Nanomanufacturing Science and Technology Focus Topic
Room: 16 - Session NM+AS+MS-MoM

Metrology and Environmental Issues in Nanomanufacturing
Moderator: N.A. Burnham, Worcester Polytechnic Institute, L.J. Gamble, University of Washington

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Nanoparticles, the primary building blocks of many nanomaterials, may become suspended in air or get into water systems, e.g. drinking water systems, ground water systems, estuaries and lakes etc. Therefore, manufactured nanoparticles can become a component of the air we breathe or the water we drink. One important issue in understanding the environmental fate, transport, toxicity and occupational health hazards of nanoparticles is in characterizing the nature and state of nanoparticles in air, water or in vivo. For the nanoparticles of interest in these studies, metals and metal oxides, it can be asked: (i) will metal oxide and metal nanoparticles be present in air or water as isolated particles or in the form of aggregates? (ii) will metal oxide and metal nanoparticles dissolve in aqueous solution or in vivo? and (iii) under what conditions will metal oxide and metal nanoparticles aggregate or dissolve? As the size regime will be very different depending on the state of the nanoparticles, as dissolved ions, isolated nanoparticles or nanoparticle aggregates, these questions are important to address as it impacts the size regime that needs to be considered or modeled in for example environmental transport or lung deposition models. Furthermore, the effect on biological systems including nanoparticle-biological interactions and toxicity will depend on the state of nanoparticles. In the studies discussed here, macroscopic and molecular-based probes that includes quantitative solution phase adsorption measurements, molecular based probes, light scattering and zeta-potential measurements to investigate the behavior of nanoparticles in aqueous suspensions. We have focused on several different metal and metal oxide nanoparticles in including Fe, Ag, Zn, Cu, Ce and Ti. Some of our newest results which focus on aggregation and dissolution, including detailed size-dependent studies, in the presence and absence of organic acids will be discussed. This research is beneficial as it significantly contributes to the growing database as to the potential environmental and health implications of nanoscience and nanotechnology and how nanomaterials will behave in the environment and impact human health.

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