. Lodge, M. Ishigami*, University of Central Florida

It is now widely accepted that surface contaminants have large effects on the performance of graphene-based field effect transistors. Various techniques are now available to clean processing residues from graphene, yet some of these techniques are chemically aggressive leaving concerns that they may damage graphene and affect the device performance. In addition, there are no consensus on the best method to produce the cleanest and, therefore, the best graphene devices.

Here, we have performed a study on the impact of various chemical treatments on the performance of field effect transistors fabricated from graphene grown using chemical vapor deposition. By measuring the impact of hydrogen-annealing, oxygen-annealing, and various solvent-based cleaning on 50 graphene field effect transistors, we generate a statistically-significant conclusion on the best cleaning technique for producing the highest performance. We will present our results along with our scanning tunneling microscopy images and Raman spectra to shed a light on the mechanism involved in each cleaning technique.

11:40am **GR+EM+ET+MS+NS-FrM11 High Efficiency Graphene Solar Cells by Chemical Doping.** *X. Miao, S. Tongay, M.K. Petterson, K. Berke, A.G. Rinzler, B.R. Appleton, A.F. Hebard*, University of Florida

We demonstrate single layer graphene/n-Si Schottky junction solar cells that under AM1.5 illumination exhibit a power conversion efficiency (PCE) of 8.6%. This performance, achieved by doping the graphene with

bis(trifluoromethanesulfonyl)amide, exceeds the native (undoped) device performance by a factor of 4.5 and is the **highest PCE** reported for graphene-based solar cells to date. Current-voltage, capacitance-voltage, and external quantum efficiency measurements show the enhancement to be due to the doping-induced shift in the graphene chemical potential that increases the graphene carrier density (decreasing the cell series resistance) and increases the cell's built-in potential (increasing the open circuit voltage) both of which improve the solar cell fill factor.

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