## Nanomanufacturing Science and Technology Focus Topic
## Room: 207 - Session NM+MS+NS+TF-MoM

### ALD for Nanomanufacturing
**Moderator:** B. Lu, AIXTRON Inc.

9:00am **NM+MS+NS+TF-MoM3 Industrialization of Atomic Layer Deposition: From Design to Deposition**, ***J.S. Becker***, *A. Bertuch, R. Bhatia, L. Lecordier, G. Liu, M. Sershen, M. Sowa, R. Coutu, G.M. Sundaram*, Cambridge NanoTech, Inc. **INVITED**

The demonstrated benefits provided by Atomic Layer Deposition (ALD) in producing films of exceptional uniformity, and conformality, has set the stage for its use in large area, batch processing, and Roll-to-Roll applications. In this work we discuss the use of Computational Fluid Dynamics (CFD) as a means of gaining insight into the system performance of such industrial instruments, but also as a technique for refining system design. Additionally we describe the basic underpinnings of design for ALD systems operated under atmospheric conditions, (for Roll-to-Roll use), along with the design factors which must be considered for zone separated ALD methods. Finally we will present film results taken from a zone-separated ALD system, and discuss the salient aspects of the deposition process.

9:40am **NM+MS+NS+TF-MoM5 Improved MOS Characteristics of $CeO_2/La_2O_3$ and $MgO/La_2O_3$ Gate Stacks Prepared by ALD**, ***T. Suzuki***, *M. Kouda*, Tokyo Institute of Technology and AIST, Japan, *K. Kakushima, P. Ahmet, H. Iwai*, Tokyo Institute of Technology, Japan, *T. Yasuda*, AIST, Japan

$La_2O_3$ is one of the candidate materials for the next-generation high-k gate stacks because it can achieve sub-1 nm EOT by forming direct-contact La silicate with Si. There have been many ALD studies for $La_2O_3$, however, the performance of the MOSFETs incorporating ALD-$La_2O_3$ needs much improvement. Our previous studies using EB evaporation showed that capping the $La_2O_3$ dielectrics with an ultrathin layer of $CeO_2$ or metallic Mg (~1 nm) effectively improved the channel mobility [1,2]. In this paper, we report fabrication of $CeO_2/La_2O_3$ and $MgO/La_2O_3$ gate stacks by ALD/CVD for the first time, and demonstrate that these stacks show improved electrical properties (k value, channel mobility, etc.) as compared to single-layer ALD-$La_2O_3$.

The experiments were carried out using a multi-chamber ALD/CVD system which was capable of in-situ metallization and RTA. The $CeO_2/La_2O_3$ and $MgO/La_2O_3$ gate stacks were formed on H-terminated Si(100) using $Ce[OCEt_2Me]_4$, $La(^iPrCp)_3$, and $Mg(EtCp)_2$ metal sources. $La_2O_3$ and MgO films were formed by ALD using $H_2O$ as an oxidant. The ALD temperature was set at a relatively low temperature of 175°C in order to ensure the self-limiting growth [3]. $CeO_2$ films were formed in the CVD mode via thermal decomposition of $Ce[OCEt_2Me]_4$ at 350°C. The gate electrodes were formed by sputtering of W. MOSFETs were fabricated by the gate-last process.

The effective k values for the $CeO_2$(1nm)/$La_2O_3$(3nm) and MgO(0.8nm)/$La_2O_3$(4nm) stack capacitors were approximately 16, which was significantly larger than those for La silicate without any capping layer (k=10~12). The k-value improvement by the $CeO_2$ capping is presumably due to the higher k value of $CeO_2$ (~23), whereas the improvement by the MgO capping is ascribed to suppression of excessive La-silicate formation.

We have also found that the $CeO_2/La_2O_3$ gate stack leads to excellent mobility characteristics. The mobility for the MOSFET with 1.43 nm EOT was 214 $cm^2$/Vs at an effective field of 1.0 MV/cm, which was 85% of the Si universal mobility. The mobility improvement by the $CeO_2$ capping is attributed to the reduced fixed-charge density, since $V_{th}$ approached to the ideal values by the $CeO_2$ capping. On the other hand, the MgO capping induced a negative shift in $V_{th}$ and consistently degraded the mobility. These effects of ALD-MgO capping are qualitatively different from those observed for EB-evaporated Mg [2]. The mechanisms causing such a difference between EB evaporation and ALD are now under investigation.

This work was carried out in Leading Research Project for Development of Innovative Energy Conservation Technologies supported by NEDO.

**References:** [1] T. Koyanagi, et al., JJAP, **48**, 05DC02 (2009); [2] M. Kouda, et al., 2009 VLSI Symp., p. 200; [3] K. Ozawa, et al.,2010 ICSICT, p. 932.

10:00am **NM+MS+NS+TF-MoM6 Highly Uniform and Conformal Thin Film Metallization with Thermal and Plasma-Enhanced Atomic Layer Deposition**, *M. Toivola, J. Kostamo, T. Malinen, T. Pilvi, T. Lehto,* ***C. Dezelah***, Picosun Oy, Finland

Ultra-thin, nanometer-scale metal or metallic films are a crucial component in e.g. several applications of modern MEMS/NEMS (Micro/NanoElectroMechanical Systems) and other advanced IC technologies, sensors, optical devices and catalyst manufacturing. When the component sizes keep diminishing and at the same time, the level of system integration increasing (for example the so-called "System-in-a-Package" multifunctional chip devices), it creates a drive from "conventional" 2D device architecture to 3D component integration. Through Silicon Vias (TSV) are a central structure in these 3D-stacked devices and there's often a need to produce highly uniform and conformal thin films of metals or otherwise conducting materials on the insides of the vias. Due to the often very high aspect ratio (AR) of the TSV structures, Atomic Layer Deposition (ALD) is one of the only methods with which reliably uniform and conformal material layers can be deposited on the via walls.

Industrially upscalable ALD processes were developed for several metals and metallic compounds, i.e. Pt, Ir, Ru, Cu, Ag, Au, TiN and TiAlCN. Deposition of metals can be done with thermal ALD and plasma-enhanced (PEALD). The main benefits of the PEALD technique are the possibility to use reductive processes instead of oxygen, lower deposition temperatures which decreases the thermal stress on the substrates, and a wider variety of precursor chemicals.

Inductively coupled remote plasma source system was further developed to reduce any possibility of plasma damage, which can often happen in the more conventionally designed, direct plasma devices. Instead of direct ion bombardment, our plasma system utilizes highly reactive radicals. Protective flows and separating metal precursor inlets shield the plasma source from getting short-circuited by films from precursor back-diffusion. E.g. $N_2$/ $H_2$, $H_2$/Ar, $O_2$ and mixed gas plasmas can be generated with the system.

Structural design solutions were optimized for ALD reactors. Top flow delivery of the precursor gases ensures even distribution of reactive molecules inside the reactor vessel. This is beneficial especially in the case of non-optimal processes with precursor decomposition or etching or poisoning of reactive sites by reaction by-products. Less impurity and thickness gradient scan be achieved with the top flow, compared to the side-flow (cross-flow) design since all the area reacts at the same time leaving less reactive sites left for reaction with the by-products. Therefore, it is possible to get more challenging reaction chemistries working with the top-flow design, and also a forced flow for through-porous samples is possible. With modified stopped flow design, extended reaction time inside the chamber can be reached while still keeping the protective flows from the inlets on to prevent any back-diffusion of precursor and subsequent particle formation in the inlet lines.

Upscalable structure was specifically designed to bridge the gap between R&D and production. Smaller ALD tools can be used for process and chemical precursor development at for universities and research labs, whereas the larger, ALD tools can be fully automatized, upscaled and clustered into full scale high volume throughput industrial production unit capable of coating even several thousands of wafers per hour.

10:40am **NM+MS+NS+TF-MoM8 Atomic Layer Deposition for Continuous Roll-to-Roll Processing**, ***S.M. George***, *P.R. P. Ryan Fitzpatrick*, University of Colorado at Boulder **INVITED**

Atomic layer deposition (ALD) is currently being developed for continuous roll-to-roll processing. This development is significant because roll-to-roll processing would allow ALD to address many applications in a cost effective manner. This talk overviews the approaches and progress to date. The original idea of ALD with moving substrates and constant precursor flows was presented in a patent by Suntola and Antson in 1977. This scheme involved rotating the substrate between alternating precursor sources and vacuum pumping regions. One current approach under development is based on moving the substrate close to a gas source head. The ALD precursors continuously flow through slits in the gas source head that are separated and isolated by inert gas purging. A second version of this design involves using a gas bearing to set the gap spacing between the gas source head and substrate. Another ongoing approach is based on moving the substrate through separate regions of precursor pressure and inert gas purging. Limited conductance between the regions prevents the gas phase reaction of the ALD precursors. The talk examines the issues and prospects for achieving ALD for continuous roll-to-roll processing. Additional details

are presented for the dependence of precursor isolation on reactor parameters for a substrate under a model gas source head.

11:20am **NM+MS+NS+TF-MoM10 High Rate Continuous Roll-to-Roll Atomic Layer Deposition**, ***E. Dickey***, Lotus Applied Technology **INVITED**

Atomic Layer Deposition (ALD) is a unique thin film deposition process, capable of producing coatings with unmatched quality and performance. Its unique attributes include high conformality and outstanding thickness precision, enabling the deposition of dense, continuous pinhole-free films, even when extremely thin, and even on highly imperfect substrate surfaces. These qualities have made the process attractive for applications on flexible substrates, including dielectrics and semiconductors for flexible electronics devices, and high performance gas diffusion barriers to encapsulate and protect environmentally sensitive devices such as OLED displays and lighting, and CIGS photovoltaic modules.

Until recently, ALD films have generally been deposited using conventional static processing, in which the individual precursors are sequentially introduced into and purged from a common volume containing the stationary substrate. This sequence, commonly called an ALD cycle, typically requires at least several seconds and results in the growth of approximately 0.1nm thickness. As a result, the time required to deposit films of reasonable thickness can be quite long. Furthermore, the static nature of the process makes roll-to-roll processing impractical. In this presentation, we discuss the development of a new ALD process based on substrate translation, with the ALD cycle elements enabled by transport of the flexible substrate back and forth between the precursor zones. Because no time is required for introducing, saturating, and removing precursors for each cycle, the deposition speed is dramatically increased. In addition, this configuration naturally provides the unique feature of film deposition only on the substrate itself, as it is the only surface which is exposed to both precursors. In turn, this allows the use of steady-state plasma as the oxygen source, enabling a new technique of precursor isolation; "precursor separation by radical deactivation", in which the oxygen gas precursor actually mixes with the metal precursor, but is only reactive in the region of the plasma source. Together, this technology set has allowed the deposition of high quality ALD films on polymer substrates, including ultra-barrier films, at substrate speeds in excess of one meter per second.

## Nanomanufacturing Science and Technology Focus Topic
## Room: 207 - Session NM+MS-MoA

### Challenges Facing Nanomanufacturing (All Invited Session)
**Moderator:** S. Rosenthal, Vanderbilt University, S. Butler, Texas Instruments Incorporated

2:20pm **NM+MS-MoA2 Sustainable Nanomanufacturing**, ***M. Roco***, National Science Foundation **INVITED**

Nanomanufacturing has been defined as an approach to design, produce, control, modify, manipulate, and assemble nanometer-scale elements or features for the purpose of realizing a product or system that exploits properties seen at the nanoscale. Nanomanufacturing R&D has as its goal enabling the mass production of reliable and economical nanoscale materials, structures, devices, and systems. The current relatively rudimentary capabilities for systematic control and manufacture at the nanoscale are envisioned to evolve faster after 2011 as we develop new models and instrumentation and enter production of nanosystems for revolutionary new products and processes. We have estimated the global market of final products that incorporate nanotechnology increases by about 25 percent per year reaching $1 trillion by 2015. This estimation made in 2000 [1] holds in 2011, after passing two thirds of the interval.

Three challenges of nanomanufacturing will be discussed: supporting innovation (beyond scaling), realizing efficiency (beyond new functions) and sustainability (of nanoscale processes and of global development). The research trends and application opportunities in nanomanufacturing will be presented by considering four generations of products by 2020 [2]. Most of what has already made it into the marketplace is in the form of “First Generation” products (passive nanostructures with steady behavior) and more recently “Second Generation” (active nanostructures, such as advanced transistors, amplifiers, targeted drugs and chemicals, sensors, actuators, and adaptive structures), while embryonic “Third Generation” (nanosystems, such as bio-assembling; networking at the nanoscale, nanoscale robotics and multiscale architectures) products are in the pipeline. Concepts for the “Fourth Generation” products, including molecular nanosystems, are only in research. Convergence with modern biology, digital revolution, cognitive sciences and other areas is expected to accelerate nanotechnology manufacturing. The role of NNI Signature Initiative on Sustainable Nanomanufacturing will be discussed.

[1] Roco, M.C. and W. Bainbridge, Eds., "**Societal Implications of Nanoscience and Nanotechnology**", *NSF*, Springer (former Kluwer Academic Publishers), 350 pages, Boston, 2001.

[2] Roco, M.C., C.A. Mirkin and M.C. Hersam, “**Nanotechnology Research Directions for Societal Needs in 2020**”, Springer, 2010 (www.wtec.org/nano2/)

3:40pm **NM+MS-MoA6 The National Nanomanufacturing Network: Opportunities, Challenges, and Strategies**, ***M.T. Tuominen***, University of Massachusetts Amherst **INVITED**

Nanomanufacturing holds immense intellectual and economic potential for stakeholders who pursue it with a vigorous, long-term strategy. Although numerous nanomaterials are already in production and use, the breadth of possible applications and societal benefits is only in its infancy. To help nucleate and support communities of practice in the area of nanomanufacturing, the NSF provides funding for the National Nanomanufacturing Network (NNN), which facilitates cooperative activities between nanomanufacturing centers and projects in academia, industry and government, and provides a web-based information resource, InterNano. This presentation will distill key opportunities, challenges, and strategies emerging from thematic workshops, comprehensive summits, and other NNN activities focused on the issues associated with nanomanufacturing. Research, development, education and commercialization are all essential components of a robust nanomanufacturing value chain. Nanomanufacturing R & D both draws from and breaks away from conventional notions of manufacturing. Unique issues have emerged in the area of nanomanufacturing process development, scale-up, metrology, integrated nanosystems design for manufacturing, nanoinformatics, sustainable manufacturing, standards, and multiple issues associated with a robust national enterprise in nanomanufacturing.

4:40pm **NM+MS-MoA9 Nanomanufacturing: The Future of Manufacturing?**, ***K. Cooper***, Naval Research Laboratory **INVITED**

Nanomanufacturing is the fabrication of building blocks with nano-scale features and their integration into useful engineered systems. Through the precise control of materials and processes at the molecular- and nano-scale, new properties and functionalities, determined by nano-scale physics and chemistry, are possible. If successful, such a capability will have a profound impact on the future of manufacturing, which should lead to the emergence of new industries and products. The challenges for nanomanufacturing are achieving the desired functionality, product quality, process repeatability, production scalability and cost affordability. Another challenge will be to achieve manufacturing platforms capable of producing systems for a variety of applications. The ONR Manufacturing Science Program is meeting these challenges though basic research in novel nano-scale production. For example, the program supports research in direct digital nanomanufacturing, massively parallel nano-scale processing, and high-throughput (e.g., roll-to-roll) nanofabrication. It encourages system-level integration and cyber-enabled manufacturing approaches. These concepts along with a few research examples will be described.

## Nanomanufacturing Science and Technology Focus Topic
## Room: 207 - Session NM+MN+MS+TF-TuM

### Lithography Strategies for Nanomanufacturing
**Moderator:** T.S. Mayer, Penn State University

8:00am **NM+MN+MS+TF-TuM1 A SANE Approach to Programmable Soft Lithography**, ***T.W. Odom***, Northwestern University **INVITED**

The prototyping of nanoscale features has rarely been separated from the scaling of them. In order to create arbitrary patterns, serial techniques such as e-beam lithography or focused ion beam milling must start from scratch every time; also, the patterns cannot be generated over large areas. In contrast, parallel fabrication methods such as molding, imprint lithography and soft lithography can scale patterns, but they are limited to transferring the same pattern on the mold. The development of new tools that can combine the strengths of serial approaches (prototyping patterns, high resolution) with those of parallel ones (high throughput, large patterned areas) is critical for next-generation applications based on nanostructures.

This talk will describe an all-moldable nanofabrication platform that can generate—from a single master—large-area nanoscale patterns with programmable densities, fill factors, and lattice symmetries. Solvent-assisted nanoscale embossing (SANE) can increase the spacing of patterns up to 100% as well as decrease them down to 50% in a single step by stretching or heating a thermoplastic substrate. In addition, SANE can reduce critical feature sizes as small as 45% compared to those on a master by controlled swelling of patterned molds with different solvents. SANE can also produce different and reconfigurable lattice symmetries, which enables new opportunities to manipulate the electronic, photonic, and magnetic properties of nanomaterials.

8:40am **NM+MN+MS+TF-TuM3 Micromolding Surface-Initiated Polymerization: A Versatile Route for Microscale Replication onto a Solid Support**, *C.A. Escobar, J.C. Tuberquia, N. Nizamidin,* ***G.K. Jennings***, Vanderbilt University

This presentation will introduce the use of confined surface-initiated ring-opening metathesis polymerization (SI-ROMP) of perfluoroalkyl or alkyl norbornene monomers from solid substrates to synthesize surface-bound polymer structures with tunable physical and chemical properties that accurately replicate those exhibited by Nature's engineered, microscopically rough, and highly functional surfaces. This approach not only allows mimicking of highly evolved and functional surface architectures but also provides versatility in that it introduces a wide variety of chemical compositions available in materials chemistry, including partially fluorinated polymers with ultralow critical surface tensions. Optical microscopy and scanning electron microscopy confirm growth of the polymer structures and the precise replication of the microscale and nanoscale features exhibited by the target natural surface with the added freedom to expand beyond Nature's chemical building blocks. Contact angle measurements show that the surface architectures exhibit both hydrophobic and oleophobic behavior, and in some cases, superhydrophobic properties. This approach is not limited to natural surfaces and could be applied in a straightforward manner to a variety of synthetic surfaces that have microscale features.

9:00am **NM+MN+MS+TF-TuM4 Si Mold Etching with Hard Mask for Bit-Patterned Media**, ***M. Kurihara***, Hitachi, Ltd., Tokyo, *M. Satake, Y. Tsuchiya, T. Nishida,* Central Research Laboratory, Hitachi, Ltd., Japan, *Y. Tada, H. Yoshida,* Hitachi Research Laboratory, Hitachi, Ltd., Japan, *N. Negishi*, Central Research Laboratory, Hitachi, Ltd., Japan

Bit-patterned media (BPM) is one of the promising candidates for hard disk media with areal density greater than 1.0Tb/in$^2$. Nanoimprint lithography (NIL) for BPM has also been investigated as a patterning technique to reduce the production cost. One of the critical issues in NIL mold fabrication is the etching selectivity between silicon and the organic mask pattern due to the following two reasons. One is a significant decrease of pattern thickness to meet the photo-lithography requirements. This decrease remained when applying the self-assembly polymer process to fine patterning. The other is the micro-loading effect that causes the etching rate drop with pattern size shrinking.

In this work, we have developed a hard mask process to compensate for the low etching selectivity. First, the micro-loading effect in the $HBr/Cl_2/O_2$ gas chemistry was evaluated with a $SiO_2$ hard mask of 20-nm thickness. This $SiO_2$ hard mask was patterned from 30 to 50 nm by EB lithography and etched with $CHF_3$ gas chemistry. The coefficients of micro-loading in silicon etching were evaluated based on the relationship between hole depth and etching time with a hole diameter of 30, 40, and 50 nm respectively. With increase of the sidewall taper angle, the micro-loading effect could be improved by about 60%. We also confirmed that there was a hole with a depth of 87 nm with a diameter of 30 nm. Extrapolating this micro-loading effect, it is expected that a hole with a depth greater than 80 nm with a diameter of 10 nm will be achieved. This result will satisfy the pattern aspect ratio of 2, which is required in NIL. We will also demonstrate the Si mold etching with a hard mask by applying the self-assembly polymer in which the areal density is greater than 1.0Tb/in$^2$.

9:20am **NM+MN+MS+TF-TuM5 Directed Assembly of Block Copolymers to Advance the Performance of Conventional Lithography**, ***P.F. Nealey***, University of Wisconsin **INVITED**

Our research program aims to integrate self-assembling block copolymers into current manufacturing practice. The fundamental concepts of the approach are that 1) the most advanced production-oriented exposure tools (e.g. 193 nm, EUV, or electron beam lithography) and resist materials are used to create patterns of differing chemical functionality on the substrate, and 2) films of block copolymers can be directed to assemble in the presence of the chemical pattern into predictable and desirable morphologies, thereby augmenting and enhancing the lithographic process. In comparing the pattern in resist to the pattern of domains induced to assemble in the block copolymer film, directed assembly has been demonstrated to achieve high degrees of pattern perfection, placement of features at the precision of the lithographic tool used to make the chemical pattern, improved dimensional control of features, improved line edge and line width roughness, and resolution enhancement by factors of two to four. In addition, the approach has been demonstrated to robustly achieve non-regular device-oriented geometries used in the fabrication of integrated circuits also with resolution enhancement by multiplication of feature density by interpolation on low duty cycle chemical patterns. After describing current capabilities, remaining technological questions and pathways towards implementation in specific applications will be discussed.

10:40am **NM+MN+MS+TF-TuM9 Measured Backscattered Electron Profile for Optimized Proximity Effect Correction**, ***D.A. Czaplewski,*** *L.E. Ocola*, Argonne National Laboratory

Electron beam (e-beam) lithography has been used to create nanoscale patterns in myriad of resists with features as small as single nanometers. When creating resist features on the single nanometer length scale, the process window to create the desire resist structure becomes increasingly small. Overdosing or under dosing of critical features causes changes in critical dimensions. In addition to the dose required for a single feature, the contribution of additional dose due to proximity of nearby features must be considered. To solve this problem, finite element analysis software packages are available for adjusting dose assignments for different features based on size, shape, and placement with respect to other features. The FEM software can only work as good as the input parameters. These parameters come from the backscattered electron profile. Here, we present the measured electron backscattered profile using a negative e-beam resist. In order to measure the backscattered profile, we use a pattern of intersecting lines surrounded by a large annulus. The lines are measured while the annulus provides a circularly symmetric backscattered electron dose. The lines and annuli are written with varying doses. By measuring the thickness of the resist, the contribution from both the lines and the annulus can be determined for different doses and different shapes by using the resist contrast curve. By using the contrast curve to assign doses to specific resist thicknesses, the specific resist and developer effects are removed from the data. The resultant backscattered electron profile can be used as input into the FEM model to create more accurate resist dose assignments for proximity effect corrected patterns for all resists.

11:00am **NM+MN+MS+TF-TuM10 CMOS Density Scaling in Non-Planar Multi-Gate Devices: A Patterning Perspective**, ***M.A. Guillorn***, *J. Chang, S. Bangsaruntip, C.-H. Lin, W.E. Haensch*, IBM T.J. Watson Research Center **INVITED**

The use of planar Si CMOS device technology may continue beyond the 22 nm node. However, the requirements for the gate dielectric and junction depth needed to maintain control of short channel effects might prove to be unobtainable in devices scaled to meet the integration density requirements of the 14 nm node and beyond. Consequently, an additional method for improving the electrostatics of the device is required. This realization has driven a steady increase in research on non-planar multi-gate CMOS devices over the past 5 years. Raising the Si channel out of the plane of the

substrate creates the opportunity to form the gate electrode around multiple sides of the channel. This geometry results in a superior situation from an electrostatics standpoint compared to a planar device where the gate electrode is present only on the top surface of the channel.

In this talk, we will discuss the challenges of fabricating three non-planar multi-gate devices from Si on insulator (SOI) substrates: (1) the FinFET, where the gate controls two sides of a thin Si mesa or fin (2) the Trigate where the gate controls three sides of a Si fin and (3) a gate-all-around nanowire transistor where the gate electrode surrounds all sides of a suspended Si channel. We will present experimental results from advanced prototypes of these devices fabricated at dimensions and densities relevant to 14 and 10 nm node technology. An emphasis will be give to the unique role lithography and patterning play in determining the electrical behavior of these devices. These results offer insight into what may lie ahead for Si CMOS scaling and how it will impact the demands placed on patterning and metrology.

11:40am **NM+MN+MS+TF-TuM12 High Resolution Dry Development**, *D.L. Olynick,* ***D.G. De Oteyza****, P. Perera, P. Kulshreshtra, P. Ashby, M. Schmidt, S. Dhuey, B.D. Harteneck, R.M. Falch, A. Schwartzberg, P.J. Schuck, S. Cabrini*, Lawrence Berkeley National Laboratory

As features sizes continue to shrink, new approaches are required to overcome roadblocks toward high-resolution lithographic patterning. One significant roadblock towards miniaturization is pattern collapse due to capillary forces during drying.[1] We have invented a dry development method for creation of high resolution and high aspect ratio resist features. We use resists that undergo an optical absorption change after exposure to high-resolution radiation (here we use electron beam lithography). This optical change allows the material to be selectively laser ablated such that the resolution is defined by the high-resolution radiation and not limited by the laser spot size. Using methyl-acetoxy calix[6]arene, a CW 532 nm laser, and spot sizes ~300 nm, we have produced features down to 10 nm in a film 120 nm thick, with pitch resolution down to 30 nm(Fig. 1). Calixarene was introduced as a high resolution electron-beam resist [2] and has demonstrated 12.5 nm half-pitch in extreme ultra-violet lithography.[3] Typically, films are spun thin to prevent high-resolution pattern collapse in thicker films but using the dry development, the patterns are well defined even in the thick films. Note, the resist acts negative with solvent development, as the cross-linked material can not be removed, whereas it is positive under laser dry development at the same electron-beam dose conditions. This is in contrast to the thermal dry development process where calixarenes are developed in negative tone.[4] With thermal development, patterns were demonstrated at 25 nm half-pitch in a 25 nm film (1:1 aspect ratio.

We have systematically studied the optical absorption contrast behavior as a function of electron beam dose, laser wavelength, and laser dose. At 532 nm laser wavelength, we identified that the absorption is a two photon process and found one functional group which is responsible for the optical contrast. We will discuss the options for materials beyond calixarenes.

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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[1] T. Tanaka, M. Morigami, N. Atoda, Jpn. J. Appl. Phys. 32 (1993) 6059-6064.

[2] J. Fujita, Y. Ohnishi, S. Manako, Y. Ochiai, E. Nomura, T. Sakamoto, S. Matsui, Jpn. J. Appl. Phys. 36 (1997) 7769-7772.

[3] H.H. Solak, Y. Ekinci, P. Kaser, S. Park, J. Vac. Sci. Technol. B, 25 (2007) 91-95.

[4] V. Auzelyte, A. Langner, H.H. Solak, J. Vac. Sci. Technol. B, 27 (2009) 2990-2992.

## Nanomanufacturing Science and Technology Focus Topic
## Room: 207 - Session NM+NS+MS-TuA

## Manufacturable Nanoscale Devices and Processes
**Moderator:** R. Maboudian, University of California at Berkeley, R. Mu, Fisk University

2:00pm **NM+NS+MS-TuA1 Assessing Nanotechnologies for Volume Manufacturing**, ***B.E. Goodlin***, *S. Butler, L. Colombo, R. Doering*, Texas Instruments Incorporated **INVITED**

Over the past several years, we have seen significant advances in nanotechnology. Much of the underlying purpose of "nanotechnology" research and development, at least as it applies to the electronics industry, is to revolutionize mainstream technology through the use of unique properties and capabilities of nanomaterials, like Si nanowires, graphene, CNTs, in an effort to provide advantages that could not be otherwise obtained thru evolutionary technology scaling. However, the ultimate goal of adopting such technologies into volume manufacturing will most certainly rely on the same tried and tested principles that govern adoption for mainstream manufacturing. Such principles include: performance (does the process hit the desired target?), cost (is it more/less costly as compared to alternatives?), capability (how reproducible is the process?), throughput (how many product can be produced and at what rate?), yield/defectivity, reliability, controllability/metrology (can the process be controlled and what measurements are needed?), maintainability (is equipment/process required easy to maintain?). Do these same governing manufacturing principles truly apply for nanotechnologies? If so, how do some of the current nanotechnologies fare? What gaps exist? Is sufficient focus being applied to address these gaps? Can we even provide adequate answers to these questions yet? Prior to addressing these questions, one must first step back and clearly identify the important, unique requirements (process, materials, equipment) that exist for a given nanotechnology to enable delivery of the desired performance. Also, one must consider interactions and compatibility of the processes with upstream and downstream processes that are necessary for the final product. Have such requirements and interactions been thought out clearly for various nanotechnologies? If so what are the requirements? What are the interactions? This talk will seek to investigate answers to these questions in an effort to assess various emerging nanotechnologies and their capabilities for eventual adoption into volume manufacturing.

2:40pm **NM+NS+MS-TuA3 Material and Tool Design Challenges for Taking ALD to High-volume Production Beyond 30nm Node**, ***B. Lu***, *Z. Karim, S. Ramananthan*, AIXTRON Inc. **INVITED**

Atomic Layer Deposition enables conformal coating of high-quality thin film on complex nano-scale structures. It has been the preferred choice of deposition technology for high-k and metal films in high-aspect ratio capacitor structure for memory applications. Maintaining 25 fF/cell in sub 30nm DRAM devices poses multiple challenges: (a) structural - very high aspect ratio (~100:1) capacitor cell structures and (b) material - the need for advanced Hi-k oxides beyond ZrO2, which are typically multi-component oxides. Chemical precursors for a majority of the promising new high-k materials are typically low vapor-pressure liquids or even solids. Achieving excellent composition control inside these high aspect ratio structures using low vapour pressure precursors is a significant challenge. These challenges are pushing ALD technology to its limit and are testing its production-worthiness for high volume manufacturing of sub 30nm devices. Innovative technology in precursor delivery, reactor design, and platform architecture are required to overcome these challenges. This presentation will discuss the new developments in equipment design to meet the technology needs as well as practical manufacturing targets (such as throughput and cost of ownership) in order to provide a production-worthy ALD solution. Applications in new high-k oxide (La/Sr/Ba oxides), metals, and PCRAM materials (such as GST) will be discussed.

4:00pm **NM+NS+MS-TuA7 The Metal-Oxide-Metal Vacancy Drift Memristor - A CMOS Compatible, High Speed, Non-Volatile Switch for Universal Memory and Storage**, *R.S. Williams,* ***J.P. Strachan***, Hewlett-Packard Labs **INVITED**

The existence of the fourth passive circuit element was proposed by Prof. Leon Chua of UC Berkeley in 1971 from fundamental symmetry arguments to augment the familiar resistance, inductance and capacitance equations. Although he showed that such a 'memristor' had many interesting and useful circuit properties, until 2008 no one knew if such a circuit element existed or not. In fact, researchers had been making and studying memristors for decades without knowing it - examples are resistive RAM devices, STTRAM devices and phase change memory devices. At HP, we have focused primarily on metal-oxide-metal bipolar resistive switches. Memristance arises naturally in these systems via coupling of electronic and ionic transport in thin semiconducting metal-oxide films under an external bias voltage. Simple analytical models show that memristance becomes much more important as the thickness of the active device region decreases, and thus memristors are mainly nanoscale structures. Memristor theory serves as the foundation for understanding a wide range of hysteretic current-voltage behavior, including both unipolar and bipolar switching, observed over the past 50 years. We have built nanoscale titanium dioxide and tantalum pentoxide memristors in our laboratory and have demonstrated both their fundamental electrical properties and several potential uses. They can be integrated into electronic circuits using conventional fabrication techniques and materials available in standard CMOS fabrication facilities. I will discuss recent results on such topics as device switching speed, endurance, measurements required to parameterize a physics-based SPICE model, and 3D stacking of memristive crossbars.

4:40pm **NM+NS+MS-TuA9 Large Scale Graphene: Progress and Challenges**, ***R.S. Ruoff***, The University of Texas at Austin **INVITED**

Graphene-based materials hold promise due to their electronic and thermal transport properties,mechanical properties, high specific surface area, and that they can act as an atom thick layer, barrier, or membrane. Here, I focus on growth of large area graphene on metal substrates and the structure and thermal and mechanical properties of such graphene. A history of experimental work on graphene (from its discovery in 1969 until 2010) is provided at:

http://bucky-central.me.utexas.edu/ .

*Support of our work by The WM Keck Foundation, DARPA, ONR, SWAN NRI, NSF, ARO, AEC, and Graphene Energy, Inc., is appreciated.*

5:20pm **NM+NS+MS-TuA11 Laser-Assisted Electron-Beam Induced Deposition and Etching**, ***N.A. Roberts***, University of Tennessee and Omniprobe, Inc., *J.D. Fowlkes,* Oak Ridge National Laboratory, *P.D. Rack,* University of Tennessee and Oak Ridge National Laboratory, *G.A. Magel, H.M. Marchman, C.D. Hartfield, T.M. Moore*, Omniprobe, Inc.

Focused electron-beam induced deposition (EBID) and etching (EBIE) are direct-write nanofabrication techniques that allow localized deposition or etching of materials without the need for resists. These deposition and etching processes are controlled by electron-beam dissociation of a precursor gas. In both cases, by-product species are created, and if the unwanted byproduct is not desorbed from the surface it will be incorporated into the deposit or reduce the etch rate for deposition and etching, respectively. Substrate heating has been used in experiments to enhance desorption by reducing the residence time of the by-product. The substrate heating has the same impact on the residence time of the precursor gas and therefore reduces the growth or etch rate of the process. *Ex situ* treatments of deposits have also been investigated to remove impurities with some success, but these treatments results in void formation and shape changes. *In situ* laser processing at short pulse widths is ideal for electron-beam induced processing because desorption of the by-products can be achieved by local heating of the sample, but the narrow pulse width results in a short heating time and cooling time. Thus the by-products can be effectively desorbed and adequate recovery time for fresh reactant to re-adsorb.

Laser-assisted EBID and EBIE processes are made possible through the use of the OptoProbe™, which is an optical imaging and processing system that can be attached to an SEM and used in conjunction with an appropriate gas injection system. The design of this port-mounted optical accessory enables simultaneous optical imaging and delivery of laser irradiation to a sample within the SEM, without interfering with normal SEM/FIB imaging and processing modes. The optical system is mounted on a 3-dimensional nanomanipulator so that precision alignment and focusing is easily achieved. For this work, the OptoProbe™ has been optimized to deliver a high-irradiance near-infrared laser spot to provide localized time-dependent sample heating for enhancing focused electron-beam induced deposition and etching. In this presentation, we will discuss recent experimental results as well as modeling of laser-assisted EBID of Au and EBIE of $SiO_x$ using $XeF_2$.

5:40pm **NM+NS+MS-TuA12 Channel SiGe Selective Epitaxy Process for DRAM High K Peripheral Transistors**, ***J. Yeo****, H. Hwang, S. Lee, W. Yoo, S. Ahn, I. Jeon, B. Kim, S. Nam, S. Kim, K. Jung, J. Lee, S. Jang, T. Lee, K. Huh, S. Yamada*, Samsung Electronics Co., Ltd, Republic of Korea

As the DRAM technology evolved towards the sub 2x era, the need for high performance transistor grows higher for the DRAM peripheral transistors. The novel technologies such as embedded SiGe, high K gate oxide, or 3-dimensional transistor technologies are indispensible in a near future. Especially, to scale the gate oxide further and to meet the gate oxide leakage constraint at the same time, high K gate dielectrics should be adapted. For a successful application of high K dielectrics to DRAMs, it is essential to realize the effective work-function (EWF) for both n, pMOSFETs, where this EWF should be maintained even after huge back-end thermal budget of DRAM process. Therefore, so called 'gate-first approach' has been examined, i.e. LaO, or MgO capping layers for NMOS [1,2], and AlO capping layer, F implantation, and ion implantation on metal for PMOS [2,3], respectively. A SiGe channel has been also examined by many research groups [4-7]. When SiGe epitaxial layer is introduced to the PMOS channel, interface trap density (Dit) has been increased by order of magnitudes, which consequently results in the degradation of transistor performance and reliability [4]. To control this interface degradation, Si capping layers often deposited on the SiGe channels, which reduces the Vt gain that can be gained by SiGe only. In this research, SiGe selective epitaxial growth (SEG) condition has been set-up first, Si capping condition has been optimized by tuning growth temperature, process pressure, and Cl/Si ratio in a LPCVD chamber. The process pressure was precisely controlled to grow Si capping layer 'selectively' as well as to avoid SiGe migration. When we increased the process pressure, surface atomic mobility can be decreased, which effectively reduced SiGe migration. However, when the pressure is increased too high, resulting in growth rate too high, selective growth condition fails. HCl/SiH4 flow rates were also tuned to get a margin for selective growth condition. When introduced to DRAM peripheral transistors, a SiGe channel reduces PMOS Vth by 290 mV, and Si capped SiGe channel by 170 mV, respectively, which has good agreement with the expected value by Energy Band Simulation. This reduced Vt controllability could be recovered by increasing Ge content of SiGe channel. To conclude, the channel SiGe channel SEG process has been successfully applied for DRAM integration, and robust pMOSFET Vt tuner method was realized.

## Vacuum Technology Division
## Room: 111 - Session VT+MN+NS+SS+AS-TuA

## Surface Science for Future Electronic Materials and Accelerator Applications
**Moderator:** M. Wüest, INFICON Ltd, Liechtenstein

2:00pm **VT+MN+NS+SS+AS-TuA1 New UHV Low Temperature Scanning Probe Microscopy Facility for the Study of Future Electronic Materials**, ***J.A. Stroscio***, National Institute of Standards and Technology **INVITED**

Since the beginning of the last century new frontiers in physics have emerged when advances in instrumentation achieved lower experimental operating temperatures. Notable examples include the discovery of superconductivity and the integer and fractional quantum Hall effects. New experimental techniques are continually adapted in order to meet new experimental challenges. A case in point is scanning tunneling microscopy (STM) which has seen a wealth of new measurements emerge as cryogenic STM instruments have been developed in the last two decades. In this talk I describe the design, development and performance of a scanning probe microscopy facility operating at a base temperature of 10 mK in magnetic fields up to 15 T [1]. The STM system can be connected to, or disconnected from, a network of interconnected auxiliary UHV chambers used for sample and probe tip preparation. Results from current measurements on graphene and topological insulators will be described.

[1] *A 10 mK Scanning Probe Microscopy Facility*, Y. J. Song, A. F. Otte, V. Shvarts, Z. Zhao, Y. Kuk, S. R. Blankenship, A. Band, F. M. Hess, and J. A. Stroscio, Rev. Sci. Instrum. **81**, 121101 (2010).

2:40pm **VT+MN+NS+SS+AS-TuA3 Contact Resistance of RF MEMS at a Randomly Rough Surface in the Presence and Absence of Adsorbed Organic Monolayers**, ***D. Berman****, J. Krim, M.J. Walker*, North Carolina State University

Understanding of current flowing through the asperities is interesting for many applications: in RFMEMS, Molecular electronics, Nanotube tunneling etc.

Previous results [2] suggest that the films are displaced from the contacts themselves, but remain present in nearby regions. The increase in resistance is associated with elimination of vacuum electrical tunneling currents in those regions. This raises the question of the relative proportions of contact resistance (Rc) and effective tunneling resistance (Rt).

Measurements on the gold on gold contacts adhered in the closed position, where the contamination film cannot possibly be placed inside the contacts are reported, to investigate vacuum tunneling current contributions to the total current at the contact. Electrical Contact Resistance measurements are reported for RF micro-electromechanical switches with Au/Au and Au/$RuO_2$ contacts, situated within an ultrahigh vacuum system equipped with *in situ* oxygen plasma cleaning capabilities. Fused Au/Au switch resistance increases by 3-5% (which corresponds to 20W tunneling resistance in parallel) after adding pentane to the switch environment. Moreover, the results are repeated with a different substrate (Ruthenium rather than Au), known for higher resistance, to change the resistance values with almost the same work function. If this is tunneling, the same effective tunneling resistance is expected, because tunneling depends on the work functions of the tip and substrate, which are close for gold and ruthenium oxide. In addition, the results are investigated for two different adsorbates, pentane and dodecane. Measurements have been recorded as the function of film coverage and the same tunneling resistance impact is observed. This is consistent with elimination of vacuum tunneling when adsorbed films are present.

Theoretical analysis of two possible mechanisms of the impact of molecular uptake is performed to interpret the experimental results: a) parallel connection of contact resistance and effective tunneling resistance before molecular adsorption, followed by molecules blocking the tunneling current; b) in series connection of contact resistance and pentane layer after adsorption. The data are more consistent with model a).

This work was supported by US National Science Foundation, AFOSR MURI and DARPA. We are grateful to C. Nordquist at Sandia National Lab and J. Hammond at RF Micro Devices for providing the experimental switches.

[1] D. Berman, M. Walker, C. Nordquist, J. Krim, *in preparation for Journal of Applied Physics*

[2] M. Walker, C. Nordquist, J. Krim, *in preparation for Tribology Letters…*

3:00pm **VT+MN+NS+SS+AS-TuA4 Surface Issues for Solid Niobium SRF Accelerator Cavities**, ***M. Kelley***, College of William and Mary

The world-wide physics community looks forward to a slate of accelerator projects of unprecedented magnitude and diversity. Certainly its sheer size makes the International Linear Collider the most visible to the public eye, with 16,000 solid niobium cavities performing at historically high gradient, and built (and operated) for historically low unit cost. Net performance makes superconducting radiofrequency (SRF) technology the approach of choice.

Solid niobium is the material most widely used for construction of SRF cavities because it has the highest critical transition temperature ($T_c$ = 9.2 K) of the pure metals, sufficiently high critical magnetic field ($H_c$ > 2 k Oe) for SRF applications, and metallurgical properties adequate for fabrication and service load. Studies of the SRF performance of niobium cavities began to be reported more than 30 years ago and continue now with the application of improved experimental techniques. Niobium metal superconductivity is a nanoscale, near-surface phenomenon because of the shallow RF penetration. Considerable evidence indicates that cavity interior surface chemistry and topography strongly impact SRF accelerator performance, motivating investigation of how they are affected by post-fabrication treatments.

Current status and prospects are discussed with respect to accelerator needs and opportunities.

4:00pm **VT+MN+NS+SS+AS-TuA7 Examples of Surface Related R&D on Nb Samples and SRF Cavities for Particle Accelerators at JLab**, ***A.T. Wu***, Thomas Jefferson National Accelerator Facility

This contribution will review some examples of surface related R&D on small and flat niobium (Nb) samples and single cell Nb superconducting radio frequency (SRF) cavities done at Jefferson Lab in the past few years. Most of the surface measurements were performed via the experimetal systems available in the surface science lab that was set up[1] at JLab to study the various problems on the Nb surfaces in the SRF field.

The first topic is about a new Nb surface polsihed technique called buffered electropolishing (BEP) that was developed at JLab[2]. This technique can produce the smoothest surface finish ever reported in the literature[3]. It was also demonstrated that under a suitable condition, a Nb removal rate higher than 10 µm/min could be realized. Efforts have been made to try to understand the polishing mechanism through experiments with a well defined experimental geometry on small flat Nb samples. A unique versatile

vertical polishing system was constructed to perform BEP on Nb single cell cavities. Small flat samples, Nb dumbbells and Nb single cell cavities were also studied and treated at CEA Saclay in France and Peking Universty in China and the cavities were RF tested at JLab. Experimental results will be analyzed and summarized. It is showed that BEP is a very promising cadidate for the next generation surface polishing technique for Nb SRF cavites.

A second topic will deal with a new Nb surface cleaning technique employed gas cluster ion beam (GCIB)[4]. This is a result of collaboration with Epion Corporation, Fermi Lab, and Argonne Lab. Beams of Ar, $O_2$, $N_2$, and $NF_3$ clusters with accelerating voltages up to 35 kV were employed in this technique to bombar on Nb surfaces. The treated surfaces of Nb flat samples were examined by sevral surface experimental systems such as SEM, EDX, AFM, SIMS, and 3-D profilometer. The experiments revealed that GCIB technique could not only modify surface morphology of Nb, but also change the surface oxide layer structure of Nb and reduce the number of field emission sites on the surface dramatically. Computer simulation via atomistic molecular dynamics and a phenomenological surface dynamics was employed to help understand the experimental results. A system was set-up at Epion Corporation to do treatments on Nb single cell cavities and then RF-tested at JLab. The experimental results will be summarized and the perspective of this technique for real appliactions is discussed.

Finally, I will show two typical examples of surface studies of Nb using a high resultion transmission electron microscope[5] and a home-made scanning field emission microscope[6] respectively.

4:20pm **VT+MN+NS+SS+AS-TuA8 Early Stages of Nb Growth on Cu for SRF Accelerator Applications**, ***C. Clavero,*** The College of William and Mary*, N.P. Guisinger,* Argonne National Laboratory*, R.A. Lukaszew*, The College of William and Mary

Among the large range of possible applications for superconducting Nb thin films, coatings for superconducting radio-frequency (SRF) cavities in linear accelerators have greatly aroused the interest of researchers in the last years[1]. Superconducting thin films and multilayer coatings are expected to increase further the maximum field gradients that SRF cavities can withstand, pushing them above 100 MeV/m [2]. In this regard, Nb coated Cu cavities have been proposed as a prototypical system for this purpose since they combine the better thermal stability of Cu due to its much higher thermal conductivity and the superconducting properties of Nb thin films [3]. Nevertheless, it is well know that structural dislocations and localized surface resistive defects on the thin films have a dramatically negative influence on their superconducting properties and resonator quality. Indeed, the quality of the films is strongly conditioned by the growth mode bellow the single atomic layer coverage at the very early stages of growth, and thus special attention needs to be devoted to this range. Here we present a complete study on the early stages of growth of Nb on Cu(111). Different growth and annealing temperatures ranging from room temperature (RT) to 600 ºC were used in order to investigate the characteristic growth mode of Nb in the sub-monoatomic coverage range. Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) were used to investigate morphology and chemical composition of the surfaces with atomic resolution. Growth of sub-monolayer coverages at RT leads to amorphous Nb islands with 1 and 2 AL heights. Annealing at 350 ºC gives rise to crystallization of the islands pseudomorphically with the substrate, *i.e.* Nb(111). Further annealing at 600 ºC promotes interdiffusion of Nb atoms into the Cu substrate and alloying of the islands. Growth of higher coverages above 1 AL at 350 ºC reveals preferential Volmer-Weber growth mode.

1. H. Padamsee, Annual Review of Nuclear and Particle Science , 635 (1993).

2. A. Gurevich, Applied Physics Letters (1), 012511 (2006).

3. C. Benvenuti, S. Calatroni, I. E. Campisi, P. Darriulat, M. A. Peck, R. Russo and A. M. Valente, Physica C: Superconductivity (3-4), 153-188 (1999).

4:40pm **VT+MN+NS+SS+AS-TuA9 Epitaxial Niobium Thin Films for Accelerator Cavities**, ***W.M. Roach****, D. Beringer, C. Clavero,* College of William and Mary*, C. Reece,* Thomas Jefferson National Accelerator Facility*, R.A. Lukaszew*, College of William and Mary

The currently proven superconducting radio frequency (SRF) technology used in linear accelerators is based on bulk niobium cavities. Since this has a high cost and these cavities are approaching the maximum field gradients that they can withstand [1], development of a suitable, reliable, cost effective alternative to bulk niobium SRF cavities is needed. Attempts have been made to replace bulk niobium cavities with niobium-coated copper cavities since the thermal conductivity of a suitable base material such as copper is better than bulk niobium [2]. Coating niobium on SRF cavities is a promising but also challenging path, since there are several difficulties associated with various thin film deposition techniques and a lack of systematic studies pertinent to niobium thin film nucleation and growth leading to surfaces of greatest benefit.

Our systematic studies show that the transport properties, in particular the residual resistance ratio (RRR), are improved when niobium is epitaxially grown on crystalline ceramic substrates such as MgO and Al2O3, compared to niobium grown on (001) copper templates. Since grain boundaries are typically one of the main obstacles to superconducting transport, we show how the increased number of crystallographic domains that can occur during epitaxial niobium growth onto copper surfaces leading to higher density of grain boundaries can explain our results. We will discuss a route to improved transport properties while maintaining thermal efficiency by using alternative seed-layers grown on copper templates that can limit increased grain boundary density. We will show our correlated studies of microstructure and surface morphology (RHEED and AFM) and the resulting transport/magnetic properties (four point probe and SQUID magnetometry) illustrating possible mechanisms to improve SRF cavity performance of such niobium films.

This work is funded by HDTRA1-10-1-0072 from the Defense Threat Reduction Agency as well as a subcontract from Thomas Jefferson National Accelerator Facility under contract DE-AC05-06OR23177 from the Department of Energy as supplemented by ARRA funds.

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[1] P. Kneisel *et al*., Proceedings of 2005 Particle Accelerator Conference, Knoxville, TN, TPPT076 (2005).

[2] S. Calatroni, Physica C **441**, 95 (2006).

5:00pm **VT+MN+NS+SS+AS-TuA10 Development via Energetic Condensation of Niobium Thin Films Tailored for Superconducting RF Applications**, ***A.-M. Valente-Feliciano***, Jefferson Lab

For the past three decades, bulk niobium has been the material of choice for SRF cavities applications. In the recent years, RF cavities performances have approached the theoretical limit for bulk niobium. For further improvement of RF cavity performance for future accelerator projects, an interesting alternative has been recently proposed by Alex Gurevich with the Superconductor-Insulator-Superconductor multilayer approach, using the benefit of the higher critical field $H_{c2}$ of higher-$T_c$ superconductors without being limited with their lower $Hc_1$.

JLab is pursuing this approach with the development of multilayer structures based on NbTiN via magnetron sputtering and High Power Impulse Magnetron Sputtering (HiPIMS). Insulators such as, AlN, $Al_2O_3$ and MgO are being investigated as candidates for the insulator layers.

This paper present the the characteristics of NbTiN and insulator layers produced and results on NbTiN-based multilayer structures on bulk Nb and thick Nb films.

5:20pm **VT+MN+NS+SS+AS-TuA11 Evaluation of Secondary Electron Emission Yield Suppression Coatings at CesrTA**, ***Y. Li****, X. Liu, J. Calvey, J. Conway, J.A. Crittenden, M.A. Palmer, J.P. Sikora,* Cornell University*, S.De. Santis*, Lawrence Berkeley National Laboratory

The performance of particle accelerators may be significantly limited due to buildup of electron cloud (EC) in the vacuum chambers. The EC buildup intensity is strongly affected by secondary electron emission from interior surfaces of the chambers. Application of coatings with reduced secondary electron yield (SEY) onto vacuum chamber interior surfaces is one of the most economical EC suppression techniques. As a part of the International Linear Collider (ILC) R&D program, the Cornell Electron Storage Ring (CESR) has been successfully reconfigured as a Test Accelerator (CesrTA) to study EC buildup and suppression techniques. During the CesrTA program, various passive SEY-reduction coatings (TiN, amorphous-carbon and diamond-like carbon thin films) have been applied to diagnostic vacuum chambers in CESR in order to evaluate the efficacy of the EC suppression and the vacuum performance of these coatings in an accelerator environment. These chambers are equipped with both vacuum instrumentation (ion gauges and residual gas analyzers), as well as EC diagnostics (retarding field analyzers and RF-shielded pickups). In this paper, we present the results of studies of the vacuum conditioning and EC mitigation performance of these coatings.

5:40pm **VT+MN+NS+SS+AS-TuA12 Electron Cloud Mitigation for the Large Hadron Collider (LHC)**, *V. Baglin, G. Bregliozzi,* ***P. Chiggiato****, P. Costa Pinto, J.M. Jimenez, G. Lanza, M. Taborelli, C. Yin Vallgren*, CERN, Switzerland

One of the main issues for the vacuum system of the Large Hadron Collider (LHC) is the build-up of electron clouds generated by electron multipacting in presence of beams. The occurrence of spatially distributed negative charges can lead to beam instabilities and emittance blow-up, pressure rises with a consequent background growth in the experimental areas, and increased thermal load in the cryogenic sections. The development of electron clouds depends on beam intensity and structure, magnetic field, and, in particular, the secondary electron emission of the beam pipe walls. With respect to this latter point, electron clouds can be eradicated whenever the maximum secondary electron yield becomes lower than a critical threshold. In the LHC the problem has already been tackled at the design phase by introducing TiZrV non-evaporable getter thin film coatings as the baseline for most of the room temperature sectors of the ring. After activation by in situ heating, this material provides maximum secondary electron yield lower than 1.1. In addition, during operation, dedicated scrubbing runs are carried out by generating intentionally electron clouds and electron impingement onto the non-coated vacuum chambers, in a way to reduce their secondary electron yield. Recently magnetron sputtered carbon coatings have been also studied because they can reach exceptionally low secondary electron emission without any heating; their application in the LHC injectors and future LHC components is under investigation.

The effect of electron clouds in the pressure variations during the first months of LHC operation will be presented, together with the effects ascribed to the mitigation techniques.

## Nanomanufacturing Science and Technology Focus Topic
## Room: 111 - Session NM+AS+MS-WeM

## Nanomanufacturing Issues: Metrology and Environmental Concerns
**Moderator:** J. Johnson, University of Tennessee Space Institute, W. Collins, Fisk University

9:00am **NM+AS+MS-WeM4 Particle Characterization Issues in Evaluating the Toxicity and Environmental Impact of Manufactured Nanomaterials**, ***K.W. Powers***, University of Florida

Nanostructured materials and nanoparticles promise to revolutionize many key areas of science and technology, however, the environmental effects of nanomaterial enabled products need to be considered throughout their lifecycle, from manufacture to environmental disposal. As nanomaterials become more commonplace in commercial applications, there is a need to assess the potential health and safety effects on human and other biological organisms. Materials at the nanoscale often possess properties that are different from the equivalent bulk or molecular scale. It is clearly shortsighted to assume that toxicological profiles of nanomaterials are the same as in the bulk or molecular forms. As they address these issues, toxicologists often need assistance in understanding and accommodating many of the unique attributes of nanoscale materials as they begin to assess potential health and environmental effects. Though the interpretation of the biological markers of toxicity are well developed, there are a number of issues relating to dosage, size, shape, detection and characterization that are problematic. There is a growing consensus that the complexity of these issues requires a multidisciplinary approach to nanoparticle toxicology that includes medical personnel, environmental and physical scientists as well as engineers trained in particle technology.

Keywords: nanoparticles, nanocharacterization, nanotoxicology, toxicity,

9:40am **NM+AS+MS-WeM6 Sampling for Airborne Nanoparticles and Selecting Respiratory Protection**, ***S.M. Hays***, Gobbell Hays Partners, Inc., *J.R. Millette*, MVA Scientific Consultants

As the manufacture and use of nanomaterials continue to increase, appropriate questions are raised about the release of airborne nanoparticles into the general environment and specifically into the breathing zone of people. The development of monitoring procedures specific to carbon nanotubes and other nanoparticles is crucial in determining the effectiveness of engineering controls and personal protection. This presentation will review experiments conducted to determine the efficacy of using asbestos air sampling methodology for sample collection with standard membrane filter cassettes and analysis using transmission electron microscopy (TEM). Tests done to evaluate the use of cartridge style respirator filters in carbon nanotube aerosols will also be presented. These laboratory tests will be discussed in relation to air samples collected in a variety of actual field use situations. Proposed methodology for the analysis for nanotubes in settled dust will be presented. Finally, one author is chairing an ASTM committee that is developing a consensus method to collect and analyze airborne nanotubes. The current state of that committee's work will be summarized.

10:40am **NM+AS+MS-WeM9 Local Probes Enabling Science and Manufacturing**, ***D.A. Bonnell***, University of Pennsylvania **INVITED**

The last decade has witnessed significant advances in measuring nanoscale phenomena. These advances have enabled scientific discovery and provided a framework to support some nanomanufacturing processes. Nevertheless, both scientific advance and to a greater extent manufacturing are limited by our current capabilities in nanoscale metrology. This talk will highlight some of the exciting advances in probe based metrology, project future developments and outline the challenges that are critical to realizing a robust nanomanufacturing sector. The outcome of a recent global assessment of Nano Metrology will also be summarized.

11:20am **NM+AS+MS-WeM11 The Influence of Surrounding Materials on the Optical Properties of Nanoscale Films: An Unforeseen Complication in Nanoscale Metrology**, ***A.C. Diebold***, *V.K. Kamineni*, University at Albany

Optical measurement of film thickness requires knowledge of the complex refractive index (dielectric function) of each material in the film stack. Practical experience has shown that the dielectric function changes with film thickness for many poly crystalline metal films and single crystal semiconductor layers. (1, 2) Previous studies pointed to quantum confinement induced changes in the dielectric function of thin silicon nanofilms between 10 nm and 2 nm. Extra Thin silicon on insulator (ET-SOI) films were used for this study. These films are often referred to as crystalline silicon quantum wells (c—SI QW). Our most recent study shows that the dielectric function of c-Si QWs can be further altered by the presence of a dielectric layer above the nano silicon top layer.(3) Based on an elastic theory description of the acoustic phonon modes, the dielectric function of the c-Si QWs is found to be strongly influenced by electron – phonon scattering. We illustrate this point using low temperature measurements of the dielectric function of a series of c-Si QWs and by comparing room temperature measurements of the dielectric function of 5 nm c-Si QWs with native oxide, 10 nm $SiO_2$, and 10 nm $HfO_2$.

1. Observation of quantum confinement and quantum size effects, A.C. Diebold and J. Price, Phys. Stat. Sol. (a) **205**, No. 4, (2008), pp 896–900.

2. Optical Metrology of Ni and NiSi thin films used in the self-aligned silicidation process, V. K. Kamineni, M. Raymond, E. J. Bersch, B. B. Doris, A. C. Diebold, J. Appl. Phys., **107,** (2010), pp 093525 1-8.

3. Evidence of phonon confinement effects on the direct gap transitions of nanoscale Si films, V.K. Kamineni and A.C. Diebold, submitted

## Spectroscopic Ellipsometry Focus Topic
## Room: 209 - Session EL+AS+EM+MS+PS+TF-ThM

### Spectroscopic Ellipsometry of Biological Materials and Organic Films
**Moderator:** M. Creatore, Eindhoven University of Technology, the Netherlands, K.G. Lloyd, DuPont Corporate Center for Analytical Sciences

8:00am **EL+AS+EM+MS+PS+TF-ThM1 Application of Various Spectroscopic Ellipsometry Techniques for In Situ Studies of Thin Polymer Films on Solid Substrates**, ***K.-J. Eichhorn***, Leibniz-Institut für Polymerforschung Dresden e.V., Germany **INVITED**

Thin films of functional polymers are not only widely integrated into modern micro- and nanoelectronic devices, but also used to modify solid surfaces for biosensor, biomedical and antifouling applications.

Therefore, in the first part I will report on improved temperature-dependent spectroscopic Vis-ellipsometry experiments to study confinement effects on the polymer dynamics in thin films to address a question which is controversially discussed in the polymer physics community for a long time past: Is there really a significant change of the glass transition temperature Tg of polymers when confined in nanoscopic films (studied here down to about 10 nm thickness)? We compared well-known linear polystyrenes of different molecular weights /1/ and hyperbranched polyesters having different architectures and functional groups /2/. Films of different thickness were prepared by spin-coating on silicon wafers, carefully equilibrated and measured in dependence on temperature (up to 250°C) in an inert gas atmosphere. The Tg data were determined from the ellipsometric results and discussed.

In the second part, “smart” surfaces will be presented which can be used for controlled adsorption and release of biomolecules. For that, different types of stimuli-responsive polymer brushes were prepared on solid substrates by a “grafting-to” procedure. The brush properties (e.g. swelling/collapsing) as well as the resulting adsorption/desorption of model proteins (e.g. Human Serum Albumin, Chymotrypsin) can be switched in an appropriate aqueous medium with temperature (PNIPAAM) and/or pH (PAA-P2VP). The corresponding processes at the solid-liquid interface were studied in-situ by spectroscopic Vis- and IR-ellipsometry /3,4/.

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8:40am **EL+AS+EM+MS+PS+TF-ThM3 Hard Matter Meets Thin Polymer Films-Spectroscopic Ellipsometry as a Versatile Tool to Investigate Properties of Responsive Poly(N-isopropylacrylamide) Systems with Incorporated Magnetic Nanoparticles**, ***S. Rauch***, Leibniz-Institut für Polymerforschung Dresden e. V., Germany

Responsive polymer systems designed by using polymer brushes or hydrogels are interesting systems, which can exhibit reversible or irreversible changes in their physical and structural properties to special environmental conditions (e.g. temperature or magnetic fields). The temperature responsive poly(*N*-isopropylacrylamide) (PNiPAAm) is one of such polymers. It undergoes a phase transition in aqueous solution at its lower critical solution temperature (LCST) of 32 °C which induces an increase in hydrophobicity. Combined with the properties of magnetic nanoparticles (NP) (e.g. $Fe_3O_4$ or $CoFe_2O_4$) these systems can lead to new surface functionalities with new interesting properties for many applications, as sensing, wettability or (bio)adhesion.

For the design of such thin film systems a basic knowledge of the film characteristics is essential. Therefore it is first necessary to know how much nanoparticles are inside or attached to the system. By using spectroscopic Vis-Ellipsometry (SE) it is not only possible to investigate optical properties of these films but also the composition of it, e.g. volume fraction of $Fe_3O_4$-NP.

We studied two types of films and present results for a thin NP-composite film prepared by pre-mixing of the PNiPAAm with hydrophobic $Fe_3O_4$-NP, spin-coated and grafted to a silicon substrate (System 1) and a film prepared by adsorption of hydrophilic functionalized $Fe_3O_4$-NP onto PNiPAAm brushes (System 2). The former system was chosen to develop an optical model starting from a simple two component effective-medium-approach (Maxwell-Garnett-EMA) using the optical constants of the pure polymer measured by SE and of $Fe_3O_4$ with averaged data taken from three different publications. The SE best fit-results were validated against scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

After transferring this optical model to System 2, the adsorption of hydrophilic functionalized $Fe_3O_4$-NP onto PNiPAAm brushes was investigated and will be discussed with additional results obtained from contact angle (CA) and phase transition (LCST) measurements.

9:00am **EL+AS+EM+MS+PS+TF-ThM4 The White Scarab Beetle *Cyphochilus insulanus* –Scattering and Polarization Properties**, ***C. Akerlind***, Swedish Defence Research Agency / Linköping University, Sweden, *H. Arwin*, Linköping University, Sweden, *T. Hallberg, H. Kariis*, Swedish Defence Research Agency, Sweden, *J. Landin, K. Järrendahl*, Linköping University, Sweden

Three methods were used to characterize the optical properties of the light scattering white scarab beetle *Cyphochilus insulanus*. Spectral directional hemispherical (DH) reflectance measurements in the wavelength region 250 nm to 25 µm were performed using integrating spheres. The general spectral appearance shows a relatively strong reflectance band in the range 400 - 1600 nm. The Bidirectional Reflection Distribution Function (BRDF) was measured over a semi-circle in the plane of incidence at the wavelengths 633 nm and 3.39 µm, using s- and p-polarized light. In the visible the BRDF data shows a near Lambertian behaviour with a constant BRDF for most angles, *i.e.* the light is diffusely scattered. For large incident angles and in the infrared the BRDF is more specular. Full Mueller-matrix spectroscopic ellipsometry (MMSE) measurements were performed in the wavelength range 250 - 1000 nm at angles of incidence between 45° and 75° using a dual rotating compensator ellipsometer. The Mueller data show that the reflected light in general has a high degree of polarization *P* even for nonpolarized incident light. The angular dependence of *P* was pronounced for incident p-polarized light and was very low near the Brewster angle. In comparison, *P* was high for all measured angles for incident s-polarized light. Close to the Brewster angle, the reflected light showed a high ellipticity for incident p-polarized light. The optical data is used to model the structure and optical response of the beetle cuticle. With input from the DH and BRDF-data analysis of the Mueller Matrix data was made using Fresnel-based layer modelling. 2-, 3- and n-phase models are compared. The obtained optical properties are also used to calculate color data in terms of chromaticity and whiteness. The scattering properties of the *Cyphochilus insulanus* cuticle are also discussed by combining the BRDF and MMSE data as well as recently obtained Mueller matrix imaging polarimetry results.

9:20am **EL+AS+EM+MS+PS+TF-ThM5 Real-time Spectroscopic Ellipsometry and Quartz Crystal Microbalance with Dissipation Characterization of Biomolecule Adsorption within Sculptured Thin Films**, *T. Kasputis, D. Schmidt*, ***K.B. Rodenhausen***, *H. Wang, A.K. Pannier, M. Schubert*, University of Nebraska - Lincoln

Recent improvements in nanofabrication strategies have led to the development of precisely crafted nanostructures with intricate features. Incorporating biomolecules such as proteins, DNA, drugs, and even whole cells could allow for functionalization of nanostructured surfaces for biological applications including biosensing, tissue engineering scaffolds, and drug and gene delivery. Along with the nanofabrication of biological devices, there is a need to develop instrumentation capable of probing and characterizing the dynamic evolution of these bio-functionalized interfaces. Spectroscopic ellipsometry combined with quartz crystal microbalance with dissipation (SE/QCM-D) is a non-destructive optical/mechanical characterization technique that reveals dynamic properties, including average film thickness (with sub-angstrom resolution), adsorbed mass, and porosity.

Nanostructures in the form of sculptured thin films (STF) were fabricated by glancing angle deposition via electron beam evaporation of titanium onto gold-coated quartz sensors. The sensors were then mounted within an SE/QCM-D liquid cell, and proteins of varying sizes were deposited and characterized, *in-situ*. Protein adsorption was detected shortly after introducing the protein solutions by SE and QCM-D as a change in the optical response and decrease of vibration frequency, respectively. QCM-D reported greater adsorbed mass for larger proteins (fibronectin) than smaller

proteins (bovine serum albumin). The adsorbed mass of proteins within the nanostructured scaffold exceeded that of proteins on flat surfaces, confirming that the STFs are capable of trapping proteins. Analysis of the anisotropic optical response from the nanostructures, which is very sensitive to environmental changes, adds complementary information on protein adsorption; the optical quantification is in agreement with QCM-D results. In addition, the adsorption of other biomolecules, such as cells and DNA complexes, has also been accomplished. The use of combinatorial SE/QCM-D to characterize and monitor the attachment of biomolecules on complex nanotopographies will improve the design and fabrication strategies for a wide array of biotechnological devices.

9:40am **EL+AS+EM+MS+PS+TF-ThM6 Characterization of Multilayer Organic Thin Film for Use as an Aptamer Biosensor with Hybrid Spectroscopic Ellipsometry and Quartz Crystal Microbalance with Dissipation**, ***J.Y. Gerasimov***, *K.B. Rodenhausen, H. Wang, R.Y. Lai, M. Schubert*, University of Nebraska - Lincoln

DNA aptamer molecules passivated by alkanethiols can be used for biological detection and screening. Through the use of spectroscopic ellipsometry (SE, optical) and quartz crystal microbalance with dissipation (QCM-D, mechanical) techniques, selective binding of analytes to chemisorbed aptamer probes can be observed *in-situ*. The system analyzed consists of a gold-coated quartz substrate, a multilayer organic thin film (containing aptamer probe, alkanethiol, and single-stranded DNA analyte), and physiological buffer solution. The attachment and detachment of material, the hybridization efficiency of the aptamer probes, and changes in the porosity of the multilayer organic thin film were all determined by SE/QCM-D.

In this contribution, we present the real-time SE/QCM-D characterization of (a) the formation of the aptamer probe layer, (b) the subsequent chemisorption of alkanethiol, and (c) the interrogation of single-stranded DNA that is non-complementary or complementary to the sequence found on the aptamer probe. The aptamer DNA sequence encodes codon 12 of the *K-ras* gene; mutations of this gene are frequently found among pancreatic cancer patients. We found that introduction of either complementary or non-complementary DNA caused increases of the multilayer organic thin film thickness. However, our SE/QCM-D analysis showed that the porosity of the multilayer organic thin film responded differently depending on the compatibility of the DNA analyte. The SE/QCM-D technique provides evidence for different surface attachment mechanisms and can be useful in characterizing biological interfaces.

10:40am **EL+AS+EM+MS+PS+TF-ThM9 Contamination Processes of EUV Optics Characterized by Spectroscopic Ellipsometry**, ***L.J. Richter***, *C. Tarrio, S. Grantham, S.B. Hill, T.B. Lucatorto,* National Institute of Standards and Technology, *N.S. Faradzhev*, University of Virginia

Extreme ultraviolet (EUV) lithography using 13.5 nm light is emerging as a viable tool for semiconductor fabrication at design rules below 32 nm. Tool performance critically depends on limiting and mitigating degradation of the EUV optical elements. A primary degradation mechanism is the EUV induced deposition of carbon from ambient species originating from outgassing of the unbaked vacuum system and/or outgassing from the EUV irradiation of the resist. Using the high brightness of the Synchrotron Ultraviolet Radiation Facility (SURF-III) at NIST both fundamental studies of EUV induced contamination and practical (“witness plate”) studies of resist out gassing are performed. Typical deposits are hydrogenated amorphous carbon features with peak thicknesses of about 1 nm and nominal lateral extent of 1 mm. Both ex-situ, small spot mapping spectroscopic ellipsometry (SE) and in situ single-wavelength imaging nulling-ellipsometry are used for rapid, sensitive, contamination metrology. Fundamental studies of contamination by admitted gases indicate that the process is a complex function of both gas pressure and photon dose. Correlations between SE and XPS are suggestive that, at high EUV fluxes, densification can occur resulting in spatial variation in the deposit dielectric function. The use of principal component analysis of the SE images to highlight the spatial diversity will be discussed.

11:00am **EL+AS+EM+MS+PS+TF-ThM10 Characterization of Organic Solar Cells Materials and Structures by Spectroscopic Ellipsometry**, *J.P. Piel,* ***L. Kitzinger***, *A. Bondaz, C. Defranoux*, SEMILAB-SOPRALAB, France

Spectroscopic Ellipsometry (S.E) is a well known optical technique widely used for the characterisation of all types of thin films for determination of film thickness and optical indices on glass or plastic substrates.

S.E. is also being applied to the characterization of materials and multilayer structures of organic materials like organic light-emitting diodes (OLEDs) or Organic Solar Cells.

We present the determination of the refractive indices of organic Solar Cells materials like P3HT, PCBM, Pentacene, Perylene, and their blends. Complex organic materials can be analyzed accurately and fully characterized from their absorption bands in the visible and UV range (190nm to 900nm).

Transmission and absorption can be also measured at the same time and be used to determine the optical properties of these materials.

Using these refractive indices, analysis of real multi-layer stacks can be done. The refractive indices can be used afterwards to automatically optimise and balance the energy flow dissipation Q inside an organic solar cell composed of a thin film stack. We present an example performed on a single cell and on a tandem bi-layer cell structure.

Since these materials are sensitive to moisture and pollution, it can be necessary to measure their optical properties and thickness values through an encapsulated media. We will demonstrate how we can measure single layer properties and multi-layer stacks, through encapsulated samples, from the back side of the substrate. This technique can be applied to test structure or real Organic Solar Cell monitoring. Backside measurement combined with a water vapour cell used for ellipsometry porosimetry is used to test the efficiency of the thin film encapsulation.

We also present the characterization of ITO and ZnO transparent electrodes by S.E. and how near infra-red ellipsometry is used to determine the ITO resistance, without contact, by using the Drude behaviour on encapsulated samples.

## Spectroscopic Ellipsometry Focus Topic
## Room: 209 - Session EL+AS+EM+MS+PS+TF-ThA

### Spectroscopic Ellipsometry for Photovoltaics, Metals and Oxide Thin Films
**Moderator:** M. Creatore, Eindhoven University of Technology, the Netherlands

2:00pm **EL+AS+EM+MS+PS+TF-ThA1 Applications of Ellipsometry in Photovoltaics**, ***D. Levi***, National Renewable Energy Laboratory **INVITED**

With the growing possibility of anthropomorphic-induced climate change there has come increasing concern over energy-related emissions of carbon dioxide into the atmosphere. The search for low or no-carbon energy sources has intensified. This has lead to a twenty first century gold rush into photovoltaics research and technology startups. Although the PV industry has maintained its exponential growth rate through the global economic downturn, electricity from photovoltaics is still a long ways from economic competitiveness with fossil fuel-based electricity sources. The U.S. Department of Energy recently announced the Sunshot program, with the expressed goal of $1/Watt installed cost for utility scale PV plants by 2017. This aggressive goal will require radical advances in new and existing PV technologies.

This presentation will begin with an overview of the major PV technologies and the state of the rapidly evolving global photovoltaics industry. Photovoltaics is a natural arena for application of spectroscopic ellipsometry. Nearly all PV devices are made of multiple thin films of semiconductors and transparent conducting oxides. New materials are constantly being introduced. Film thickness, optical properties, interfaces, electronic properties, and film growth dynamics are all critical aspects of these devices and lend themselves to investigation through the use of spectroscopic ellipsometry. I will present several case studies of how we have applied spectroscopic ellipsometry in our research in photovoltaics at the National Renewable Energy Laboratory.

2:40pm **EL+AS+EM+MS+PS+TF-ThA3 Comparison between Ex Situ and Real Time Spectroscopic Ellipsometry Measurements of Structurally Graded Si:H Thin Films**, ***N.J. Podraza***, University of Toledo

Analysis of spectroscopic ellipsometry measurements of graded thin films remains challenging, although analysis procedures and software have improved over the past several decades. Practical use of these processes remains somewhat time consuming and is often not fully utilized by the casual user. In this work, ex situ ellipsometric spectra collected for static samples and real time spectroscopic ellipsometry (RTSE) measurements collected during film growth will be compared to illustrate differences in results arising from the measurement procedures and analysis. As an application, consider hydrogenated silicon (Si:H) thin films used for solar cells. Devices typically incorporate either amorphous silicon (a-Si:H) or “nanocrystalline” silicon (nc-Si:H) absorber layers, although the best “nanocrystalline” absorber layers actually consist of mixed-phase amorphous+nanocrystalline (a+nc) material. Si:H thin films may initially (i) nucleate as amorphous and remain amorphous throughout growth; (ii) immediately nucleate as nanocrystallites; or (iii) initially evolve in the amorphous regime but nucleate crystallites which subsequently grow preferentially over the surrounding amorphous material until nanocrystallite coalescence. Analysis of ellipsometric spectra collected for (i) or (ii) simply involve using a substrate / bulk film / surface roughness model and complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) for the bulk material. For (iii), RTSE is ideally used to monitor the growth of Si:H that evolves through the amorphous, nanocrystalline, and mixed-phase regimes and a virtual interface analysis (VIA) procedure is used to extract $\varepsilon$ for the amorphous and nanocrystalline components, the bulk and surface roughness thicknesses versus time, and the nanocrystalline fraction depth profile in the (a+nc) growth regime. For (a+nc)-Si:H films only measured with a single static ex situ measurement at the end of the deposition, obtaining $\varepsilon$ and structural parameters of the film become less precise. Specifically, sensitivity to the variation in the nanocrystallite fraction with thickness may be lost and inaccurate $\varepsilon$ for the component materials may be obtained. This works seeks to compare the structural and optical properties of (a+nc)-Si:H obtained by RTSE and VIA with those from analysis of static ex situ spectra with models using different structures, parameterizations in $\varepsilon$, and spectral range restrictions. These comparisons will be used to identify appropriate structural and dielectric function models to more accurately analyze structurally graded thin films under different material and measurement circumstances.

3:00pm **EL+AS+EM+MS+PS+TF-ThA4 Real-Time Spectroscopic Ellipsometry of Cu(In,Ga)$Se_2$ Thin Film Deposition: Copper Transition in 3-Stage Co-Evaporation Process**, ***D. Attygalle***, University of Toledo, *V. Ranjan*, Old Dominion University, *P. Aryal*, University of Toledo, *S. Marsillac*, Old Dominion University, *R.W. Collins*, University of Toledo

With record efficiencies above 20%, Cu(In,Ga)$Se_2$ (CIGS) based solar cells have shown the greatest potential for success among the thin film photovoltaics technologies. Thermal co-evaporation of individual elements has proven to produce extremely high quality CIGS materials, provides a high level of flexibility, but also generates greater challenges in process optimization. The limitations of existing process monitoring capabilities, hence the challenge of correcting process fluctuations in real time, has led the industrial community toward more controllable CIGS deposition processes. Real time spectroscopic ellipsometry (RTSE) can be used successfully in the monitoring of complicated processes -- including CIGS film preparation by co-evaporation using precursor films of $(In_xGa_{1-x})_2Se_3$. Information extracted from RTSE includes the evolution of bulk layer and surface roughness layer thicknesses, the composition and phase, as well as the layer dielectric functions, all of which can assist in understanding the fabrication process and in optimizing solar cells. In this study, the focus is on the transitions of Cu-poor to Cu-rich CIGS and vice versa by observing the changes in ($\psi$, $\Delta$) spectra obtained by RTSE. The commonly used monitoring method, which involves observing the changes in emissivity of the film, largely depends on the apparatus design, the substrate, and the bulk layer thickness. When a CIGS film is prepared by exposing a precursor film of $(In_xGa_{1-x})_2Se_3$ to Cu and Se fluxes, thereby becoming Cu-rich, a semi-liquid $Cu_{2-x}Se$ phase is believed to form on top of a bulk layer consisting of mixed phases of Cu(In,Ga)$Se_2$ and $Cu_{2-x}Se$ [1]. A multilayer optical model, with appropriate effective medium approximation layers to represent this scenario, has shown good agreement with the observed ($\psi$, $\Delta$) spectra. Since RTSE is highly sensitive to monolayer-level changes in the top-most layer, RTSE gives superior sensitivity in Cu-rich to Cu-poor end point detection, which occurs when the top $Cu_{2-x}Se$ phase drops below detectable limits. Furthermore this method is less affected by the substrate and bulk layer thickness. Although careful analysis of RTSE can give a wealth of information about CIGS material properties and their evolution, this type of end point detection can be successful simply by monitoring the real time changes in the ($\psi$, $\Delta$) spectra.

[1] J. AbuShama, R. Noufi, Y. Yan, K. Jones, B. Keyes, P. Dippo, M. Romero, M. Al-Jassim, J. Alleman, and D.L. Williamson, "Cu(In,Ga)$Se_2$ Thin-film evolution during growth from $(In,Ga)_2Se_3$ precursors", *Mat. Res. Soc. Symp. Proc.* paper H7.2.1, (2001).

3:40pm **EL+AS+EM+MS+PS+TF-ThA6 Bulk Hetrojunction Solar Cell Characterization by Phase Modulated Spectroscopic Ellipsometry**, ***K. Uppireddi***, *L. Yan*, HORIBA Scientific

The blend morphology, phase separation as well as crystallinity of organic photovoltaic solar cell are important properties to increase the efficiency. The performance of such cells is strongly influenced by blend composition and thermal annealing conditions. In this work we demonstrate the use of ellipsometry as a powerful and sensitive metrology means of monitoring organic solar cell based on the blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-buytric acid methyl ester (PCBM). Ellipsometric measurements were performed on P3HT/c-Si, PCBM/c-Si and P3HT:PCBM/c-Si at an angle of incidence of 70 degree, across the spectral range 190 – 2100 nm (0.6-6.5 eV). Two different analysis protocols were used to model the P3HT:PCBM blend structure. In the first protocol effective medium theory was used to represent the optical constant of layer, where as in the second one the blend was treated as one single homogenous material. The approach renders investigation of final morphology and composition.

4:00pm **EL+AS+EM+MS+PS+TF-ThA7 *In Situ* Spectroscopic Ellipsometry during Atomic Layer Deposition of Pt, Pd and Ru**, ***N. Leick***, *J.W. Weber, M.J. Weber, A.J.M. Mackus, H.C.M. Knoops, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

The precise thickness control of atomic layer deposition (ALD) and its conformal growth make ALD the method of choice for nanometer thin film deposition. Platinum-group metals such as Pt, Pd and Ru have many applications in the areas of nanoelectronics and catalysis and recently there has been considerable interest to deposit films of these materials by ALD. Spectroscopic ellipsometry (SE) is a powerful, noninvasive optical technique that can be used *in situ* during ALD to precisely monitor the thickness of the films. SE also provides information on the optical and

electrical properties of the films which is very relevant for their applications. Choi et al. [1] previously investigated the dielectric functions of Pt-group metal films with a thickness of ~400 nm as prepared by physical vapor deposition. For the aforementioned applications, however, the films are required to be much thinner, which leads to differences in film morphology as well as to dielectric functions that can be different from those of bulk films. In the spectroscopic ellipsometry work to be presented in this contribution we have therefore focused on films with thicknesses from 5 nm to 35 nm. *In situ* data was obtained during ALD in the photon energy range of 0.7 – 6.5 eV. Using a Kramers-Kronig consistent B-spline model to account for the thickness-dependent dielectric functions, we were able to obtain accurate ALD growth-per-cycle values for Ru, Pt and Pd (1.00 ± 0.06 Å, 0.47 ± 0.04 Å, 0.14 ± 0.02 Å). Furthermore, the contributions from free-carriers (Drude term) and interband absorptions (Lorentz-oscillator contributions) were investigated by combining the SE data with FT-IR reflectance data such that the photon energy range of 0.04 eV – 6.5 eV was covered. In this range, it was possible to represent each film with a unique Drude-Lorentz model although some ambiguities about the Lorentz oscillator contributions remained in the case of Ru. It will be shown that the extracted thicknesses and electrical resistivities from this model are in line with data obtained from X-ray reflectometry and four-point probe measurements (for example Ru: $\rho_{SE}$ ~23 μΩ.cm and $\rho_{FPP}$ ~16 μΩ.cm). Furthermore, in the case of Ru also the influence of the film roughness will be addressed.

[1] Choi *et al.*, Phys. Rev. B **74**, 205117 (2006)

4:20pm **EL+AS+EM+MS+PS+TF-ThA8 Manipulating the Optical Properties of Metals: Sculptured Thin Films Coated by Atomic Layer Deposition**, *D. Schmidt, N. Ianno, E. Schubert,* ***M. Schubert***, University of Nebraska - Lincoln

The fabrication of three-dimensional metal nanostructures with tailored geometry is one of the central challenges of nanotechnology because geometrical and material parameters are responsible for the optical, electrical, mechanical, chemical, or magnetic properties of such nanostructured thin films. Engineered artificial sculptured thin films (STFs) with designed anisotropies are potential candidates for applications in various fields such as optics, magneto-optics, as well as chemical and biological sensing and detection. However, in order to utilize metallic nanostructures for novel applications their size-, structure-, and material-driven physical properties have to be understood and quantified.

We utilize glancing angle electron-beam deposition, which exploits physical atomic-scale shadowing and dynamically varying particle flux azimuth for fabrication of three-dimensional highly spatially coherent STFs with different morphologies. Subsequently, nanostructures are individually covered with a thin conformal coating (cladding) by means of atomic layer deposition (ALD).

We will present the anisotropic optical properties of highly anisotropic ALD coated metal STFs determined by generalized spectroscopic ellipsometry in the visible and near-infrared spectral region. The analysis of our multilayer slanted columnar thin films deposited at glancing angle ($\theta_i$ = 85°) revealed that such STFs possess monoclinic optical properties, and the optical response may be described by an effective medium dielectric homogenization approach. It will be discussed how the anisotropic Bruggeman effective medium approximation (AB-EMA) allows for determination of structural parameters as well as fractions of individual film constituents. Furthermore, the AB-EMA analysis reveals that the anisotropic dielectric properties of the metal core changes upon deposition of a dielectric cladding.

4:40pm **EL+AS+EM+MS+PS+TF-ThA9 Ellipsometric Characterisation of Porous Aluminium Oxide Supports**, *W. Ogieglo, N.E. Benes,* ***H. Wormeester***, MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

Porous aluminium oxide is widely used as a support material for thin film inorganic micro- and mesoporous membranes. Such membranes are used in energy-efficient gas separation, pervaporation and nanofiltration processes. Ellipsometry can be used to determine material properties of the thin membrane films, as well as the penetrant loading [1]. Interpretation of the ellipsometry data requires a detailed knowledge of the porous aluminium oxide support. This support is made of aluminium oxide particles that are sintered together. In between the particles voids are present that amount to 38% porosity. We have studied the influence of the size of the voids on the optical response of the support material. For this study, voids with a diameter of around 60, 80 and 160 nm were used. We noted a strong decrease of the normal incidence specular reflection with void size and a subsequent increase in off specular reflection. In ellipsometry, only a limited depolarization of the specular reflected light was noted in the wavelength range between 300 and 1750 nm. The angle dependent ellipsometry measurements showed that the optical properties of these supports can not be obtained from a direct inversion. The reason for this is that at the interface the more or less spherical voids are cut, which leads to a distribution of openings at the surface, i.e., a substrate with a very rough surface. This roughness was modelled with a graded porosity changing from 38% in the bulk to 75% at the outer surface. This measured variation in porosity is very similar to the cumulative height distribution of the surface layer obtained from AFM. The validity of this graded porosity model was verified from the analysis of a sample with a thin polysulfone (PSU) layer deposited on the support. The PSU layer partly fills the open pores at the surface. This results in an interface with a graded variation in aluminium oxide, void and PSU.

The proper treatment of the surface layer also provides the optical properties of the porous aluminium oxide bulk material itself. These optical properties can in a limited wavelength range be modelled with Bruggeman's effective medium approximation. As a consequence of the size of the inclusions, their diameter is no longer negligible with respect to the wavelength of light in the UV part of the spectrum. For the material with the largest pore size, also a large part of the visible range has to be excluded. A more elaborate approach than the standard effective medium approach has to be used in this case.

[1] H. Wormeester, N.E. Benes, G.I. Spijksma, H. Verweij and B. Poelsema

Thin Solid Films **455-456**, 747-751 (2004)

5:00pm **EL+AS+EM+MS+PS+TF-ThA10 Optical Properties and Structure of Vanadium Oxide Thin Films**, ***M.A. Motyka****, M.W. Horn,* Pennsylvania State University*, N.J. Podraza*, University of Toledo

Vanadium oxide ($VO_x$) thin films are common materials used as imaging layers in uncooled microbolometer based thermal imaging devices. These films are used in this application largely due to the controllable resistivity of the film (ρ), the high temperature coefficient of resistance (TCR), and the low electrical noise. One of the main difficulties of this material system relates to the multiple valence states of vanadium, each of which results in materials with different electrical properties. Bolometer quality $VO_x$ may consist of a composite of nanocrystalline face centered cubic (FCC) VO phase and amorphous materials. The thin film oxygen content via Rutherford back scattering (RBS) has suggested that the typical ratio V:O should be near 1:1.7-2.0, significantly higher than the stability window of the FCC phase. This off-stoichiometry ratio suggests that the amorphous material is a mixture of higher oxygen valence states similar to $V_2O_5$ and $VO_2$. The higher quality $VO_x$ thin film material also has been observed via transmission electron microscopy (TEM) to contain $VO/V_2O_3$ nano-twin crystalline domains. The presence of each of these phases impacts the electrical and optical properties of the resulting $VO_x$ film. Films with various oxygen contents and structures were studied with spectroscopic ellipsometry (SE) over a spectral range of 0.05 to 5.15 eV using a multichannel dual rotating compensator near-ultraviolet to near infrared instrument in conjunction with Fourier transform infrared spectroscopic ellipsometry (FTIR-SE). Thus, the complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) can be obtained for these materials over the full spectral range. Differences in ε due to variations in the film structure are observed as functions of processing, indicating that SE is a means of probing the material composition and structure. Specifically, ε are compared for various film composites fabricated by unbiased pulsed DC magnetron sputtering as well as composite films prepared by reactive ion beam sputtering and pulsed DC magnetron sputtering with a substrate bias. The microstructure and ε are correlated with films exhibiting the desirable device electrical properties. In situ real time spectroscopic ellipsometry (RTSE) has shown that environmental conditions alter the as-deposited $VO_x$ thin films grown via pulsed DC-magnetron reactive sputtering of a metallic vanadium target. In order to prevent undesired atmospheric effects to the thin film, it is a common practice to encapsulate the thin film with a more environmentally stable material. In this study, the material chosen was $SiO_2$ grown in the same deposition chamber, pre-atmospheric exposure, via rf sputtering.

5:20pm **EL+AS+EM+MS+PS+TF-ThA11 Sensitivity of Dielectric Properties of Vanadium Dioxide Thin Films to Growth Conditions**, *D.W. Ferrara,* ***R.E. Marvel****, J. Nag, R.F. Haglund*, Vanderbilt University

Vanadium dioxide ($VO_2$) is a strongly-correlated electron material with a well-known semiconductor-to-metal transition (SMT) that can be induced thermally ($T_c$ = 68°C), optically, or electrically. Recently, $VO_2$ films have attracted attention as a component in active metamaterials, especially in conjunction with metal nanostructures. Since these structures are highly sensitive to the dielectric properties of the embedding material, the SMT of $VO_2$ can be used to tune the optical response of the structure. Accurately modeling the behavior of these structures requires detailed knowledge of the dielectric function of $VO_2$ as it undergoes the SMT; however, previous measurements of the optical constants of $VO_2$ reveal significant variations between experiments.

To understand systematic variations due to growth conditions, films of $VO_2$ were deposited on either silicon, glass, or sapphire substrates by pulsed laser ablation of vanadium metal targets in 10 mTorr oxygen ($O_2$) background gas, followed by annealing at 450°C in 250 mTorr of $O_2$. Anneal times were varied from 30 to 90 depending on film thickness; deposition thickness was varied from 20 nm to 200 nm. For each sample, temperature-dependent spectroscopic ellipsometry measurements at optical and near-infrared wavelengths were conducted to determine the dependence of the optical constants on film thickness, substrate and crystallinity, and temperature.

Bruggeman and Maxwell-Garnett effective-medium formulations were used to account for three constituent materials: semiconducting $VO_2$, metallic $VO_2$, and vanadium pentoxide ($V_2O_5$). The effective dielectric functions were modeled using Lorentz and Tauc-Lorentz oscillators. Our results show that the contribution of $V_2O_5$ to the effective dielectric function increases with annealing time, consistent with previous studies. The results are also substantiated using Rutherford backscattering, X-ray photoelectron spectroscopy and X-ray diffraction.

## Energy Frontiers Focus Topic
## Room: 102 - Session EN+MS+VT-ThA

### Photovoltaics Manufacturing
**Moderator:** V. Ku, Satcon Technology Corporation

2:00pm **EN+MS+VT-ThA1 Waste Not, Want Not**, ***L.V. Maness, Jr.***, South Park Platinum, Inc. **INVITED**

Rapidly increasing demand for certain geological commodities, in particular semi-conductors, rare earth elements (REE) and those with other desirable characteristics, are making the extraction of formerly ignored elements of significant financial interest for miners, recyclers and other commodity producers. This need is tempered by legal and regulatory requirements that minimize pollution. Historically, miners, smelters and others have used almost all the physical, chemical and electromagnetic characteristics of ores as a means of extraction and concentration – with the exception of the unique benefits afforded by processing in vacuums. Vacuum use enables the clean separation and capture of many commodities that heretofore were wasted, either up smokestacks, in water, or in waste dumps, etc. As a side-benefit, the coating with certain REE, etc., of heated surfaces will enable the selective emission of optimized thermal frequencies for use in generating electricity using Thermal PhotoVoltaics (TPV) technologies: this major improvement in TPV efficiency will result from the suppression in a vacuum of transfer of energy via conduction and convection. In addition, for the many commodities that vaporize selectively in vacuums, a vacuum-smelter would enable the non-polluting capture of all processed materials. Such capabilities will enable revolutionizing the economics of many operations, since the removal of one component from a mix will increase proportionally the relative percentages of the other components. This development will bring closer the goal of "***No Waste Mining***" and of the separation and use of certain otherwise useful constituents, such as arsenic, which are considered harmful, are tightly regulated and whose disposal is presently a very high cost-item.

2:40pm **EN+MS+VT-ThA3 The U.S. PV Manufacturing Consortium – Bringing the Supply Chain Together**, *P. Haldar*, ***H. Efstathiadis***, College of Nanoscale Science & Engineering and U.S. Photovoltaic Manufacturing Consortium **INVITED**

The U.S. Photovoltaic Manufacturing Consortium (PVMC) – a $300 million partnership between SEMATECH and the College of Nanoscale Science and Engineering (CNSE) of the University at Albany – will bring together the entire supply chain of companies to enable the development of advanced PV-related manufacturing processes. Created as part of the U.S. Department of Energy's (DOE) SunShot initiative, which is designed to reduce the cost of photovoltaic solar energy systems by about 75 percent over the next decade, the PVMC will engage over 40 companies and organizations from throughout the solar community. Through PVMC, SEMATECH and CNSE will spearhead a unique research and development collaboration through which industry, academia and government will accelerate the development, commercialization and manufacturing of next-generation copper indium gallium selenide (CIGS) thin film PV manufacturing technologies, increasing performance while driving down the cost and risk of bringing them to the marketplace. By integrating the industrial research consortium and manufacturing development facilities models, PVMC offers lab-to-fab capabilities that will support rapid commercialization of new technologies and incubation of new start-up firms. PVMC offers the Federal government an unparalleled opportunity to promote the competitiveness of the U.S. PV industry.

4:20pm **EN+MS+VT-ThA8 Potentials and Challenges for High Efficiency Multi Junction Solar Cells**, ***Bedair***, North Carolina State University **INVITED**

The developments of multi junction solar cell will be outlined. The major challenges facing this structure will be discussed. There are several current approaches to improve the efficiency of MJ solar cells. They include: lattice matched structure, metamorphic s structure, inverted structure and GaAsN based approach. We will discuss the concept of strain balanced strained layer super lattices in improving the conversing efficiencies of lattice matched MJ solar cells.

The advantages and the limitations of each of these approaches will be presented and discussed. We also discuss the limitations facing the applications of MJ solar cell at high solar concentrations. We will address the tunnel junction issues for concentration exceeding 1000 suns. Series resistance and heat dissipation issues will also be outlined.

Finally the cost issues will be addressed with their limitations on the potential applications of this approached.

## Spectroscopic Ellipsometry Focus Topic
## Room: 209 - Session EL+AS+EM+MS+PS+TF-FrM

## Spectroscopic Ellipsometry: Future Directions and New Techniques
**Moderator:** H. Wormeester, MESA, The Netherlands

8:20am **EL+AS+EM+MS+PS+TF-FrM1 Current Trends and Future Outlook for Spectroscopic Ellipsometry**, ***J.N. Hilfiker***, *B. Johs, C.M. Herzinger, T.E. Tiwald*, J.A. Woollam Co., Inc. **INVITED**

This talk reviews the significant developments in spectroscopic ellipsometry (SE) in areas including extending spectral range, improving accuracy, and enhancing speed. Current SE applications owe much to hardware and software developments of the past. Thus, today's research efforts may reach full potential for applications years or even decades from now. With this in mind, we point to the current state-of-the-art and what this may mean for future SE applications.

Three important areas will be explored. First, there has been a continual trend to expand SE wavelength range. This has included extensions to both shorter and longer wavelengths. For the latter, there is current development into the THz. More immediate benefit may come from smaller SE extensions from the ultraviolet to the near infrared. For example, further near-infrared extensions help to characterize modern transparent conductive oxides (TCOs), used in both inorganic and organic photovoltaic stacks.

Second, we look at the search for improved SE accuracy. Substantial improvements have come with the development of new ellipsometer technologies, progressing from rotating analyzer/polarizer to rotating compensator and now dual-rotating compensator ellipsometers. In addition to improved accuracy, this technology provides advanced measurements, including the complete Mueller-matrix. This will open SE characterization to new applications of anisotropic, nanostructured, and even patterned thin films. Accuracy enhancements must be compatible with the expanding SE spectral range. Infrared SE has overcome many non-ideal optical components to provide measurements competitive to standard FTIR measurements.

Third, we look at the quest for improved measurement speed. This development is constrained by the previous requirements. The benefits of a wide spectral range generally outweigh speed requirements; otherwise laser-based ellipsometry would still have a strong foot-hold. Thus, compromises are made depending on application. Current instrumentation typically utilizes detector arrays for multi-channel SE measurements.

To conclude, we will look at the SE outlook and how it may take advantage of wavelength range, accuracy, and speed. In-line and in-situ SE measurements show special promise. Significant improvements in instrumentation, computing speed, and software are now making these applications more feasible. In addition, there are novel ideas to provide sample access and overcome non-ideal measurement conditions for in-line and in-situ SE. Significant progress in many different areas promises to extend ellipsometry into new areas – many of which are being studied by researchers today.

9:00am **EL+AS+EM+MS+PS+TF-FrM3 THz Optical Hall-effect and MIR-VUV Ellipsometry Characterization of 2DEG Properties in a $HfO_2$ Passivated AlGaN/GaN HEMT Structure**, ***S. Schöche***, U. of Nebraska - Lincoln, *J. Shi*, Cornell U., *A. Boosalis, P. Kühne*, U. of Nebraska - Lincoln, *C.M. Herzinger, J.A. Woollam*, J.A. Woollam Co., Inc., *W.J. Schaff, L.F. Eastman*, Cornell U., *V. Darakchieva*, Linkoping U., Sweden, *M. Schubert, T. Hofmann*, U. of Nebraska - Lincoln

Nitride based high electron mobility transistors (HEMT) utilize the formation of a two-dimensional electron gas (2DEG) at the interface between GaN and AlGaN due to a difference in spontaneous polarization. It is known that surface traps significantly influence the electrical properties of this 2DEG. Accurate knowledge about the influence of surface passivation on the channel properties is crucial. The device performance is governed by the mobility, the sheet charge density, and the effective mass of electrons in the 2DEG. These parameters are typically determined by electrical Hall effect (EHE), Shubnikov-de Haas (SdH), or cyclotron resonance (CR) measurements. Commonly these experiments require very low temperatures and high magnetic fields. Complex contact configurations are required for SdH and EHE and the ability to locate the 2DEG and possible parallel current paths is limited.

We present non-contact, optical measurements of free-charge carrier mobility, sheet density, and effective mass parameters of the 2DEG for a $HfO_2$-passivated AlGaN/GaN HEMT structure at room temperature. Spectroscopic ellipsometry in the spectral range from THz and Mid-IR to VUV and THz optical Hall-effect (generalized ellipsometry in magnetic field) (OHE) are employed.

The MIR measurements are performed for analysis of the heterostructure constituents' layer thickness, phonon modes, and volume free charge carriers. The phonon mode parameters were found to be in excellent agreement with literature values and the existence of significant volume charge carrier concentrations could be excluded. NIR to VUV ellipsometry is used to determine the thickness of the thin top layers. From a line-shape analysis in the VUV spectral range the optical constants of the $HfO_2$ passivation layer could be extracted. An amorphous structure of the HfO2 passivation layer could be confirmed by comparison with existing studies in literature.

OHE in the THz spectral range is performed for characterization of the 2DEG channel parameters. A classical Drude model for free charge carrier contribution to the dielectric function was applied to determine the sheet density, the carrier mobility, and the effective mass of the 2DEG electrons. The electron effective mass of ($0.22\pm0.04$) $m_0$ extracted here using OHE corroborates the values found in previous SdH and CR studies. The values for the high-frequency sheet density and carrier mobility obtained by the optical investigations in the THz spectral range are in excellent agreement with results from dc EHE measurements indicative within linear Boltzmann transport theory for frequency-independent carrier scattering mechanisms of the 2D carrier distribution.

9:20am **EL+AS+EM+MS+PS+TF-FrM4 Vector-Magneto-Optical Generalized Ellipsometry on Sculptured Thin Films**, ***D. Schmidt***, *C. Briley, E. Schubert, M. Schubert*, University of Nebraska - Lincoln

Sculptured thin films are self-organized and self-assembled three-dimensional nanostructures with tunable geometries. These artificial nanostructured thin films exhibit highly anisotropic physical properties, which mainly depend on their specific geometry.

Slanted, highly-spatially coherent, columnar nanostructure samples were prepared by glancing angle electron-beam deposition. Glancing angle deposition is a bottom-up fabrication technique that employs a physical vapor deposition process at oblique angles where the trajectory of the incoming particle flux is not parallel to the substrate normal. The technique allows to engineer the columnar film structure and is today amongst the most promising self-organized fabrication processes in micro- and nanotechnology.

We present and discuss the novel approach of vector-magneto-optical generalized ellipsometry on ferromagnetic permalloy nanostructured thin films carried out at room temperature. Investigations have shown that the metal alloy thin films are highly transparent, reveal strong form-induced birefringence, and exhibit intriguing magneto-optical anisotropy. Spatial magnetization orientation hysteresis and magnetization magnitude hysteresis properties are studied using a three-dimensional Helmholtz coil arrangement. This particular octupole setup allows for arbitrary magnetic field directions at the sample position with field strengths up to 200 mT while optical access is granted for reflection and transmission-type ellipsometry measurements. Analysis of data obtained within this unique vector-magneto-optic setup reveals magnetization anisotropy of the permalloy slanted nanocolumns and gives insight into switching behavior of confined magnetic domains.

9:40am **EL+AS+EM+MS+PS+TF-FrM5 THz Dielectric Anisotropy of Metal Slanted Columnar Thin Films**, ***T. Hofmann***, *D. Schmidt, A. Boosalis, P. Kühne, R. Skomski*, University of Nebraska-Lincoln, *C.M. Herzinger, J.A. Woollam*, J.A. Woollam Co., Inc., *M. Schubert, E. Schubert*, University of Nebraska-Lincoln

Sculptured thin films (STFs) present an interesting class of self-organized, artificially made materials with three-dimensional, highly spatially coherent arrangements of nanostructures. Contemporary interest in materials for terahertz (THz) electronic, optoelectronic, and optical applications is redrawing attention to STFs that may enable designed optical properties for the THz frequency region.

We report on the anisotropic optical dielectric functions of a metal (cobalt) slanted columnar thin film deposited by electron-beam glancing angle deposition for the THz frequency domain using generalized spectroscopic ellipsometry. A simple anisotropic Bruggeman effective medium dielectric function homogenization approach is successfully employed to describe the observed optical response. This approach describes isolated, electrically conductive columns which render the thin film biaxial (orthorhombic). The anisotropy induced by the columnar film structure is very large. The anisotropic Bruggeman effective medium approach predicts upon slight modifications of Drude, fraction and/or depolarization parameters that

targeted optical properties of STF in the THz range can be achieved by variation of slanting angle, lateral column density, and material.

10:00am **EL+AS+EM+MS+PS+TF-FrM6 A Compact High-speed Spectroscopic Ellipsometer**, ***G. Chin***, ULVAC Inc., Japan

Recently, we developed a compact, high-speed spectroscopic ellipsometer. It analyzes the spectrums obtained from the polarization interference occurring between two multiple-order retarders which snapshot the wavelength distribution of the sample's spectroscopic polarization parameters. This innovative spectroscopic ellipsometer can measure the thickness and optical constants of thin films at a dramatically fast speed. Its acquisition time is as short as 10 ms. It does not require the conventional complex mechanical or active components for polarization-control, such as a rotating compensator and an electro-optical modulator. It can open great opportunities for new applications of the spectroscopic ellipsometry in which the compactness, the simplicity and the rapid response are extremely important. For example, it was integrated into the deposition tool and successfully measured thin films in the vacuum chamber.

This paper describes the principle, system configuration and our innovative efforts on developing the compact high-speed spectroscopic ellipsometer. Some typical application data will be also introduced, such as in line and in situ measurements for photovoltaic, flat panel display and semiconductor industries.

10:20am **EL+AS+EM+MS+PS+TF-FrM7 Ellipsometry Porosimetry (EP): In Situ Spectroscopic Ellipsometry Measurements Coupled with Pressure Controlled Adsorption of Organic Vapors to Study Properties of Nano-Porous Thin Films**, *J.P. Piel, L. Kitzinger,* ***A. Bondaz****, C. Defranoux*, SEMILAB-SOPRALAB, France

Ellipsometric porosimetry (EP) is a non contact, non destructive technique that is cited as a reference technique for porous thin film analysis [1, 2]. As it is based on a spectroscopic ellipsometric measurement, the technique allows the precise determination of the refractive indices and thickness of the porous films. The advantage of these EP tools is that the combination of this well established spectroscopic ellipsometric (SE) technique with a suitably adapted adsorption chamber permits access to all the information obtained by classic adsorption experiments (e.g. BET) on thin films with an excellent sensitivity. Information such as open and closed porosity, pore size distribution etc... can be thus obtained.

In addition the EP allows access to a multitude of information that the classic equipment does not. For example, Spectroscopic Ellipsometry allows to follow the variation of the sample thickness during the adsorption experiment, leading to the determination of the Young's Modulus for the thin films. This will be presented. The technique is highly sensitive to the detection of interfaces; it is thus possible to detect a porosity gradient or to study a multilayer structure and thereafter simultaneously plot the two corresponding adsorption isotherms [3]. In the same manner, the instrument permits the use of a range of different gases adsorptive in order to tailor the probe molecule to the morphology and to the chemistry of the porous layer at ambient temperature [4]. We thus obtain information on the chemistry of the pores within the layer, before, during and after the adsorption experiment. Recent developments include the implementation of the FTIR interferometer SE extension to the EP system. It allows a precise characterization of the chemistry of the pores within the layer. We thus obtain information on the chemical bonds present in the layers before, during and after the adsorption experiment. Preliminary results will be presented.

Specifically, this fundamental technique permits the thorough characterization of porous thin film samples. We will demonstrate some of the different features of the EP technique with regards to the morphological and chemical properties of the porous thin films. Additionally, we will illustrate the technique for various thin film applications such as solgel thin films, nanofilms for catalysis, photovoltaic cells, fuel cells, optical sensors, and bio-compatible materials to name but a few.

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[2] C. Wongmanerod et al, *Appl. Surf. Sci.* **172**, 117 (2001).

[3] A. Bourgeois et al, *Thin Solid Films* **455-456**, 366 (2004).

[4] A. Bourgeois et al, *Adsorption* **11**, 195 (2005).

## Graphene and Related Materials Focus Topic
## Room: 208 - Session GR+MS+EM-FrM

## Graphene Device Physics and Applications
**Moderator:** M. Arnold, University of Wisconsin-Madison

8:20am **GR+MS+EM-FrM1 Fabrication and Characterization of Graphene p-n Junction Devices**, ***J.U. Lee***, University at Albany-SUNY **INVITED**

Graphene is a newly discovered material composed of two-dimensional array of hexagonal carbon atoms. It has a number of unique electronic properties, the most remarkable of which is the zero band-gap light-like linear electronic dispersion, giving rise to Dirac fermions. This feature can be used to make devices based on previously unexplored physical properties. For example, in analogy to optics, we describe new devices based on *optics-like manipulation of electrons*.

Our devices are based on graphene and bi-layer graphene *p-n* junctions doped using electrostatic doping techniques from buried split gates. In the present context, graphene *p-n* junctions do not rectify, i.e. behave as semiconductor diodes. Instead, in graphene p-n junctions, carriers launched from a point contact from one side of the junction are able to refocus back to a point on the other side of the junction. This behavior, known as the Veselago effect, can be the basis for new logic devices for replacing Si CMOS. In addition, using the same platform, we describe interconnect structures that can be reconfigured. Together, we envision a new circuit paradigm based on components that seamlessly reconfigure between devices and interconnect components.

In this talk, we describe the details of graphene *p-n* junction fabrication and characterization, and circuits that are enabled by the *p-n* junction devices. The devices are fabricated at CNSE's state-of-the-art 300mm Si wafer fabrication line using processing techniques that leave atomically flat top oxide surface above the patterned split gates. For characterizing the p-n junctions, we perform transport and SPM measurements.

9:00am **GR+MS+EM-FrM3 Assembled Bilayer Graphene for Electronic Applications**, ***G.G. Jernigan****, T.J. Anderson, J.T. Robinson, J.D. Caldwell, M.D. Ancona, V.D. Wheeler, L.O. Nyakiti, J. Culbertson, A.L. Davidson, A.L. Friedman, P.M. Campbell, D.K. Gaskill*, U.S. Naval Research Laboratory

Graphene has shown successful application in RF transistors and frequency doublers where its high mobility and high saturation velocity translate into operation at high frequencies while utilizing little power. However, a major detraction to graphene development for other device applications is that it does not have a band gap. The lack of a band gap means that graphene's current cannot be turned off. Bilayer graphene is regarded as one possible solution to this problem, since bilayer graphene is capable of developing a band gap if the symmetry of the system can be broken. That said, bilayer graphene (from exfoliation or growth) forms a highly ordered A-B stack of the two graphene sheets resulting in little to no band gap, unless a high electric field can be applied.

In this presentation, we will demonstrate a novel method for creating bilayer graphene where a single layer of CVD graphene grown on Cu is bonded to a single layer of epitaxial graphene grown on Si-face SiC. This process results in a bilayer system that has a built-in asymmetry that yields unique physical and electrical properties not previously observed. For example, we demonstrate that the transfer of CVD graphene to epitaxial graphene results in a smoother morphology than transfer onto SiO2 and that bonding of CVD graphene to epitaxial graphene can avoid the damage caused by the drying step necessary in the poly (methyl methacrylate) transfer method. X-ray photoelectron spectroscopy and Raman microscopy demonstrate that the sheets are coupled together but strained differently, in contrast to a naturally formed bilayer. Electrical characterization of Hall devices fabricated on the novel bilayer show higher mobilities and lower carrier concentrations than the individual CVD graphene or epitaxial graphene sheets alone. Modeling of the electric field produced by opposite doping in the graphene sheets will also be presented, as CVD graphene is typically p-type and epitaxial graphene is typically n-type.

10:00am **GR+MS+EM-FrM6 Rectification at Graphene / Semiconductor Junctions: Applications Beyond Silicon Based Devices**, ***S. Tongay****, X. Miao, K. Berke, M. Lemaitre, B.R. Appleton, A.F. Hebard*, University of Florida

Schottky barriers are crucial and necessary device components of metal-semiconductor field effect transistors (MESFETs) and high electron mobility transistors (HEMTs). Here, we report on the formation of Schottky barriers at graphene-multilayer graphene/semiconductor junction interfaces which have been characterized by current density vs. voltage (J-V) and

capacitance vs. voltage (C-V) measurements. After graphene transfer onto various semiconductors such as Si, GaAs, GaN and SiC, we observe a strong rectification at the interface, i.e., high (low) resistance in the reverse (forward) bias directions. The J-V characteristics have been analyzed using thermionic emission theory and the extracted barrier height values are consistent with the Schottky-Mott model. When capacitance is plotted as $1/C^2$ vs V, a linear dependence is observed, which by extrapolation to the intercept identifies a built in potential that is consistent with the Schottky barrier height extracted from J-V measurements. Graphene's low Fermi energy together with its robust thermal, chemical, structural and physical properties provide numerous advantages when used to form Schottky barriers in device applications: namely, voltage tunability of the Schottky barrier height, stability to high temperatures, resistance to impurity diffusion across the interface, and the use of absorbates to chemically tune the Fermi energy and hence the Schottky barrier height.

10:20am **GR+MS+EM-FrM7 Imaging of Electron Beam Induced Current in Epitaxial Graphene**, ***S. Mou***, *J. Boeckl, W.C. Mitchel, J.H. Park,* Air Force Research Laboratory, *S. Tetlak,* Wyle Laboratories, *W. Lu*, Fisk University

It has been known and observed that there forms a Schottky junction between graphene and SiC in epitaxial graphene due to the work function difference and the charge transfer between them. As a result, it is viable to apply the electron beam induce current (EBIC) technique on the epitaxial graphene directly due to the fact that it needs a built-in field and ample electron generation volume to generate EBIC. EBIC is an important characterization technique, which identifies electrically active impurities/defects, detects local built-in field, and measures minority carrier diffusion length. In this paper, we use a FEI SEM equipped with a current amplifier to investigate the spatial mapping of EBIC generation and collection in a two terminal geometry. The incident electron beam generates excited electron-hole pairs in SiC and the minority carriers are collected through the Schottky junction before flowing into graphene. EBIC imaging reveals mesoscopic domains of bright and dark contrast areas due to local EBIC polarity and magnitude, which is believed to be the result of spatial fluctuation in the carrier density in graphene. We also investigate the electron energy dependence, which modulates the EBIC magnitude. With an analytical drift-diffusion current model, we are able to extract the minority carrier diffusion length in the SiC, which is on the order of micro meter and agrees well with other published data.

10:40am **GR+MS+EM-FrM8 Potassium-Ion Sensors Based on Valinomycin-Modified Graphene Field-Effect Transistors**, ***Y. Sofue***, *Y. Ohno, K. Maehashi, K. Inoue, K. Matsumoto*, The Institute of Scientific and Industrial Research, Osaka University, Japan

Highly sensitive ion sensors based on valinomycin-modified graphene field-effect transistors (VGFETs) have been developed to selectively detect K ions, which are an essential element for biological activity including human life. Graphene single-layers were obtained by mechanical exfoliation. Graphene FETs were fabricated by conventional e-beam lithography and lift-off method on a thermally grown $SiO_2$ layer. To demonstrate selective detection of K ions, the graphene channels were covered with ion selective membrane, which consisted of polyvinyl chloride and valinomycin. Transfer characteristics of VGFETs in a 100 mM Tris-HCl buffer solution with various KCl concentrations over the range from 10 nM to 1.0mM. With increasing K ion concentration, the solution-gated voltage at the Dirac point shifted toward negative direction. The shifts are due to the accumulation of positively charged K ions surrounded by valinomycin on the graphene surfaces. The electrostatic potential of graphene surfaces exhibit a rather linear dependence on log[K]. These results indicate that VGFETs effectively detected K ions with concentration from 10 nM to 1.0 mM. To investigate selectivity in VGFETs, Na-ion concentration dependence was also measured. The transfer characteristic in VGFETs remained almost constant over the Na ion concentration range between 10 nM and 1.0 mM. These results indicate that VGFET selectively detected K ions with high sensitivity.

11:00am **GR+MS+EM-FrM9 Band-gap Generation by using Ionic-Liquid Gate in Bilayer Graphene**, ***Y. Yamashiro***, *Y. Ohno, K. Maehashi, K. Inoue, K. Matsumoto*, Osaka University, Japan

Electric fields were applied to a bilayer graphene to generate a band gap using an ionic-liquid gate instead of the general top-gate structures. The ionic-liquid gate can apply higher electric field than other type of the gates because of its large capacitance and electric strength. In this abstract, the graphene layers were extracted from kish graphite by a mechanical exfoliation and were put on highly *n*-doped Si substrates covered with a 300-nm-thick $SiO_2$ layer. Side-gate electrodes were patterned approximately 20 mm away from the channels. An ionic liquid (DEME-TFSI) was put on the bilayer graphene and the side-gate electrode. Electrical characteristics at 300 K revealed that the electrical double layer in the ionic-liquid, which works as a very thin insulator, had 200 times larger capacitance than a 300-nm-thick $SiO_2$ layer. The thickness of electrical double layer was estimated to be 3.75 nm. In electric field dependence measurements, an increase in a sheet resistance of the bilayer grapheme channel was clearly observed with increasing the magnitude of electric field in bilayer graphene. On the other hand, the increase in the sheet resistance didn't appear in the monolayer- and trilayer- graphene. That is why the increasing of the sheet resistance was caused by a band gap generated in ionic-liquid gated bilayer graphene by the electric field.

11:20am **GR+MS+EM-FrM10 Electronic Transport in Hydrogenated Graphene Films**, ***B.R. Matis***, *J.S. Burgess,* NRC/NRL Postdoctoral Associate, *A.L. Friedman, J.T. Robinson,* Naval Research Laboratory (NRL), *F.A. Bulat,* Sotera Defense Solutions, Inc., *B.H. Houston, J.W. Baldwin*, Naval Research Laboratory (NRL)

Graphene films grown by chemical vapor deposition on copper foils and exfoliated graphene flakes were hydrogenated using low kinetic energy plasma processing. The film sheet resistance can be tuned over a wide range (1 kΩ/square – 300 kΩ/square), increasing proportionally with hydrogen coverage. Variable temperature measurements demonstrate a transition from semi-metallic behavior for graphene to semiconducting behavior for hydrogenated graphene. Sheet resistance measurements as a function of temperature also suggest the emergence of a band gap in the hydrogenated graphene films. Interesting surface doping effects will be discussed in conjunction with the location of the charge neutrality point. This work was supported by the Office of Naval Research.

11:40am **GR+MS+EM-FrM11 First-principles Study of Electronic Properties of Two Dimensional Carbon and Boron Nitride Nanomaterials**, ***S. Mukherjee***, S.N. Bose National Centre for Basic Sciences, India

First principles pseudopotential plane wave method was used to study ground state electronic properties of Graphene, hexagonal Boron Nitride (h-BN), Graphene doped with Boron and Nitrogen, and multilayers of Graphene and h-BN. Our results on doped Graphene indicate that upon electron (hole) doping, the Dirac-point in the electronic bandstructure shifts below (above) the Fermi level and a gap appears at the high-symmetric K-point. Upon co-doping of Graphene by both Boron and Nitrogen a small energy gap between the conduction and valence band appears at the Fermi level, making the CBN nanomaterial a narrow band semiconductor. The energy gap depends sensitively on the degree of doping and on the thickness of CBN layer. These results are in agreement with recent experimental measurements [1,2]. Our bandstructure calculations on the multilayers of Graphene and h-BN indicate that these nanostructured multilayers exhibit semiconducting behaviour with band gap in the range 60-600 meV depending on the relative orientation and thickness of the layers. (Author: Sugata Mukherjee, work done in collaboration with T.P. Kaloni)

1. X. wang et al, Science **324**, 768 (2009)

2. L. Cie et al, Nature Materials **9**, 430 (2010).

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Czaplewski, D.A.: NM+MN+MS+TF-TuM9, **4**

**— D —**

Darakchieva, V.: EL+AS+EM+MS+PS+TF-FrM3, 16
Davidson, A.L.: GR+MS+EM-FrM3, 17
De Oteyza, D.G.: NM+MN+MS+TF-TuM12, **5**
Defranoux, C.: EL+AS+EM+MS+PS+TF-FrM7, 17; EL+AS+EM+MS+PS+TF-ThM10, 12
Dezelah, C.: NM+MS+NS+TF-MoM6, **1**
Dhuey, S.: NM+MN+MS+TF-TuM12, 5
Dickey, E.: NM+MS+NS+TF-MoM10, **2**
Diebold, A.C.: NM+AS+MS-WeM11, **10**
Doering, R.: NM+NS+MS-TuA1, 6

**— E —**

Eastman, L.F.: EL+AS+EM+MS+PS+TF-FrM3, 16
Efstathiadis, H.: EN+MS+VT-ThA3, **15**
Eichhorn, K.-J.: EL+AS+EM+MS+PS+TF-ThM1, **11**
Escobar, C.A.: NM+MN+MS+TF-TuM3, 4

**— F —**

Falch, R.M.: NM+MN+MS+TF-TuM12, 5
Faradzhev, N.S.: EL+AS+EM+MS+PS+TF-ThM9, 12
Ferrara, D.W.: EL+AS+EM+MS+PS+TF-ThA11, 14
Fowlkes, J.D.: NM+NS+MS-TuA11, 6
Friedman, A.L.: GR+MS+EM-FrM10, 18; GR+MS+EM-FrM3, 17

**— G —**

Gaskill, D.K.: GR+MS+EM-FrM3, 17
George, S.M.: NM+MS+NS+TF-MoM8, **1**
Gerasimov, J.Y.: EL+AS+EM+MS+PS+TF-ThM6, **12**
Goodlin, B.E.: NM+NS+MS-TuA1, **6**
Grantham, S.: EL+AS+EM+MS+PS+TF-ThM9, 12
Guillorn, M.A.: NM+MN+MS+TF-TuM10, **4**
Guisinger, N.P.: VT+MN+NS+SS+AS-TuA8, 8

**— H —**

Haensch, W.E.: NM+MN+MS+TF-TuM10, 4
Haglund, R.F.: EL+AS+EM+MS+PS+TF-ThA11, 14
Haldar, P.: EN+MS+VT-ThA3, 15
Hallberg, T.: EL+AS+EM+MS+PS+TF-ThM4, 11
Harteneck, B.D.: NM+MN+MS+TF-TuM12, 5
Hartfield, C.D.: NM+NS+MS-TuA11, 6
Hays, S.M.: NM+AS+MS-WeM6, **10**
Hebard, A.F.: GR+MS+EM-FrM6, 17
Herzinger, C.M.: EL+AS+EM+MS+PS+TF-FrM1, 16; EL+AS+EM+MS+PS+TF-FrM3, 16; EL+AS+EM+MS+PS+TF-FrM5, 16
Hilfiker, J.N.: EL+AS+EM+MS+PS+TF-FrM1, **16**
Hill, S.B.: EL+AS+EM+MS+PS+TF-ThM9, 12
Hofmann, T.: EL+AS+EM+MS+PS+TF-FrM3, 16; EL+AS+EM+MS+PS+TF-FrM5, **16**
Horn, M.W.: EL+AS+EM+MS+PS+TF-ThA10, 14
Houston, B.H.: GR+MS+EM-FrM10, 18
Huh, K.: NM+NS+MS-TuA12, 7
Hwang, H.: NM+NS+MS-TuA12, 7

**— I —**

Ianno, N.: EL+AS+EM+MS+PS+TF-ThA8, 14
Inoue, K.: GR+MS+EM-FrM8, 18; GR+MS+EM-FrM9, 18
Iwai, H.: NM+MS+NS+TF-MoM5, 1

**— J —**

Jang, S.: NM+NS+MS-TuA12, 7
Järrendahl, K.: EL+AS+EM+MS+PS+TF-ThM4, 11
Jennings, G.K.: NM+MN+MS+TF-TuM3, **4**
Jeon, I.: NM+NS+MS-TuA12, 7
Jernigan, G.G.: GR+MS+EM-FrM3, **17**
Jimenez, J.M.: VT+MN+NS+SS+AS-TuA12, 9
Johs, B.: EL+AS+EM+MS+PS+TF-FrM1, 16
Jung, K.: NM+NS+MS-TuA12, 7

**— K —**

Kakushima, K.: NM+MS+NS+TF-MoM5, 1
Kamineni, V.K.: NM+AS+MS-WeM11, 10
Kariis, H.: EL+AS+EM+MS+PS+TF-ThM4, 11
Karim, Z.: NM+NS+MS-TuA3, 6
Kasputis, T.: EL+AS+EM+MS+PS+TF-ThM5, 11
Kelley, M.: VT+MN+NS+SS+AS-TuA4, **7**
Kessels, W.M.M.: EL+AS+EM+MS+PS+TF-ThA7, 13
Kim, B.: NM+NS+MS-TuA12, 7
Kim, S.: NM+NS+MS-TuA12, 7
Kitzinger, L.: EL+AS+EM+MS+PS+TF-FrM7, 17; EL+AS+EM+MS+PS+TF-ThM10, **12**
Knoops, H.C.M.: EL+AS+EM+MS+PS+TF-ThA7, 13
Kostamo, J.: NM+MS+NS+TF-MoM6, 1
Kouda, M.: NM+MS+NS+TF-MoM5, 1
Krim, J.: VT+MN+NS+SS+AS-TuA3, 7
Kühne, P.: EL+AS+EM+MS+PS+TF-FrM3, 16; EL+AS+EM+MS+PS+TF-FrM5, 16
Kulshreshtra, P.: NM+MN+MS+TF-TuM12, 5
Kurihara, M.: NM+MN+MS+TF-TuM4, **4**

**— L —**

Lai, R.Y.: EL+AS+EM+MS+PS+TF-ThM6, 12
Landin, J.: EL+AS+EM+MS+PS+TF-ThM4, 11
Lanza, G.: VT+MN+NS+SS+AS-TuA12, 9
Lecordier, L.: NM+MS+NS+TF-MoM3, 1
Lee, J.: NM+NS+MS-TuA12, 7
Lee, J.U.: GR+MS+EM-FrM1, **17**
Lee, S.: NM+NS+MS-TuA12, 7
Lee, T.: NM+NS+MS-TuA12, 7
Lehto, T.: NM+MS+NS+TF-MoM6, 1
Leick, N.: EL+AS+EM+MS+PS+TF-ThA7, **13**
Lemaitre, M.: GR+MS+EM-FrM6, 17
Levi, D.: EL+AS+EM+MS+PS+TF-ThA1, **13**
Li, Y.: VT+MN+NS+SS+AS-TuA11, **8**
Lin, C.-H.: NM+MN+MS+TF-TuM10, 4
Liu, G.: NM+MS+NS+TF-MoM3, 1
Liu, X.: VT+MN+NS+SS+AS-TuA11, 8
Lu, B.: NM+NS+MS-TuA3, **6**
Lu, W.: GR+MS+EM-FrM7, 18
Lucatorto, T.B.: EL+AS+EM+MS+PS+TF-ThM9, 12
Lukaszew, R.A.: VT+MN+NS+SS+AS-TuA8, 8; VT+MN+NS+SS+AS-TuA9, 8

**— M —**

Mackus, A.J.M.: EL+AS+EM+MS+PS+TF-ThA7, 13
Maehashi, K.: GR+MS+EM-FrM8, 18; GR+MS+EM-FrM9, 18
Magel, G.A.: NM+NS+MS-TuA11, 6
Malinen, T.: NM+MS+NS+TF-MoM6, 1
Maness, Jr., L.V.: EN+MS+VT-ThA1, **15**
Marchman, H.M.: NM+NS+MS-TuA11, 6
Marsillac, S.: EL+AS+EM+MS+PS+TF-ThA4, 13
Marvel, R.E.: EL+AS+EM+MS+PS+TF-ThA11, **14**
Matis, B.R.: GR+MS+EM-FrM10, **18**
Matsumoto, K.: GR+MS+EM-FrM8, 18; GR+MS+EM-FrM9, 18
Miao, X.: GR+MS+EM-FrM6, 17
Millette, J.R.: NM+AS+MS-WeM6, 10
Mitchel, W.C.: GR+MS+EM-FrM7, 18
Moore, T.M.: NM+NS+MS-TuA11, 6
Motyka, M.A.: EL+AS+EM+MS+PS+TF-ThA10, **14**
Mou, S.: GR+MS+EM-FrM7, **18**
Mukherjee, S.: GR+MS+EM-FrM11, **18**

**— N —**

Nag, J.: EL+AS+EM+MS+PS+TF-ThA11, 14
Nam, S.: NM+NS+MS-TuA12, 7
Nealey, P.F.: NM+MN+MS+TF-TuM5, **4**
Negishi, N.: NM+MN+MS+TF-TuM4, 4
Nishida, T.: NM+MN+MS+TF-TuM4, 4
Nizamidin, N.: NM+MN+MS+TF-TuM3, 4
Nyakiti, L.O.: GR+MS+EM-FrM3, 17

**— O —**

Ocola, L.E.: NM+MN+MS+TF-TuM9, 4
Odom, T.W.: NM+MN+MS+TF-TuM1, **4**
Ogieglo, W.: EL+AS+EM+MS+PS+TF-ThA9, 14
Ohno, Y.: GR+MS+EM-FrM8, 18; GR+MS+EM-FrM9, 18
Olynick, D.L.: NM+MN+MS+TF-TuM12, 5

**— P —**

P. Ryan Fitzpatrick, P.R.: NM+MS+NS+TF-MoM8, 1
Palmer, M.A.: VT+MN+NS+SS+AS-TuA11, 8
Pannier, A.K.: EL+AS+EM+MS+PS+TF-ThM5, 11
Park, J.H.: GR+MS+EM-FrM7, 18

Perera, P.: NM+MN+MS+TF-TuM12, 5
Piel, J.P.: EL+AS+EM+MS+PS+TF-FrM7, 17; EL+AS+EM+MS+PS+TF-ThM10, 12
Pilvi, T.: NM+MS+NS+TF-MoM6, 1
Podraza, N.J.: EL+AS+EM+MS+PS+TF-ThA10, 14; EL+AS+EM+MS+PS+TF-ThA3, **13**
Powers, K.W.: NM+AS+MS-WeM4, **10**

**— R —**

Rack, P.D.: NM+NS+MS-TuA11, 6
Ramananthan, S.: NM+NS+MS-TuA3, 6
Ranjan, V.: EL+AS+EM+MS+PS+TF-ThA4, 13
Rauch, S.: EL+AS+EM+MS+PS+TF-ThM3, **11**
Reece, C.: VT+MN+NS+SS+AS-TuA9, 8
Richter, L.J.: EL+AS+EM+MS+PS+TF-ThM9, **12**
Roach, W.M.: VT+MN+NS+SS+AS-TuA9, **8**
Roberts, N.A.: NM+NS+MS-TuA11, **6**
Robinson, J.T.: GR+MS+EM-FrM10, 18; GR+MS+EM-FrM3, 17
Roco, M.: NM+MS-MoA2, **3**
Rodenhausen, K.B.: EL+AS+EM+MS+PS+TF-ThM5, **11**; EL+AS+EM+MS+PS+TF-ThM6, 12
Ruoff, R.S.: NM+NS+MS-TuA9, **6**

**— S —**

Santis, S.De.: VT+MN+NS+SS+AS-TuA11, 8
Satake, M.: NM+MN+MS+TF-TuM4, 4
Schaff, W.J.: EL+AS+EM+MS+PS+TF-FrM3, 16
Schmidt, D.: EL+AS+EM+MS+PS+TF-FrM4, **16**; EL+AS+EM+MS+PS+TF-FrM5, 16; EL+AS+EM+MS+PS+TF-ThA8, 14; EL+AS+EM+MS+PS+TF-ThM5, 11
Schmidt, M.: NM+MN+MS+TF-TuM12, 5
Schöche, S.: EL+AS+EM+MS+PS+TF-FrM3, **16**
Schubert, E.: EL+AS+EM+MS+PS+TF-FrM4, 16; EL+AS+EM+MS+PS+TF-FrM5, 16; EL+AS+EM+MS+PS+TF-ThA8, 14
Schubert, M.: EL+AS+EM+MS+PS+TF-FrM3, 16; EL+AS+EM+MS+PS+TF-FrM4, 16; EL+AS+EM+MS+PS+TF-FrM5, 16; EL+AS+EM+MS+PS+TF-ThA8, **14**; EL+AS+EM+MS+PS+TF-ThM5, 11; EL+AS+EM+MS+PS+TF-ThM6, 12
Schuck, P.J.: NM+MN+MS+TF-TuM12, 5
Schwartzberg, A.: NM+MN+MS+TF-TuM12, 5
Sershen, M.: NM+MS+NS+TF-MoM3, 1
Shi, J.: EL+AS+EM+MS+PS+TF-FrM3, 16
Sikora, J.P.: VT+MN+NS+SS+AS-TuA11, 8
Skomski, R.: EL+AS+EM+MS+PS+TF-FrM5, 16
Sofue, Y.: GR+MS+EM-FrM8, **18**
Sowa, M.: NM+MS+NS+TF-MoM3, 1
Strachan, J.P.: NM+NS+MS-TuA7, **6**
Stroscio, J.A.: VT+MN+NS+SS+AS-TuA1, **7**
Sundaram, G.M.: NM+MS+NS+TF-MoM3, 1
Suzuki, T.: NM+MS+NS+TF-MoM5, **1**

**— T —**

Taborelli, M.: VT+MN+NS+SS+AS-TuA12, 9
Tada, Y.: NM+MN+MS+TF-TuM4, 4
Tarrio, C.: EL+AS+EM+MS+PS+TF-ThM9, 12
Tetlak, S.: GR+MS+EM-FrM7, 18
Tiwald, T.E.: EL+AS+EM+MS+PS+TF-FrM1, 16
Toivola, M.: NM+MS+NS+TF-MoM6, 1
Tongay, S.: GR+MS+EM-FrM6, **17**
Tsuchiya, Y.: NM+MN+MS+TF-TuM4, 4
Tuberquia, J.C.: NM+MN+MS+TF-TuM3, 4
Tuominen, M.T.: NM+MS-MoA6, **3**

**— U —**

Uppireddi, K.: EL+AS+EM+MS+PS+TF-ThA6, **13**

**— V —**

Valente-Feliciano, A.-M.: VT+MN+NS+SS+AS-TuA10, **8**

**— W —**

Walker, M.J.: VT+MN+NS+SS+AS-TuA3, 7
Wang, H.: EL+AS+EM+MS+PS+TF-ThM5, 11; EL+AS+EM+MS+PS+TF-ThM6, 12
Weber, J.W.: EL+AS+EM+MS+PS+TF-ThA7, 13
Weber, M.J.: EL+AS+EM+MS+PS+TF-ThA7, 13
Wheeler, V.D.: GR+MS+EM-FrM3, 17
Williams, R.S.: NM+NS+MS-TuA7, 6
Woollam, J.A.: EL+AS+EM+MS+PS+TF-FrM3, 16; EL+AS+EM+MS+PS+TF-FrM5, 16
Wormeester, H.: EL+AS+EM+MS+PS+TF-ThA9, **14**
Wu, A.T.: VT+MN+NS+SS+AS-TuA7, **7**

**— Y —**

Yamada, S.: NM+NS+MS-TuA12, 7
Yamashiro, Y.: GR+MS+EM-FrM9, **18**
Yan, L.: EL+AS+EM+MS+PS+TF-ThA6, 13
Yasuda, T.: NM+MS+NS+TF-MoM5, 1
Yeo, J.: NM+NS+MS-TuA12, **7**
Yin Vallgren, C.: VT+MN+NS+SS+AS-TuA12, 9
Yoo, W.: NM+NS+MS-TuA12, 7
Yoshida, H.: NM+MN+MS+TF-TuM4, 4