Tuesday Morning, October 20, 2015

Nanometer-scale Science and Technology
Room: 212B - Session NS+SP-TuM

Nanoscale Imaging and Materials Characterization
Moderator: Mehmet Z. Baykara, Bilkent University

8:00am **NS+SP-TuM1 Influence of Focused Electron Beam on Electrical Characterization of Advanced MOSFETs**, *Jonghyuk Kang*, *S.H. Lee*, Samsung Electronics Co., LTD., South Korea, *B.D. Choi*, Sungkyunkwan University, Republic of Korea

The focused electron beam based inspection instruments such as Scanning Electron Microscope (SEM) have become widespread in the semiconductor manufacturing and failure analysis of scaled devices. Also, nano-probing systems with SEM guidance have become important in the failure analysis area to evaluate the localized device in the actual LSI [1] . However, electron beam leads to device degradation [2] and its damage are increasing with the scaling. As CMOS scaling is going to be sub-10nm regime [3], electron beam damages are becoming critical issue in performing electrical characterization at the contact level in integrated devices using nano-probe technique. To avoid the electron damage, the acceleration voltage should be lower. However, the lower acceleration voltage of electron beam leads to lower resolution of image created by SEM guidance.

In this work, we evaluated NMOS FinFET in SRAM cells manufactured in a 10nm CMOS process with Atomic Force Microscopy (AFM) based nano-probing system. AFM based nano-probing system has no electron beam damage because it uses topography image created by AFM instead of SEM for guidance at contact level [4] . After deprocessing the samples to the contact level, we irradiated electron beams to samples to investigate a dependency of the device characteristics on electron beam acceleration voltage. Compared to a non-exposed reference transistor, the exposure of electron beam on the target transistor lead to significant changes on device characteristics such as saturation current (I_{DS}), sub-threshold voltage (V_{TH}) and sub-threshold swing (S). This might be due to trapped charges in the gate oxide and interface state [5] . Our studies show that it is critical to avoid electron beam exposure before electrical device characterizations are carried out at the contact level using nano-probe system since electron beam induced device parameter changes are not negligible in the failure analysis of sub-10nm devices.

References

[1] S. Ikeda, Y. Yoshida, K. Ishibashi, Y. Mitsui, Electron Devices, IEEE Transactions on, 50 (2003) 1270-1276.

[2] K. Nakamae, H. Fujioka, K. Ura, Journal of Applied Physics, 52 (1981) 1306-1308.

[3] K. Okano, T. Izumida, H. Kawasaki, A. Kaneko, A. Yagishita, T. Kanemura, M. Kondo, S. Ito, N. Aoki, K. Miyano, Electron Devices Meeting, 2005. IEDM Technical Digest. IEEE International, IEEE2005, pp. 721-724.

[4] R. Mulder, S. Subramanian, T. Chrastecky, INTERNATIONAL SYMPOSIUM FOR TESTING AND FAILURE ANALYSIS, ASM International; 2006, pp. 503.

[5] S. Shabde, A. Bhattacharyya, R.S. Kao, R.S. Muller, Solid-state electronics, 31 (1988) 1603-1610.

8:20am **NS+SP-TuM2 *In Situ* Synthesis and Characterization of Core-Shell Nanoparticle Arrays Using Dynamic Transmission Electron Microscopy**, *Joseph McKeown*, Lawrence Livermore National Laboratory, *Y. Wu*, University of Tennessee, *J.D. Fowlkes*, Oak Ridge National Laboratory, *P.D. Rack*, University of Tennessee, *G.H. Campbell*, Lawrence Livermore National Laboratory

Core-shell nanoparticles have attracted much attention due to their unique and tunable properties relative to bulk structures of the same materials, making them candidates for a variety of energy- and catalysis-related applications. Intriguing magnetic behavior can be tailored by variation of size, interface, crystal orientation, and composition, and core-shell nanoparticles with noble-metal shells yield novel optical responses and enhanced electrocatalytic activity. The immiscible Co-Cu alloy system is of particular interest, because it combines a strong magnet (Co) with an effective conductor (Cu) that also has a tunable plasmonic resonance. The ability to monitor and characterize these dewetting processes in situwhile the system is evolving can potentially lead to increased control and directed self-assembly. However, in situcharacterization of the dynamics of self-assembly processes has proven extremely challenging, particularly in materials systems that utilize metallic nanoparticles as the dynamics of these processes evolve extremely fast over very small spatial scales. Here, we present a method to synthesize Co@Cu nanoparticles via pulsed-laser-induced dewetting of Co-Cu alloy thin films. We show that this technique effectively synthesizes Co@Cu core-shell particles with controllable sizes ranging from tens to several hundred nanometers. The assembly dynamics during pulsed-laser-induced dewetting of Co-Cu alloy films were revealed using the high spatiotemporal resolution of the dynamic transmission electron microscope (DTEM) at Lawrence Livermore National Laboratory.

8:40am **NS+SP-TuM3 Investigation of Nickel-assisted Growth of Silicon Carbide Nanowires**, *Lunet E. Luna*, *R. Maboudian, C. Carraro*, University of California at Berkeley

Silicon carbide (SiC) based electronics hold promise for pushing past the limits of current technology to achieve small, durable devices that can function in high-temperature, high-voltage, corrosive, and biological environments. SiC is an ideal material for such conditions due to its high mechanical strength, excellent chemical stability, and its biocompatibility. Consequently, SiC nanowires have attracted interest in applications such as biological sensors, field emission cathodes, and energy storage devices. To realize SiC nanowire based devices for large-scale use, the growth mechanism must be further understood to enable strict control of nanowire crystal structure and orientation. Here we report on recent studies to understand the growth mechanism of Ni-assisted silicon carbide nanowires using single-source precursor methyltrichlorosilane. The effects of growth parameters, such as temperature and precursor flow rate, on the structure and morphology of the resulting nanowires will be presented. This study identifies the key parameters that may be varied to tailor nanowire growth for various applications.

9:00am **NS+SP-TuM4 Homogeneous Nucleation and Characterization of Nanodiamonds Synthesized in an Atmospheric-Pressure Microplasma**, *Jonathan Cole*, *R.M. Sankaran*, Case Western Reserve University

Nanodiamonds possess striking properties such as exceptional mechanical and chemical stability, low cytotoxicity, tunable active surface chemistry, and tunable photoluminescence-inducing color centers, but their synthesis remains a challenge. At normal temperature and pressure, graphite is the thermodynamically stable phase of bulk carbon, while the diamond phase requires high temperatures and pressures. Nanodiamonds have thus been produced via high-pressure, high-temperature (HPHT) conversion of graphite in the presence of carbonaceous precursors and via detonation of carbon-containing explosives. Alternatively, nanocrystalline diamond films have been deposited at low pressure (~1 Torr) by chemical vapor deposition (CVD). Supporting theoretical predictions[1] have shown that at the nanoscale, hydrogenated forms of carbon prefer sp^3 bonding, even at normal conditions, up to a certain size.

Here, we present a study of a plasma process for the synthesis of nanodiamonds at low temperature (<1000 $^{\circ}$C) and atmospheric pressure. C-H-O-containing vapor precursors diluted in Argon are continuously fed into a DC hollow cathode plasma discharge. Nanoparticles nucleate from radical moieties such as C_2 and CH, whose radiative transitions (specifically, C_2 516 nm vibrational band and CH 431 nm electronic band) are monitored by optical emission spectroscopy (OES). Particles are carried as an aerosol to either a filter for *ex situ* materials analysis or an *in situ* scanning mobility particle sizer system (SMPS). SMPS measurements confirm particle formation and allow us to correlate particle yield and size distribution with OES results. Specifically, we have compared results for ethanol and methanol precursors and find that C_2 formation is favored by ethanol, while CH formation is favored by methanol, and that an increase in both radical populations (measured as the aforementioned peak intensities normalized to Ar 750 nm intensity) increase with both particle number density and average diameter.

Analogous to CVD of diamond films[2], we find from TEM analysis that the selectivity of diamond phase is dependent on the C-H-O atomic ratio of the precursor. Specifically, methanol is found to produce a significant amount of sub-5 nm nanodiamonds, while ethanol mostly yields larger amorphous

and graphitic carbon. We suggest that the radical chemistry observed via OES (i.e., C_2 versus CH populations) plays an important role in such observations, and we demonstrate that addition of H_2 gas to ethanol vapor will recover the results given by methanol.

References

[1] P. Badziag et al., Nature **343**, 244-245 (1990).

[2] P. Bachmann et al., Diamond and Related Materials **1**, Issue 1, 1-12 (1991).

9:20am **NS+SP-TuM5 Chemically-specific Intramolecular Imaging with Atomic Force Microscopy**, *Ozgur Sahin*, Columbia University **INVITED**

Atomic force microscopy (AFM) is a powerful tool for imaging and chemical characterization of biological samples at molecular resolution in physiologically relevant environments. However, the localized tip-sample interactions limit high-resolution images to the topmost layer of surfaces. Consequently, characterizing the three-dimensional (3-D) inner structures of molecules has been a challenge. Here we demonstrate three-dimensional localization of chemical groups within a protein complex using AFM. We employ short DNA sequences to label specific chemical groups inside the protein complex. T-shaped cantilevers functionalized with complementary probe DNAs allow locating each label with sequence specificity and sub-nanometer resolution. We measure pairwise distances between labels and reconstruct the 3-D loci of the target groups using simple geometric calculations. Experiments with the biotin-streptavidin complex showed that the 3-D loci of carboxylic acids of biotins are within 2-Angstroms of their respective 3-D loci in the corresponding crystal structure, suggesting AFM may complement existing structural biological techniques in solving structures that are difficult to study due to their size and complexity.

11:00am **NS+SP-TuM10 Time-Resolved Small-Angle X-ray Scattering of Detonating Composition B-3 at the Advanced Photon Source**, *Rachel Huber, D. Podlesak,* Los Alamos National Laboratory (LANL), *M. Bagge-Hansen,* Lawrence Livermore National Laboratory (LLNL), *D. Dattelbaum, M. Firestone,* LANL, *T. Graber,* Washington State University, *R. Gustavsen,* LANL, *R. Hodgin,* LLNL, *B.J. Jensen,* LANL, *L.M. Lauderbach,* LLNL, *P. Rigg,* Washington State University, *B. Ringstrand,* LANL, *S. Seifert,* Argonne National Laboratory, *N. Sinclair,* Washington State University, *E. Watkins,* LANL, *T.M. Willey, T. van Buuren*, LLNL

High explosive (HE) detonations drive chemical reactions under extreme conditions, in which explosive molecules are rapidly converted to small molecular products such as carbon, H_2O, CO_2 and N_2. Solid carbon products are known to be comprised of several allotropes including amorphous carbon, graphite, onion-like graphitic carbon, fullerenes, and nanodiamonds (NDs). The formation of different allotropes arises from the temperatures and pressures conditions on the nanocarbon phase diagram accessed during the detonation. Previously, only the starting explosive samples, and post-mortem soot were available for structural analysis. However, a fundamental understanding of how carbon particles form and evolve during a detonation must occur in real-time on the nanosecond timescale. New developments in *in-situ* time-resolved small angle X-ray scattering (TR-SAXS) has allowed for the measurement of multiple SAXS spectra of detonating Composition B-3 (60% TNT, 40% RDX) at the Dynamic Compression Sector (Sector 35-B) at the Advanced Photon Source (Argonne National Laboratory). The TR-SAXS measurements coupled to the detonation on the ns-timescale are the first of their kind in the United States. Through Guinier and Porod analysis of the TR-SAXS data, we are able to determine the size, morphology, and phase of the carbon allotropes at time delays behind the detonation front.[1,2] In addition, electron microscopy, X-ray photoelectron spectroscopy, and static SAXS were used to study the carbon solids in the post-detonation soot. By understanding the formation of solid carbon behind the detonation front, an improved theoretical framework may be applied to modeling the products equation of state for explosives.

1 Ten, K. A., Pruuel, E. R. & Titov, V. M. SAXS Measurement and Dynamics of Condensed Carbon Growth at Detonation of Condensed High Explosives. *Fullerenes, Nanotubes and Carbon Nanostructures* **20**, 587-593, doi:10.1080/1536383x.2012.656542 (2012).

2 Titov, V. M., Tolochko, B. P., Ten, K. A., Lukyanchikov, L. A. & Pruuel, E. R. Where and when are nanodiamonds formed under explosion? *Diamond and Related Materials* **16**, 2009-2013, doi:10.1016/j.diamond.2007.09.001 (2007).

11:20am **NS+SP-TuM11 LEEM Imaging of Growth of Au on Ge(110)**, *Bret Stenger, A. Dorsett, M.S. van Zijll, C.A. Gabris, C.K.B. Paw U, S. Chiang*, University of California, Davis

The growth of Au on Ge(110) was observed with Low Energy Electron Microscopy (LEEM). The objectives of this study were to control the growth of low-dimensional nanostructures and understand the collective diffusion behavior observed. Ge(110) was heated to 800°C and dosed with 0.5 ML of Au. During deposition, islands grew to ~1-2 microns in width and ~2-3 microns in length, all oriented along the same direction. The islands were observed to move and change shape over a short period of time ($< 1s$) indicating the rapid collective movement of $\sim 4 \times 10^7$ atoms. As the temperature decreased, the island behavior was also studied and revealed rapid island contractions which left traces on the Ge(110) surface. This island growth is similar to that previously observed for Ag on Ge(110), although the Ag islands are typically a factor of 10 narrower and often 3 to 5 times longer.

11:40am **NS+SP-TuM12 Strength and Fracture of Graphene Oxide Nanosheets**, *C. Cao,* University of Toronto, Canada, *M. Daly, B. Chen, C.V. Singh, Y. Sun,* University of Toronto, ***Tobin Filleter***, University of Toronto, Canada

Graphene oxide (GO) is a layered material comprised of hierarchical features which possess vastly differing characteristic dimensions. GO has been applied as a good candidate for paper-like materials, robust fibers, and reinforcement elements in composites. The use of GO in these materials has been motivated in large part by the predicted high mechanical properties of individual GO monolayers. Recent experiments performed in our research group have measured the strength of GO monolayers to be ~25 GPa [1], which is in good agreement with previously theoretical predictions [2]. Macroscopic papers and fibers synthesized using GO, however, typically exhibit strengths on the order of 10-100's of MPa's. GO nanosheets represent the critical hierarchical structure that bridges the length-scale of these monolayer and bulk material architectures.

In this study, the strength and fracture behavior of GO nanosheets were examined *in situ* with a micro-tensile device operated inside scanning and transmission electron microscopes (SEM/TEM) [3]. The tensile strength of GO nanosheets was measured to be as high as 12 ± 4 GPa, approaching the intrinsic strength of monolayer GO, and orders of magnitude higher than bulk GO papers. During mechanical failure, the nanosheets were observed to undergo intraplaner brittle fracture in highly localized regions through the cross-section of nanosheets due to interlayer load transmission via a hydrogen bond networks as reveled by complimentary Molecular Dynamics simulations.

GO nanosheets were found to exhibit variations in strength that were strongly correlated with the effective volume. This is consistent with Weibull statistics, such that larger GO nanosheets are more likely to possess larger planar defects and adversely impact strength. Furthermore, the Young's modulus was inversely correlated to sample thickness, and approached that of monolayer GO (~380 GPa) for thin samples. These trends provide strong evidence of the scaling effects on the mechanical properties of GO materials, and help to bridge the understanding of the mechanical behavior of hierarchical GO materials which will ultimately guide application as GO papers and coatings.

[1] C. Cao et al., "High strength measurement of monolayer graphene oxide", Carbon, vol. 81, pp. 497-504, 2014.

[2] J. T. Paci et al., "Computational studies of the structure, behavior upon heating, and mechanical properties of graphite oxide," Journal of Physical Chemistry C, vol. 111, pp. 18099-18111, 2007.

[3] C. Cao et al., "Strengthening in graphene oxide nanosheets: Bridging the gap between interplanar and intraplanar fracture ", Nano Letters, In Revision, 2015.

12:00pm **NS+SP-TuM13 Low-Temperature Atomic Layer Deposition of Crystalline Platinum Nanoclusters on Graphene Nanoplatelets Using (Methylcyclopentadienyl)-Trimethylplatinum and Oxygen**, *Hao Van Bui*, Delft University of Technology, Netherlands, *R. Bevaart, F. Grillo,* Delft University of Technology, *J.R. van Ommen,* Delft University of Technology, Netherlands

The thermal atomic layer deposition of platinum using (methylcyclopentadienyl)-trimethylplatinum ($MeCpPtMe_3$) and oxygen has been investigated for more than a decade and performed on various supports, including flat surfaces [1, 2], nanoparticles [3], nanowires [4] and carbon-based nanomaterials [5, 6, 7, 8]. It has been demonstrated and widely accepted that this ALD process has a lower limit of deposition temperature of 200 °C. Here, we demonstrate the thermal Pt ALD on graphene nanoplatelets using $MeCpPtMe_3$ and dry air (20% wt. O_2), and show that highly dispersed and crystalline Pt nanoparticles can be obtained at a temperature as low as 80 °C. The feasible low-temperature deposition is attributed to the role of the graphene support that can activate molecular oxygen to form O_2^- anions [9], which consequently enhances the oxidation reactions in ALD. Importantly, the low deposition temperatures (*i.e.*, 80 °C and 100 °C) can prevent the ripening of nanoparticles and hinder the formation of new nuclei during the ALD, allowing for better control in particle size and distribution. In contrast, at higher temperatures (150-250

°C), the ripening occurs, and new nuclei are constantly formed during the deposition, resulting in a broader particle size distribution.

References

[1] T. Aaltonen et al., Chem. Mater. **13**, 1924 (2003).

[2] T. Aaltonen et al., J. Mater. Res. **19**, 3353 (2004).

[3] Y. Zhou at al., Appl. Catal. B: Environ. **101**, 54 (2010).

[4] N. P. Dasgupta et al., J. Am. Chem. Soc. **135**, 12932 (2013).

[5] J. S. King et al., Nano Lett. **8**, 2405 (2008).

[6] C. Liu et al., Small **5**, 1535 (2009).

[7] S. Sun et al., Sci. Rep. **3**, 1775 (2013).

[8] K. Kim et al., Nature Comm. **5**, 4781 (2014).

[9] E. Gao and W. Z. Wang, Nanoscale **5**, 11248 (2013).

Authors Index

Bold page numbers indicate the presenter