

# Wednesday Afternoon, October 22, 2008

## Nanomanufacturing Focus Topic

Room: 309 - Session NM+PS+AS-WeA

## Nanomanufacturing I: Plasma Processing and Materials

**Moderator:** R.M. Martin, IBM T.J. Watson Research Center

1:40pm NM+PS+AS-WeA1 **Silicon Nanocrystal Inks: Plasma Processing as a Route to Solution-Processed Silicon Films**, U.R. Kortshagen, R. Cram, D. Rowe, X.-D. Pi, University of Minnesota  
**INVITED**

Colloidal nanocrystals are studied for a wide spectrum of applications from more efficient quantum dot solar cells to printed electronics. While significant advances have been made with chalcogenide semiconductors, similar progress with silicon has been hampered for a long time by the lack of efficient synthesis approaches. However, silicon has the undoubted advantage of being non-toxic, environmentally benign, abundant and cheap. This talk describes a plasma synthesis approach for the efficient synthesis of silicon nanocrystals. Silicon crystals are synthesized in a flow through plasma reactor on time-scales of a few ms. The residence time of the silicon crystals can be used to tailor the nanocrystal size. Dopants can be introduced into the crystals and changes in the photoluminescence properties as well as surface etching studies allow to deduce the dopant location within the nanocrystal. The nanocrystal surfaces can be functionalized with organic ligands that impart solubility to the nanocrystals. By making silicon nanocrystals soluble in organic solvents, inks of doped silicon crystals can be formed that can be used to prepare silicon nanocrystal films through solution processes such as drop coating, spin coating, or ink-jet printing. Laser annealing is used to produce conducting films from the colloidal nanocrystal precursors. Structural and electrical properties of the films are determined with a wide array of characterization techniques. Properties and potential applications of these materials will be discussed.<sup>1</sup>

<sup>1</sup>This work was supported primarily by the MRSEC Program of the National Science Foundation under Award Number DMR-0212302. Partial support is acknowledged by NSF grant DMI-0556163, and by Center for Nanostructure Applications at the University of Minnesota.

2:20pm NM+PS+AS-WeA3 **Vertically Aligned Si Nanostructure Arrays formed using SF<sub>6</sub>/O<sub>2</sub> Plasma**, C. Yang, S.H. Ryu, Y.D. Lim, W.J. Yoo, Sungkyunkwan University, Korea

Arrays of high aspect ratio (>10:1) vertically aligned Si nanostructure were formed in an inductively coupled plasma (ICP) reactor using SF<sub>6</sub>/O<sub>2</sub> plasma without any masks at noncryogenic temperature. Mean diameter of the nanostructure arrays is about 100 nm and the mean height is up to 4.77 μm. These nanostructure arrays can be fabricated for large area (>100 cm<sup>2</sup>). The formation of the nanostructure arrays are studied as a function of time, bias RF-power and O<sub>2</sub>/SF<sub>6</sub> ratio. The processing condition of the SF<sub>6</sub>/O<sub>2</sub> plasma is known to markedly affect the preparation of the nanostructure arrays. O<sub>2</sub>/SF<sub>6</sub> ratio determines the formation of the nanostructure arrays. The nanostructure arrays only could be fabricated when the O<sub>2</sub> content is not too low or too high, the range is 0.5 < O<sub>2</sub>/SF<sub>6</sub> < 2.5. Two types of the nanostructure arrays formed because of the different bias RF-power, one is nanohole arrays and another is the nanopillar arrays. The formation of the nanostructure is hole when the bias power is 10 W, but the diameter is only 420 nm after etching 150 s. If the bias power increased to 30 W, the nanopillar arrays appear, the mean height is up to 4.77 μm after etching 150s. The etching time is also important for the nanostructure arrays. After etching about 40s, the nanostructure arrays appear abruptly and become longer and longer. But very long time etching has destroyed the nanostructure arrays. The mechanism of the plasma etching for fabricating the nanostructure arrays has been investigated using OES, XPS and SEM analyses. From the analyses, the properties of the plasma and the formed passivation layer are mainly reasons for the fabrication of the nanostructure arrays. The best condition to fabricate a high aspect ratio vertically aligned Si nanostructure arrays is suggested.

2:40pm NM+PS+AS-WeA4 **Structured Growth of Silver Nanoparticles Within a Hydrocarbon Matrix**, E. Körner, J.F. Lübben, G. Fortunato, D. Hegemann, EMPA, Switzerland

Low pressure plasma processes enable an extensive variety of surface adjustments for medical applications or technical textiles. Specifically, a modular plasma vacuum chamber provides the base for highly flexible and tailor-made coating technology. Different modification strategies, e.g. activation, etching, plasma polymerization or metallization by sputtering can be used separately or combined with each other. This work presents the

combination of plasma polymerization and etching with a co-sputtering process which leads to the formation of a nanoporous polymer matrix with embedded metal nanoparticles. A capacitively coupled radiofrequency power input and an asymmetric reactor geometry allow the production of such multifunctional coatings within a one-step process. The hydrocarbon matrix is built-up by using ethylene (C<sub>2</sub>H<sub>4</sub>) as a monomer gas. In addition, carbon dioxide (CO<sub>2</sub>) or ammonia (NH<sub>3</sub>) is used as the reactive gas, to structure the matrix and add functional groups to the a-C:H network. The deposition rate and the functionality of the coatings are adjusted by the ratio of reactive gas to monomer. With increasing the ratio of reactive gas the functionality of the matrix increases at the expense of the deposition rate. An excess of argon is used in the gas mixture for co-sputtering from a Ag cathode. The growth, distribution and formation of Ag particles are analyzed carefully under different conditions with respect to the gas mixture. The films are investigated with atomic force microscopy and scanning electron microscopy after different growth steps. It can be seen that the particles are more embedded in the matrix for higher film thicknesses and lower reactive gas ratios. Additionally, X-ray photoelectron spectroscopy analyses are performed to evaluate the surface chemistry and Ag surface concentration. For bulk measurements, the overall Ag content is measured with inductively coupled plasma optical emission spectrometry. Target covering or oxidation can decrease the Ag deposition rate and has to be taken into account in determining the optimal plasma conditions. In contrast to magnetron sputtering the Ag particles appear to be bigger with RF sputtering, which could provide a Ag reservoir with a slower release and a better long-term antibacterial effect. This is important for the application of the films as antibacterial coatings, where an optimal antibacterial efficiency for a minimal amount of Ag is desirable.

3:00pm NM+PS+AS-WeA5 **Photoluminescence Brightening from Freestanding Single-Walled Carbon Nanotube Bundles Prepared by Diffusion Plasma CVD**, R. Hatakeyama, T. Kato, Tohoku University, Japan

The optical property of single-walled carbon nanotubes (SWNTs) has been the subject of intense interest in recent years, since the discovery of efficient photoluminescence (PL) from isolated semiconducting SWNTs. Because it was believed that the debundle of SWNTs was the inevitable process to capture the PL signal from SWNTs, the bundle forming SWNTs were, in most cases, treated as by-products or impurities causing a spectrum broadening and shifting, and hence their optical features, especially the PL, have not attracted a great deal of attentions so far. Very recently, the PL from bundled SWNTs in an aqueous solution has been reported. Since the PL from bundled SWNTs includes outstanding advantages such as an exemption from a complicated debundle process and easy manipulation, it can be expected that the SWNT-bundle engineering has a great potential for the nanotube-based PL device fabrication. From an industrial point of view, the application of nanotube-PL to the well-organized present semiconductor technology is an inevitable factor, i.e., the establishment of bright PL emission from a solid-state material is considered to be a still remained fundamental problem. In this study we report unique PL features obtained from as-grown vertically-, and individually-freestanding SWNTs prepared by a diffusion-plasma chemical vapor deposition method.<sup>1</sup> The intensity of PL is clearly observed to increase through the morphology transition from isolated to thin-bundled of the freestanding SWNTs.<sup>2</sup> Based on the precise spectrum analysis and equation-based estimation of the PL time trace, the origin of the PL brightening is consistently explained in terms of the exciton energy transfer through the tube bundles. The PL brightening is also revealed to obviously depend on SWNT diameters. Only the small-diameter rich sample can realize the PL brightening, which can be interpreted to be due to the different concentration of metallic SWNTs causing a PL quenching. Since it appears to be possible to fabricate brightly illuminating nanotubes on various kinds of substrates, the bundle engineering with freestanding nanotubes is expected to be a potential candidate for realizing the nanotube-based PL device fabrication.

<sup>1</sup>T. Kato and R. Hatakeyama, Appl. Phys. Lett., 92 (2008) 031502.

<sup>2</sup>T. Kato and R. Hatakeyama, J. Am. Chem. Soc., accepted.

4:00pm NM+PS+AS-WeA8 **Practical Considerations for Implementation of Nanomaterials in Aerospace**, K.D. Humfeld, The Boeing Company  
**INVITED**

4:40pm NM+PS+AS-WeA10 **Large-Scale Production and Metrology of Vertically Aligned Carbon Nanotube Films**, L. Dai, K. Bosnick, National Research Council Canada

We have successfully produced carbon nanotube (CNT) films (25-50 wafers per load) on a large scale in a commercial Tystar chemical vapor deposition (LPCVD) system. Electron microscopy studies indicate that the CNT films

are consisted of densely packed and vertically aligned multi-walled CNTs. A series of catalysts and growth conditions are tested systematically to synthesize high quality CNTs by varying the catalytic metal compounds and the CVD parameters. Both Fe films and ternary metal Cr/Ni/Fe films have been found favorable for the growth of aligned CNT films. To assess the as-grown vertically aligned CNT films, we are developing a general metrology which contains various analytical techniques to qualify the CNT film morphology, size, chirality, homogeneity, purity, dispersion, etc. This metrology uses some of the measurement equipments that are broadly used for material characterizations, including scanning electronic microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, profilometry, contact angle measurement and thermo gravimetric analysis (TGA). The metrology will facilitate quality control and process optimization necessary for industry applications of CNT films.

5:00pm **NM+PS+AS-WeA11 Linewidth Measurements on sub-20 nm HSQ/Graphene Nanostructures**, *J.J. Peterson*, Intel Corporation, *M.A. Rodriguez*, *V. Tileli*, University at Albany-SUNY, *M. Sprinkle*, *C. Berger*, *W.A. de Heer*, Georgia Institute of Technology

Although linewidth measurements of patterned graphene nanoribbons using the high resolution (HR) scanning electron microscope (SEM) have been reported in the literature,<sup>1</sup> it is known that such measurements are generally destructive to the structures which are being measured. Furthermore, due to the destructiveness of the measurement, the critical dimensions may be changing even as the measurement is being made. For this reason, the atomic force microscope (AFM) and scanning probe microscope (SPM)<sup>2</sup> has become an accepted method of linewidth measurement for graphene or hydrogen silsesquioxane (HSQ) on graphene structures, but this methodology is not scalable to a manufacturing environment. For this reason, it is desired that a more manufacturable method of linewidth measurement may be developed for measurement of critical dimensions of graphene nanostructures. In this talk, we compare linewidth measurements sub-20 nm HSQ/graphene structures using the HR SEM and environmental-SEM (E-SEM) and report that E-SEM measurements will support the necessary resolution to enable linewidth measurements of graphene nanostructures without the damage associated with typical HR scanning electron microscopes. Furthermore, we make a comparison of linewidth measurements using both the SPM and E-SEM and discuss each respective method's advantages and disadvantages.

5:20pm **NM+PS+AS-WeA12 Size Distributions and Agglomeration Effects in FePtAu Nanoparticles**, *V.V. Krishnamurthy*, Oak Ridge National Laboratory, *Z. Jia*, *D. Reed*, *M. Mandal*, *G.J. Mankey*, *J.W. Harrell*, *D.E. Nikles*, The University of Alabama, *L. Porcar*, NIST Center for Neutron Research

We have investigated the effect of thermal treatment on the microstructure and positional ordering of chemically synthesized  $(\text{Fe}_{49}\text{Pt}_{51})_{88}\text{Au}_{12}$  nanoparticles using small angle neutron scattering (SANS). The as made FePtAu particles have an average diameter of 3 nm. Thin films of nanoparticles were prepared by spincoating the dispersion of FePtAu nanoparticle on Si wafers. The samples were annealed for 30 minutes in a flowing nitrogen atmosphere in order to promote FCC-L1<sub>0</sub> phase transformation. The annealing temperature of the samples was varied from 300 °C to 550 °C in steps of 50 °C. The crystal structure and the lattice constant of the samples have been determined by x-ray diffraction. The magnetization hysteresis has been measured in a vibrating sample magnetometer. SANS measurements were performed at room temperature with an incident neutron wavelength of 6 Å using the 30 m NG3 SANS instrument at NIST. The scattering vector magnitude ( $q$ ) dependence of the SANS intensity,  $I(q)$  shows strong dependence on the sample annealing temperature. The  $q$  dependence of the SANS intensity in the range of 0.2 to 3 nm<sup>-1</sup> could be fitted by modeling the nanoparticles as polydisperse spheres with Schultz distribution for the diameters and a hard sphere interaction between the particles. In this  $q$  range, the agglomerates are assumed to be polydisperse spheres. The results indicate that significant agglomeration occurs in all the samples. The average size of the agglomerates is found to increase from 18 nm at 300 °C to 53 nm at 550 °C. The data also seem to indicate the sintering of particles in the temperature range of 500-550 °C. These results will be compared with the particle size distributions in off-situ annealed  $\text{Fe}_{49}\text{Pt}_{51}$  nanoparticles and in-situ annealed  $(\text{Fe}_{49}\text{Pt}_{51})_{88}\text{Au}_{12}$  nanoparticles.

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