

Monday Morning, October 31, 2011

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 CeO₂/La₂O₃ and MgO/La₂O₃ 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

La₂O₃ 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 La₂O₃, however, the performance of the MOSFETs incorporating ALD-La₂O₃ needs much improvement. Our previous studies using EB evaporation showed that capping the La₂O₃ dielectrics with an ultrathin layer of CeO₂ or metallic Mg (~1 nm) effectively improved the channel mobility [1,2]. In this paper, we report fabrication of CeO₂/La₂O₃ and MgO/La₂O₃ 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-La₂O₃.

The experiments were carried out using a multi-chamber ALD/CVD system which was capable of in-situ metallization and RTA. The CeO₂/La₂O₃ and MgO/La₂O₃ gate stacks were formed on H-terminated Si(100) using Ce[OCEt₂Me]₄, La(PrCp)₃, and Mg(EtCp)₂ metal sources. La₂O₃ and MgO films were formed by ALD using H₂O 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]. CeO₂ films were formed in the CVD mode via thermal decomposition of Ce[OCEt₂Me]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 CeO₂(1nm)/La₂O₃(3nm) and MgO(0.8nm)/La₂O₃(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 CeO₂ capping is presumably due to the higher k value of CeO₂ (~23), whereas the improvement by the MgO capping is ascribed to suppression of excessive La-silicate formation.

We have also found that the CeO₂/La₂O₃ gate stack leads to excellent mobility characteristics. The mobility for the MOSFET with 1.43 nm EOT was 214 cm²/Vs at an effective field of 1.0 MV/cm, which was 85% of the Si universal mobility. The mobility improvement by the CeO₂ capping is attributed to the reduced fixed-charge density, since V_{th} approached to the ideal values by the CeO₂ 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. N₂/H₂, H₂/Ar, O₂ 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 can 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.

Monday Afternoon, October 31, 2011

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.

Tuesday Morning, November 1, 2011

Biofabrication and Novel Devices Focus Topic

Room: 105 - Session BN+NM-TuM

Biofabrication Applications

Moderator: G.F. Payne, University of Maryland, College Park

8:20am **BN+NM-TuM2 Electrically Controlled Biofabrication with Stimuli-Responsive Polysaccharide and Their Visualization in Microfluidic Devices**, *Y. Cheng, X.L. Luo, J. Betz, C.Y. Tsao, H.C. Wu, G.F. Payne, W.E. Bentley, G.W. Rubloff*, University of Maryland, College Park

Stimuli-responsive polysaccharides, such as chitosan and alginate, are useful biomaterials that can be induced to undergo a reversible sol-gel transition to generate biologically-relevant scaffolds. The recent discovery that their gelation can be triggered by imposing an electrical signal opens many avenues for the creation of biologically functional hybrid structures and their localization onto and within microfabricated devices for biofabrication and biosensing applications. Here we report two different mechanisms for creating polysaccharide hydrogels in microfluidics by electrical signal. The cathodic electrodeposition of the cationic chitosan hydrogel was achieved by electrochemically generated OH⁻ ions at the cathode surface, creating a localized pH gradient at the sol-gel interface. The anodic electrodeposition of calcium alginate hydrogel was achieved by electrical-signal-mediated release of Ca²⁺ ions as a result of electrochemically generated H⁺ ions at the anode surface reacting with suspended CaCO₃ particles in alginate solution. Localization of the hydrogels in transparent microfluidic devices makes them highly accessible through optical imaging and spectroscopy. The processes of *in situ* gel formation are simple, scalable, spatially controllable, and electroaddressable. Applications in protein immobilization and cell assembly with electroaddressing capability were further demonstrated. With the advantage of spatiotemporal control of gel formation coupled with microfabrication techniques, a variety of novel and useful structures such as multi-layer, multi-address, and even site-programmable arrays of biological components can also be achieved.

8:40am **BN+NM-TuM3 Biofabrication for Interrogating Cell Signaling**, *W.E. Bentley, T. Gordonov*, University of Maryland, College Park **INVITED**

The biological signal transduction process is the means by which external signals are incorporated into information that directly or indirectly alters gene expression and ultimately, phenotype. The hierarchical structure of signal transduction processes is a topic of intense research. Microbial quorum sensing (QS) is responsible for a variety of phenotypes and is rich in diversity and modes of action. As such, quorum sensing represents a “guide” for learning how signals can be translated into altered phenotype.

As microbial communities occupy a confined space over time, concentrations of extracellular signaling molecules accumulate, providing stimulus for unique and varied cellular responses as well as protection from competing microbial communities. Referred to as “quorum sensing” for its often reported and coincident dependence on high population density, extracellular signaling provides a new basis for control over molecular and cellular processes as well as population behavior, perhaps in a manner more consistent with that of native machinery. Among behaviors guided by QS are the establishment and persistence of bacterial infections.

Our laboratory has uncovered many of the molecular features of the QS autoinducer-2 (AI-2) system using traditional methods that probe bacterial physiology and by exploiting newer principles of biofabrication. That is, we employed electrodeposition methods to assemble complex biological subsystems onto specific sites on microfabricated devices and within microfluidic channels via programmable electrical signals. We have also used genetic engineering techniques to create signal activated fusion tags that covalently link proteins to the device/bio interface. We have designed and synthesized “biological nanofactories” that provide small signal molecule generation at the surface of targeted and captured cells - enabling programmable control of cell function.

Using these methods, we have discovered attributes of the natural switching mechanism that can be exploited for developing next generation antimicrobials. That is, we decomposed elements of the QS “switch” via mutation and a mathematical model of the regulatory elements and coupled this understanding with devices designed to appropriately interrogate these molecular features. Finally, we have developed alkyl analogs of AI-2 that

elucidate structural detail and have potential for affecting behavior in natural environments. Correspondingly, these serve as the basis for creating next generation antimicrobials that target the communication between bacteria rather than their survival mechanisms.

9:20am **BN+NM-TuM5 Surface Modified Magnetic Microparticles for Bioreactor Applications**, *A. Khaing, E. Milkani, A. Maziarz, C. Lambert, W. McGimpsey*, Worcester Polytechnic Institute

A magnetically-stabilized, continuous-flow bioreactor was designed and applied for the controlled growth of rat aortic smooth muscle cells (RASMC) in a pre-determined shape in a three-dimensional environment. The cells were immobilized on magnetic agarose beads (MABs) and grown into a tube-shaped tissue. By adjusting the experimental parameters, the size of the MABs were controlled. The surfaces of the MABs were biochemically modified and RASMC cell growth on the modified MABs was tested. Initial RASMC tissue rings with MABs grew in the magnetic field inside the continuous flow of culture medium in the first few days. The RASMC tissue tube was formed in a week, and allowed to mature up to about a month before removing from the bioreactor to characterize it. Histological staining of RASMC tissue tube showed that RASMC were circumferentially aligned perpendicular to the direction of the flow of culture medium. The majority of the cells in the RASMC tissue tube grown out of the MABs stabilized in the magnetic field in the continuous flow were healthy and highly proliferating. The system has applications in the fields of tissue regeneration, pharmaceutical production, stem cell amplification and biofuel production.

9:40am **BN+NM-TuM6 Bacterial Communication in Controlled 3D Microenvironments**, *X.L. Luo, H.C. Wu, C.Y. Tsao, Y. Cheng, J. Betz, G.W. Rubloff, W.E. Bentley*, University of Maryland

Antibiotic resistance is a growing and widely recognized public health issue. Today, more than 70% of bacteria are resistant to at least one of the most commonly used antibiotics. Bacteria evolve with increasing antibiotic resistance due to the selective pressure that administration of conventional antibiotics creates on cell viability, wherein those bacteria that survive antibiotics become dominant. The emergence of “super” bacteria that carry multiple resistant genes calls for the development of novel antimicrobial strategies that place *less* selective pressure on the target bacteria. Rather than killing bacteria with antibiotics, interruption of bacterial communication networks - or quorum sensing (QS) - might delay the population-scale behaviors of target bacteria in gene regulation and buy time for the host immune system to fight back. Microfluidic environments provide a controlled and attractive opportunity to study bacterial QS and to explore these strategies.

Here we report *in vitro* signaling between localized, spatially distinct cell populations in controlled 3D fluidic microenvironments. First, a freestanding chitosan membrane was fabricated by using pH gradients generated at the flow interface of two converging flows. Next, alginate membranes were fabricated by cross-linking alginate sequentially on both sides of the chitosan membrane using diffusion of calcium ions through the semi-permeable chitosan membrane. Finally, cell assembly was achieved by suspending cells in the alginate solution to embed the target cells into the alginate scaffolds, realized as a micro-sandwich structure of cells in alginate on both sides of the chitosan membrane. Signal molecules transmitted *in situ* from one cell population were transported either by diffusion to (1) surrounding cells and (2) nearby segregated cell population, or by convection to (3) cell populations that are relatively far away in a separated microchannel. Induced quorum sensing responses, the production of fluorescence proteins functionally linked to QS genes, were observed for all three configurations. Importantly, these membrane-based 3D scaffolds offer convenient top-down visualization and easy access to both sides of the scaffolds. These approaches provide a versatile and powerful platform to understand and modulate collective and interruptive cellular responses in bacterial quorum sensing.

10:40am **BN+NM-TuM9 “Body-On-A-Chip”: Combining Microfabrication, Cell Cultures, and Mathematical Models**, *M.L. Shuler*, Cornell University **INVITED**

We seek to understand the response of the human body to various pharmaceuticals. Our platform technology is an *in vitro* system that combines microfabrication and cell cultures and is guided by a computer model of the body. We called this *in vitro* system a micro cell culture analog (microCCA) or a “Body-on-a-Chip”. A microCCA device contains mammalian cells cultured in interconnected micro-chambers to represent key body organs linked through the circulatory system and is a physical representation of a physiologically based pharmacokinetic model.^(1, 2) MicroCCAs can reveal toxic effects that result from interactions between

organs as well as provide realistic, inexpensive, accurate, rapid throughput toxicological studies that do not require animals. The advantages of operating on a microscale include the ability to mimic physiological relationships more accurately as the natural length scale is order of 10 to 100 microns.

We have used a microCCA to test potential combination therapies (Tegafur and uracil) for colon cancer. ⁽³⁾ Tegafur is a prodrug for 5-FU and uracil an inhibitor of DPD, an enzyme which deactivates 5-FU. Simple microwell plates cannot probe this system, but the microCCA predicts the types of responses observed experimentally. A “pumpless” system that would be easy to utilize has been demonstrated with Tegafur also. ⁽⁴⁾ We have coupled these body modules with a micro model of the GI tract to examine the response to oral exposure of drugs, chemicals, or nanoparticles. ⁽⁵⁾

Overall, we believe that in vitro, microfabricated devices with cell cultures provide a viable alternative to animal models to predict toxicity and efficacy in response to pharmaceuticals.

References

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2. Khamsi, R. Meet the Stripped Down Rat. *Nature* (2005), 435(5 May):12-13.
3. Sung, J.H. and M.L. Shuler. A Micro Cell Culture Analog (microCCA) with 3-D Hydrogel Culture of Multiple Cell Lines to Assess Metabolism-Dependent Cytotoxicity of Anti-Cancer Drugs. *Lab Chip* (2009), 9:1385-1394.
4. Sung, J.H., C. Kam, and M.L. Shuler. A microfluidic device for pharmacokinetic-pharmacodynamic (PK-PD) model on a chip. *Lab Chip* (2010) 10: 446-455.
5. Mahler, G.J., M.B. Esch, R.P. Glahn, and M.L. Shuler. Characterization of a gastrointestinal tract microscale cell culture analog used to predict drug toxicity. *Biotechnol. Bioeng.* (2009) 104:193-205.

11:20am BN+NM-TuM11 Simultaneous Bacterial Transformation and Localization within a Microfluidic Device, J. Betz, Y. Cheng, C.Y. Tsao, G.F. Payne, W.E. Bentley, G.W. Rubloff, University of Maryland

Transformation, the process by which a bacterium takes up and incorporates extracellular DNA, is one of the primary enabling technologies in the biotechnology field. This allows a researcher to program bacteria, equipping them with a complement of genes to accomplish a task, such as producing a molecule of interest or acting as a sensor. We describe the simultaneous transformation and localization of *Escherichia coli* bacteria in response to an electric signal within a microfluidic device. We demonstrate that these transformed bacteria can act as fluorescent sensors of isopropyl β -D-1-thiogalactopyranoside (IPTG), a chemical stimulus, or low dissolved oxygen levels, an environmental stimulus.

This method focuses on bacterial transformation with the added benefit of simultaneous entrapment within an alginate hydrogel at a desired electrode address. This offers the ability to create microfluidic cell-based sensors in a single, simple step. To transform and deposit bacteria, the device was filled with a mixture of electrocompetent cells, 200ng plasmid, 0.5% alginate, and 0.125% CaCO₃ and subjected to a 30V/cm DC electric field for 3 minutes on ice. The cells were allowed to recover at 37°C for an hour, cultured for 16 hours, and induced with a chemical signal, IPTG, for 4 hours. This resulted in increased expression of DsRed, a red fluorescent protein.

Dissolved oxygen is an important parameter for many cell culture experiments. To create a dissolved oxygen sensor, *E. coli* were transformed with a plasmid that causes production of green fluorescent protein (GFP) in response to decreased dissolved oxygen concentration in the surrounding medium. Following the above transformation and culturing method, the cells were induced with media that had been deoxygenated in a vacuum chamber, resulting in an increase in GFP expression.

This method is versatile in terms of creating microfluidic cell-based sensors. We envision many exciting applications of this work, including the development of dynamically reconfigurable microfluidic biosensors and high-throughput screening methods for plasmid libraries generated by protein engineering and directed evolution experiments.

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/in². 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/Cl₂/O₂ gas chemistry was evaluated with a SiO₂ hard mask of 20-nm thickness. This SiO₂ hard mask was patterned from 30 to 50 nm by EB lithography and etched with CHF₃ 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/in².

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 desired 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 given 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 feature 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.

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Tuesday Afternoon, November 1, 2011

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. Ramanathan*, 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 SiO₂, using XeF₂.

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 indispensable 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 (D_{it}) 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 V_t 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 V_{th} 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 V_t 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 V_t tuner method was realized.

Nanomanufacturing Science and Technology Focus

Topic

Room: East Exhibit Hall - Session NM-TuP

Nanomanufacturing Science and Technology Poster

Session

NM-TuP1 Nanoscopic Polymerization of Polyaniline on the Nanostructured Alumina Surface and the Nano-Contact Transfer of the Nanofabricated Polyanil. *Y. Watanabe, T. Mori, H. Kato, S. Takemura, T. Hiramatsu*, Kanto Gakuin University, Japan

The aim of the present study is to present what types of nano-size structures and patterns made of polyaniline can be created in local polymerization in nanoscopic area such as nano-size crater or trench. The authors also intend that the fabricated polyaniline patterns can be transferred to other substrate such as silicon wafer by a nano-contact method. Nanoscopic polymerization of polyaniline was conducted locally in nanoscale craters or highly-oriented line pattern with nanoscale trenches fabricated on an aluminum surfaces by combined process of chemical treatments and anodization. Nanoscopic polymerization process was performed by a wet method. Aniline monomer solved in pure water, which was added by oxidation agent ammonium peroxodisulfate (APS) solved in HCl in a test tube, was dropped on the nanostructures as a droplet with a micropipette and was extended on the surface. Aniline monomer was being polymerized in a test tube under those conditions. As for the linked-crater structure, the size of the crater ranged from 50 nm to 100 nm by dynamic force microscopy (DFM) measurements. On the other hand, as for the highly-oriented line structure, the line distance was estimated at 30-40 nm. Nanoscopic polymerization was conducted on the two types of nanostructured templates. DFM observation and the cross section analysis were conducted on pre-deposited and deposited surfaces. For the nanoscale polymerization on the linked-crater structure, one of the characteristic patterns was a polyaniline dots pattern. The DFM image showed that each crater was filled with polyaniline creating polyaniline dots. It was also found that binding small dots formed a tree-like network made of polyaniline covering the linked-crater surface. In the case of lower concentration of APS, dots became smaller. Preliminary stage of nanowire growth was also observed. On the other hand, as for the nanoscale polymerization on the highly-oriented line structure, one of the characteristic patterns was polyaniline line pattern where polyaniline polymerized in each trenches. At the next stage, nano-contact transfer of the fabricated polyaniline patterns to Si wafers was tried. In the case of the line pattern template, it was found that a polyaniline line pattern could be transferred to a Si wafer for the lower concentration of aniline monomer. It was also confirmed that the transferred pattern was changed into dots pattern for the higher concentration of aniline. By atomic force microscopy-current imaging tunneling spectroscopy (AFM-CITS) measurements, the obtained IV characteristics indicated the gap became broaden on the transferred polyaniline pattern.

NM-TuP2 Dielectric Performance of Post Deposition Treated Al₂O₃ Films Prepared by Using Parallel-Plate Electrode PEALD. *C.C. Yu*, National Applied Research Laboratories, Taiwan, Republic of China, *H.D. Trinh*, National Chiao Tung University, Taiwan, Republic of China, *B.H. Liu, C.C. Kei, C.N. Hsiao, D.P. Tsai*, National Applied Research Laboratories, Taiwan, Republic of China

In this study, self established plasma enhanced atomic layer deposition system (PEALD) was successfully used to deposit Al₂O₃ films at room temperature. Trimethylaluminum (TMAI) and ionized oxygen ions have used as metal precursors and oxidant, respectively. PEALD cycles comprised TMA pulsing and O₂ plasma treatment steps, and all the steps followed by purging nitrogen gas for 5 second. Parallel electrodes and DC power supply have applied to ignite O₂ plasma during ALD cycles. Effects of plasma power output have investigated by preparing Al₂O₃ films with different O₂ plasma power ranged from 7 – 50 W. Film thickness measurement has been carried out by using x-ray reflection analysis (XRR), and self limiting behavior has been investigated which verified PEALD growth mechanism. Growth rate of PEALD Al₂O₃ films that analyzed by XRR was ranged from 0.8 – 1.7 Å/cyc. Microstructure analysis of PEALD Al₂O₃ films have been characterized by using scanning electron microscope (SEM) and transmittance electron microscope (TEM) and revealed pin-hole free structures with excellent interfaces between films and substrates. Results of atomic force microscope (AFM) measurement show that PEALD cycle number varied from 100 – 500 cycles would lead to the smooth surface roughness of films ranged from 0.184 – 0.35 nm. Dielectric behavior of high-k capacitors has measured by using HP4284A LCR

impedance analyzer. The relations between D_{it} values and plasma power output have characterized and evaluated. The results of C-V measurement show shifted C-V curves and hint that the films deposited with different plasma power lead to varied D_{it} values. This phenomenon implies that higher plasma power causes higher amount of interfacial charge traps on the substrate surface. To study the effects of interfacial conditions on performances of capacitors, post treatment has been used to modify the film properties. Post deposition annealing technique has been applied by using rapid thermal annealing furnace (RTA). The adopted annealing temperatures were ranged from 300 – 500 °C for 30 seconds in nitrogen atmosphere. Improvements of Shifted C-V curves were investigated and carried out the varied D_{it} values as 10⁹ – 10¹⁸ / cm² - eV.

Key : PEALD, Direct plasma, High-k material, C-V, I-V, D_{it}, Parallel electrode

NM-TuP3 Effect of Growth Temperature on Optical Properties of TiO₂ Films by Atomic Layer Deposition. *M.H. Chan, C.C. Kei, C.N. Hsiao, W.-H. Cho, C.C. Yu, B.H. Liu, W.C. Chen, D.P. Tsai*, National Applied Research Laboratories, Taiwan, Republic of China

Titanium dioxide (TiO₂) films were deposited on Si and B270 glass substrates by a horizontal-flow atomic layer deposition (ALD) system. Titanium tetrachloride and deionized water were used as metal precursor and oxidant, respectively. Precursors were separately introduced into the reactor for a pulse length of 40 ms, and the working pressure was kept at 1 torr. Deposition temperature of TiO₂ films was varied between 100 and 300°C. Absorption coefficient and refractive index were obtained by using spectroscopic ellipsometry. Crystal structure of TiO₂ films was acquired by using X-ray diffractometry. Film thickness was obtained by scanning electron microscopy. Curve-fittings of ellipsometric data was also applied to evaluate the film thickness and growth rate of TiO₂ films. It was found that the crystallinity of Rutile TiO₂ films was significantly improved as increase the processing temperature from 150 to 300 °C. This might be the reason for an increasing refractive index of TiO₂ films prepared at a higher temperature. Beside, increase of precursors' reactive rate would result in a lower absorption coefficient for samples prepared at a higher temperature. The growth rate of TiO₂ film prepared at various temperatures is around 0.6 Å/cycle. However, a slight decrease in the growth rate can be observed due to the faster desorption rate of precursors at higher temperatures.

NM-TuP4 Fabrication of Double Nanohoneycombs (Pt/ZnO) with Controllable Size using Nanosphere Lithography and Plasma Enhanced Atomic Layer Deposition. *C.-T. Lee, W.-H. Cho, B.H. Liu, C.C. Kei, D.P. Tsai*, National Applied Research Laboratories, Taiwan, Republic of China

The double nanohoneycombs (Pt/ZnO) on glass and Si substrates were fabricated by nanosphere lithography (NSL) and plasma enhanced atomic layer deposition (PEALD). The first nanohoneycomb (ZnO) was fabricated by controllable size with NSL and magnetron sputtering. In this study, platinum thin films were deposited on ZnO nanohoneycomb by using PEALD using MeCpPtMe₃ and oxygen plasma as precursors. The effects of the thickness of platinum thin films on the structural and optical properties of the double nanohoneycombs (Pt/ZnO) were investigated by field emission scanning electron microscopy, X-ray diffraction and spectrometer. X-ray diffraction analysis revealed that the platinum thin films are polycrystalline with a preferred orientation along (111). This technique forming double nanohoneycombs, especially with desired period, is expected to be a candidate for wide nanostructure applications such as field emission, sensors, etc.

NM-TuP7 Fabrication of Nanopattern Sapphire Substrate by Nanosphere and Nanoimprint Lithography Technology. *C.M. Chang, M.H. Shiao, D.Y. Chiang*, National Applied Research Laboratories, Taiwan, Republic of China, *C.T. Yang*, Industrial Technology Research Institute, Taiwan, Republic of China, *M.J. Huang*, National Applied Research Laboratories, Taiwan, Republic of China, *W.J. Hsueh*, National Taiwan University, Taiwan, Republic of China

In this study, nanosphere lithography (NSL) and nanoimprint lithography (NIL) methods were used to fabricate metal pit and polymer pillar etching masks for sapphire substrate etching process, respectively. The metal mask contains 500 nm hole array and polymer pillar array mask which each pillar's size was 350 nm in diameter and height. Then inductively-coupled-plasma reactive ion etching (ICP-RIE) technique was used to etch sapphire substrate, which introduced both boron trichloride (BCl₃) and Argon (Ar) mixture etchant gases with 1 : 6 flow rate ratio. After etching processes were finished, two types of nanopattern structure were obtained on the sapphire substrate surface. One type of sapphire substrate was nano-pit array structure with 400 nm in diameter and 200 nm in depth, another type

of sapphire substrate was nano-cone array structure with 400 nm diameter and 100 nm in thickness. The contact angles of two patterned sapphire substrates were measured to be 101.02° and 98.14° for nano-pit array and nano-cone array structure, respectively. From the contact angle measurement results, it can be found that the surface property of sapphire substrate changed from hydrophilic, which contact angle was 24.46°, to be hydrophobic.

NM-TuP8 Fabrication of Single-Electron Transistor Utilizing Multi-Coated Self-Assembled Monolayer, N. Kwon, K. Kim, I. Chung, Sungkyunkwan Univ., Republic of Korea

We have fabricated quantum dots with the precise sizes from 30 nm to sub-10 nm at the controllable position. First, Au electrodes with the unique shape were obtained using a conventional lithography. Then, self-assembled multilayers, composed of alternating layers of α , ω -mercaptoalkanoic acids (~2 nm) and copper (II) ions, were deposited on Au electrode patterns to form the controllable gap between adjacent Au electrodes. After reaching to nanometer-scale gap, the second Au was deposited again. Finally, lift-off both e-beam resist and molecular resist were removed by lift-off, thereby resulting in quantum dot with nano-gap between gold electrodes. The physical properties were analyzed using scanning probe microscopy (SPM) and field emission scanning electron microscopy (FE-SEM). The electrical properties were evaluated using Keithley-4200.

NM-TuP9 Photoluminescence Studies of Nanostructured Alumina Surfaces Coated by Polythiophene Film and Copper Phthalocyanine, A. Ishii, R. Nakashima, H. Kato, S. Takemura, H. Kobe, Y. Watanabe, T. Hiramatsu, Kanto Gakuin University, Japan

Photoluminescent properties of the nanostructured alumina surfaces and the surfaces coated by polythiophene (PT) nanofilm and Copper phthalocyanine (CuPc) were investigated. Nanostructures such as linked-crater structure and highly-oriented line structure were prepared on an Al surface by a combined process of chemical and electrochemical treatments. The nanoscale linked crater structure was fabricated on an Al surface by treatment with Semi Clean and successive electrochemical anodization in H₂SO₄ solution created a nanoscale finer linked-crater structure on the surface. The crater size was estimated at 80-150 nm in diameter by dynamic force microscopy (DFM) measurements. Regarding the highly-oriented line structure, the anodization process applied to the original fiber-like surface structure on the Al plate. The anodization fabricated the finer line structure on the Al surface. The line distance was estimated at 40 nm. The fabricated nanostructured surfaces were identified as alumina by Fourier transform infrared spectroscopy (FT-IR) and x-ray photoemission spectroscopy (XPS) measurements. Conducting polymer polythiophene nanofilm growth on the nanostructured Al surface was conducted by an electrochemical synthetic method in an electrochemical cell. Polythiophene nanofilm was polymerized on the nanostructured Al used as an anode in acetonitrile containing thiophene monomer and (Et)₄NBF₄ by applying positive voltage to the anode. It was observed by DFM that nanofilm was grown along the crater structures or the line structures. CuPc deposition on the nanostructured surfaces was carried out by casting method. Photoluminescent properties of the nanostructured alumina surfaces and the surfaces topped by the nanofilm and CuPc were investigated. It was shown that characteristic ripples of several emission peaks appeared in the wavelength range of 350-550 nm in both cases of linked-crater and highly-oriented line structures while no ripple-shaped emission peaks were observed in the case of the original native Al oxide surface. The emission spectral profile was different in peak positions, number of ripples and intensities between two types of nanostructures. Photoluminescence measurements on the polythiophene nanofilm-grown linked-crater structure also showed that the rippled emission peaks clearly appeared. It was also clearly confirmed that the observed rippled emission patterns were significantly enhanced in both cases of CuPc deposited and nanofilm-coated nanostructures. The mechanism of generation of the rippled peaks and the enhancement were discussed by considering nanosize effects and Al-O vibration modes.

NM-TuP11 Optimization of Criss-Cross Photolithography for 3D NAND, J. Germain, J. Smith, J.M. Kim, K.Y. Ko, Applied Materials, Inc.

The patterning of small contact holes is an ever present challenge in the field of photolithography. Recently, the importance of this challenge has expanded both because of the development of 3D NAND architectures such as BiCS and because of the need to pattern even smaller contact holes for DRAM applications.

As the required critical dimensions and pitches of contact holes become smaller, the methods typically used for lithography become insufficient. One approach to solving this problem is the use of criss-cross lithography. In criss-cross lithography, two sets of lines are patterned perpendicular to each other, and a freeze step is used to bind them in place. In the first

portion of this work, criss-cross lithography is used to pattern 60 nm holes, with an argon freeze applied to harden the first layer of polymer before patterning the second layer. In this application, two types of problems were discovered: underexposure which causes patterns to become unstable due to gaps at the bottom of the structure and non-optimized dosing which results in patterns which, while circular before etch, exhibit X/Y directionality when any of a wide range of etch processes is applied to the pattern. We explain the causes of these two problems and demonstrate a consistent relationship between etch depth and X/Y directionality for these types of patterns.

In the later portion of this work we demonstrate the applicability of an alternate technique, thermal freeze, to the patterning of 60 nm contact holes. This technique has been applied and optimized such that it enables the criss-cross patterning approach to produce patterns that are consistent and circular even after the etch process. Along with demonstrating that thermal freeze can be used to produce criss-cross wafers, we also identify the exposure relationships required to achieve circular patterns.

Wednesday Morning, November 2, 2011

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 SiO₂, and 10 nm HfO₂.

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

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