Plasma Science and Technology

Room: 606 - Session PS1+NS-WeM

Plasmas in Nanotechnology

Moderator: S. Kodambaka, University of California, Los Angeles

8:00am **PS1+NS-WeM1 Spectroscopic, Spatial, and Temporal Investigation of Fe Nanoparticle Synthesis by Through Thin Film Ablation**, ***A.R. Waite,*** University of Dayton, Air Force Research Laboratory and UTC, Inc., *P.T. Murray,* University of Dayton, *J.G. Jones,* Air Force Research Laboratory, *E. Shin,* University of Dayton, *A.A. Voevodin*, Air Force Research Laboratory

Nanoparticles of Fe have been formed by the process of Through Thin Film Ablation (TTFA). In the TTFA process, the target consists of a thin film (10-20 nm thick) of material that has been applied to an optically transparent support. The thin film target is ablated in vacuum through the transparent support, and this produces a directional plume of nanoparticles. Optical Emission Spectroscopy (OES), Time-of-Flight (TOF) analysis, and high-speed Intensified Charge Coupled Device (ICCD) imaging are utilized to study the plume dynamics and characteristics. OES measurements indicate the ejected nanoparticles to have a temperature of 2232 K, suggesting they are liquid. TOF analysis indicated that there are two main size constituents in the ablation plume, higher speed atomic species and slower nanoparticles. ICCD imaging is used to further study the plume dynamics in both time and space. Ablation in vacuum and in the presence of a background gas will be discussed.

8:20am **PS1+NS-WeM2 Size Manipulation and Control of Nanoparticles Produced from Atmospheric-Pressure Microplasmas**, ***N.A. Brunelli***, *K.P. Giapis*, California Institute of Technology

Size manipulation and control of nanoparticles produced from atmospheric-pressure microplasmas Atmospheric-pressure microdischarges have been shown to produce silicon nanoparticles between 1-2 nm in diameter, which exhibit intense photoluminescence emission at 420 nm with quantum efficiency of 30%.[1] For imaging applications, it is desirable to have an emission at longer wavelengths which requires larger diameter nanoparticles. However, it has been exceedingly difficult to manipulate the nanoparticle size in a single microdischarge, where perturbations to the growth conditions seem to only influence the number of particles produced while the size remains invariant. We demonstrate here that the combination of a microdischarge with a CVD reactor can overcome this problem by achieving overgrowth of the seed particles produced in the microdischarge. For example, silicon nanoparticles can be enlarged from 2.5 nm to 3.5, 4.5 and 5 nm by mixing an additional 150, 300 and 600 ppm of sila4ne in argon, respectively. In fact, the CVD overgrowth allows not only tuning of the particle size but also permits selection of an alternate overgrowth layer, creating core-shell structures. Examples of Ge and Fe cores overgrown with Si will be shown. We quantify this claim by using a new ultrafine radial differential mobility analyzer immediately after the furnace to monitor in real-time the particle size. We characterize the nanoparticles by AFM, photoluminescence (PL) spectroscopy and transmission electron microscopy. As oxidation has been shown to affect the PL emission,[2] we have encapsulated the particles in thin films to ensure observed light emission is from radiative recombination. Beyond enlarging the seed particle diameter, we demonstrate the synthesis of core-shell structures consisting of an inexpensive metallic core and a thin overlayer of catalytically active material as the shell. Electrochemical measurements demonstrate the catalytic activity and performance of Fe-Pt and Co-Pt core-shell nanoparticles for fuel cell type applications.

[1] Sankaran, R. M., D. Holunga, et al. (2005). "Synthesis of blue luminescent Si nanoparticles using atmospheric-pressure microdischarges." Nano Letters 5(3): 537-541.

[2] Biteen, J. S., N. S. Lewis, et al. (2004). "Size-dependent oxygen-related electronic states in silicon nanocrystals." Applied Physics Letters 84(26): 5389-5391.

8:40am **PS1+NS-WeM3 Ionic Plasmas Yielding Novel-Structured and -Functional Nanocarbons**, ***R. Hatakeyama***, *T. Kaneko, W. Oohara, Y.F. Li*, Tohoku University, Japan **INVITED**

Nanocarbons of carbon allotropes have attracted a great deal of attention due to their high potential for novel properties and a variety of applications. Since fullerenes and carbon nanotubes among them are furnished with hollow inner nanospaces, it is a fascinating challenge to inject various kinds of atoms and molecules into the nanospaces based on plasma nanotechnology, which could lead to innovative functionalization of the pristine ones. For that purpose original approaches using nanoscopic plasma processing mainly in ionic plasmas have been performed in order to develop fullerene-, SWNT(single-walled carbon nanotube)- and DWNT(double-walled carbon nanotube)-based materials with new functions corresponding to electronic and biological applications. Firstly, the encapsulation of charge-exploited alkali atoms inside the fullerene is realized (Li@C_{60} etc.) using alkali-fullerene plasmas as ionic plasmas, which consist of positive alkali ions and negative C_{60} ions. Then the atomic nitrogen as a spin-exploited atom is also encapsulated inside C_{60} (N@C_{60}). In relation to the inner nanospace modification of the carbon nanotubes, another ionic plasmas, i.e., alkali-halogen plasma and pair-ion plasma are generated, which consist of positive alkali ions and negative halogen ions, and positive-C_{60} and negative-C_{60} ions with an equal mass, respectively. Furthermore, an electrolyte solution plasma including DNA negative ions is prepared. The substrate bias method is utilized mainly in these plasmas, where positive and negative ions with their energies and fluxes controlled are irradiated to an immersed substrate coated with the pristine carbon nanotubes . In addition, a thermal and plasma combined process is also devised for the treatment of both charge- and spin-exploited atoms. Consequently, we have innovatively created alkali-metals encapsulated SWNTs and DWNTs (Cs@SWNTs, Cs@DWNTs), halogen-elements encapsulated SWNTs (I@SWNTs), ferromagnetic-atoms encapsulated SWNTs (Fe@SWNTs), fullerene molecules encapsulated SWNTs and DWNTs (C_{60}@SWNTs, C_{60}@DWNTs, C_{70}@DWNTs, C_{84}@DWNTs), and DNA molecules encapsulated SWNTs (DNA@SWNTs) . Finally, their electronic and magnetic properties are intensively investigated. As a result, we have for the first time succeeded in realizing the continuous transition of air stable electronic transport from p-type to n- type semiconducting property by adjusting an amount of dosed atoms and molecules inside SWNTs and DWNTs (Cs@SWNTs, Cs@DWNTs, I@SWNTs, C_{60}@SWNTs, C_{60}@DWNTs), and in forming nano structures of magnetic semiconductor (Fe@SWNTs), nano pn junctions with rectifying characteristic [(Cs/I)@SWNTs)], and nano structures with distinct negative differential resistance of high peak-to-valley ratio (C_{60}@DWNTs, C_{70}@DWNTs, C_{84}@DWNTs) . In the case of DNA@SWNTs an experimental system utilizing an interfacial region between the gas and liquid phases has been constructed in order to enhance the DNA encapsulation rate. Here an ionic liquid consisting of only positive and negative molecules is introduced into the liquid phase, which can be regarded as an ionic plasma, i.e., fully ionized electrolyte plasma.

9:20am **PS1+NS-WeM5 Continuous-Flow Microplasma Synthesis of Metal Nanoparticles for Catalytic Growth of Carbon Nanotubes**, *W.-H. Chiang,* ***R.M. Sankaran***, Case Western Reserve University

Carbon nanotubes (CNTs) have been synthesized in a continuous-flow, gas-phase catalytic process. The synthesis technique consists of two steps: 1) production of well-defined metal nanoparticles in an atmospheric-pressure microplasma and 2) catalytic growth of carbon nanotubes in a tube furnace reactor. In the first step, nanoparticles are generated using a direct-current (dc) hollow cathode microplasma made-up of a stainless steel cathode with a pin-hole (d~180 µm) and an arbitrarily-shaped tube anode. Gaseous precursors are introduced into the microplasma at atmospheric-pressure and decomposed non-thermally by electron impact to generate reactive radical species. Under appropriate precursor saturation conditions, the radicals polymerize to nucleate particles homogenously in the gas phase. Particle growth is limited to the small reactor volume (less than 1 nL) created by the microplasma geometry. As a result of the large concentration gradients and short residence time, the technique is capable of producing very small (1-3 nm diameter) nanoparticles with narrow size distributions. The particle-laden flow is then continuously fed to a second reactor to grow carbon nanotubes in free flight with addition of acetylene and hydrogen and heating at fixed temperatures between 500 and 1000 ^{o}C. Nanotube size and distribution are determined on line using a gas-phase electrophoretic mobility macromolecular analyzer (GEMMA). In situ aerosol classification allows experimental conditions to be directly related to growth parameters. We have recently investigated the catalytic properties of iron and nickel nanoparticles toward growth of carbon nanotubes. Process parameters were optimized to prevent amorphous carbon formation and obtain high-quality CNTs. Ex-situ techniques such as Raman spectroscopy and transmission electron microscope (TEM) were used to characterize the structure of the carbon nanotubes. The combination of continuous-flow synthesis using microplasmas and the GEMMA system opens new possibilities for nanocatalyst synthesis and provides a methodology for enhancing our fundamental understanding of catalytic behavior.

9:40am **PS1+NS-WeM6 Low Temperature Growth of Single-Walled Carbon Nanotubes by Oxygen-Assisted Inductively Coupled Plasma Chemical Vapor Deposition**, ***C.-H. Hsiao***, *C.-H. Weng, Z.-Y. Juang, K.-C. Leou, C.-H. Tsai*, National Tsing Hua University, Taiwan

Single-walled carbon nanotubes (SWNTs) have attracted a great deal of attention recently due to their unique physical properties and a wide range of potential applications, in particular, field effect transistors (FET) and nano-photonic devices. It is highly desirable to develop a method compatible with standard semiconductor microfabrication processes for direct synthesis of high quality SWNTs. In this work, we demonstrated a low temperature growth process of SWNTs on silicon substrates by inductively coupled plasma chemical vapor deposition (ICP-CVD) method with CH_4/H_2 gas mixture as base processing gases. A unique Ni/Al/SiO_2 nanocatalysts/support system has also been developed to allow the growth of high quality SWNTs. To further improve the crystalline structure of SWNTs, oxygen was added to the processing gas mixture to remove amorphous carbons during the growth process. Both the scanning electron microscopy and micro-Raman spectra were employed for characterizations of the SWNTs. Parametric experiments were conducted to optimize the O_2 fraction in the gas mixture. The SWNTs were successfully synthesized at a temperature as low as 600°C.

10:40am **PS1+NS-WeM9 Fabrication of Defect-Free and Diameter-Controlled Silicon Nanodisks for Future Quantum Devices by using Neutral Beam Etching**, *T. Hashimoto*, ***T. Kubota***, *C.H. Huang,* Tohoku Univ., Japan, *M. Takeguchi,* National Inst. for Mtls Sci., Japan, *K. Nishioka,* Japan Adv. Inst. of Sci. and Tech., *Y. Uraoka, T. Fuyuki,* Nara Inst. of Sci. and Tech., Japan, *I. Yamashita,* Matsushita Electric Industrial Co., Ltd, Japan, *S. Samukawa*, Tohoku Univ., Japan

Nanometer-scale structures, such as quantum dots, are widely studied because of their possible application in the development of quantum-effect devices, such as quantum-dot lasers and single-electron transistors. To develop practical and robust quantum-effect devices, manufacturers must be able to fabricate selectively arranged, defect-free, sub-10-nm-scale structures of uniform size on substrates. To realize a nanometer-scale structure, we used a ferritin iron core (7 nm in diameter) as a uniform and high-density template and our developed neutral beam (NB) etching process for damage-free etching. We fabricated a "nanodisk,"a nanometer-thick disk-shaped silicon structure by patterning <3.5-nm poly-Si layer / 1.4-nm SiO_2 layer / Si substrate> by using NB etching with a ferritin iron-core mask. To precisely control the diameter of the nanodisk, we must selectively remove the surface native silicon oxide layer before Cl neutral beam etching because the Cl neutral beam has extremely high selectivity to SiO_2 film. SEM and TEM observations revealed that the nanodisk was successfully fabricated and that the buried SiO_2 layer was not damaged during etching. When the nanodisk was only etched by using the Cl neutral beam with the iron core mask, the diameter of the nanodisk was about 13 nm. To shrink the diameter of nanodisk, we developed a dry process to remove native oxide by using NF_3 gas and hydrogen radicals ("NF_3 treatment"). By using the NF_3 treatment to remove the native oxide, we decreased the nanodisk diameter to 10 nm. We found that removing the surface native oxide is very important for controlling the diameter of nanodisk. We then measured the I-V characteristics by using atomic force microscopy (AFM) with a conducting probe. Coulomb staircases were observed from the I-V measurements of the nanodisks at 25 K and at room temperature. These results indicate that the nanodisks we fabricated have a precise quantum-effect structure, and they attained single-electron properties. This research has great potential in the development of practical and robust fabrication processes for future quantum-effect devices. A part of this work was supported by the Nanotechnology Support Project and the Leading Project of the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan.

11:00am **PS1+NS-WeM10 Parallel Writing of Complex Nanofeatures using Nanopantography**, ***L. Xu***, *A. Nasrullah, M. Jain, Z. Chen, V.M. Donnelly, D.J. Economou, P. Ruchhoeft*, University of Houston

Nanopantography is a technique for massively parallel writing of nano-sized features. A broad-area, collimated, monoenergetic ion beam is directed to an array of sub-micron-diameter electrostatic lenses fabricated on a conductive substrate (e.g., doped Si wafer). By applying appropriate voltages to the lens electrodes, each "beamlet" entering the lens is focused to a spot on the wafer surface. The spot size can be up to 100X smaller than the diameter of the lens. With the choice of an Ar^+ beam in the presence of Cl_2 gas, 10 nm-dia holes were etched in Si; while with the choice of a Ni^+ beam, ~10 nm nickel dots were deposited on Si. Nanopantography has the capability to write arbitrary nano-sized features since the focal points can be displaced by tilting the substrate. A second-generation nanopantographic system was built to allow writing of complex nano-features. The improved system design had an ion flux ~ 15X higher than the first generation reactor. A LabView-controlled motorized stage could be tilted in both the X- and Y-axes with an accuracy of 0.011° degrees. This corresponds to translation of the focal point by 1.5 nm on the substrate. The energy distribution of the extracted ion beam was measured to have a spread of 2.2 eV, for a 100 eV beam. By continuously tilting the substrate in one direction, nanotrenches with ~15 nm (FWHM) width and ~40 nm depth were etched in a Si wafer. More complex patterns, such as letters of the alphabet, were also etched into Si in a massively parallel fashion by two-dimensional tilting of the substrate.

11:20am **PS1+NS-WeM11 High Aspect Ratio Deep Trench Chamber and Process Development for Silicon Etch in DRAM Applications below 50 nm**, ***S. Wege***, *S. Barth,* Qimonda Dresden, Germany, *A. Kersch,* Qimonda Munich, Germany, *M. Reinicke,* Dresden University of Technology, Germany, *G. Wenig,* Qimonda Munich, Germany, *M. Rudolph, J. Sobe, A. Steinbach*, Qimonda Dresden, Germany

For QimondaÂ´s DRAM Technology the deep trench etched into silicon is the base for the capacitor concept. The shrink of lateral dimensions at approximately constant capacity specifications leads to increased deep trench aspect ratio requirements. Therefore high selectivity to the etch mask and excellent uniformity is needed, especially for technologies below 50nm. In this paper we describe the development of advanced DT plasma etch chamber and process to fulfill these requirements. New process regimes, e.g., RF pulsing and high temperature showed promising results. Simulations were combined with in-situ plasma measurement techniques, e.g., QMS with ion energy analysis, high resolution OES, insitu IR absorption spectroscopy, and technological experiments, to characterize hardware features and process conditions. To achieve high Si etch rate and selectivity, plasma density and electron energy distribution in the plasma bulk, and ion energy distribution on the wafer surface can be optimized through multi frequency cathode excitation. The selectivity is further enhanced by using advanced hard mask materials and combining with RF pulsing. The optimization of the side wall passivation stoichiometry is a key for high aspect ratio silicon etch. In addition, the etch process chamber includes new features for process control, in-situ wafer surface temperature and trench depth measurement. The equipment and process development was accomplished through close cooperation between Qimonda and the tool supplier.

11:40am **PS1+NS-WeM12 Etch Selectivity and Surface Roughening of Polystyrene and Poly(methyl methacrylate) in Plasma Etching of Block Copolymers**, ***Y.-H. Ting***, *S.-M. Park, C.-C. Liu, X. Liu, F.J. Himpsel, P.F. Nealey, A.E. Wendt*, University of Wisconsin-Madison

Polystyrene -block-poly(methyl methacrylate), (PS-b-PMMA) diblock copolymers are a promising lithography alternative for nanometer scale features. The two components segregate into nanoscale domains when the polymer solution is spun on to form a thin film and annealed above the glass transition temperatures of both components. Preferential removal of PMMA domains through plasma etching to leave behind a PS mask for subsequent etching of underlying layers is the focus of this work. The quality of the PS mask is characterized by the thickness and lateral dimension of the PS structures after removal of the PMMA, as well as the smoothness of its surfaces. We have characterized the effects of different plasma chemistries including O2, Ar/O2, Ar, CF4 and CHF3/O2 on etch selectivity and surface/sidewall roughness for PS and PMMA. The surface roughness of PS and PMMA after Ar/O2 plasma etching (which gave the best overall etch performance) was further examined as a function of ion bombardment energy to understand the roughening mechanisms, as the two polymers show different responses to changing plasma conditions. Specifically, the surface roughness of PMMA increases with increasing ion bombardment energy, while that of PS decreases. An oxidation-induced micro-masking process on PS surfaces upon plasma exposure has been proposed to explain the different in roughening of PS and PMMA. Surface chemical analysis using NEXAFS shows that chemical change occurs on the PS surface during exposure to oxygen containing plasmas. Evidence of inhomogeneities in the composition of the PS film suggests that surface inhomogeneities in chemical composition may persist and change chemically upon plasma exposure. Variations in etch resistance associated with the inhomogeneities may in turn be responsible for observed surface roughness. Roughening caused by this "micro-masking" effect is reduced under conditions that minimize selectivity, such as high ion bombardment energies. We acknowledge support from the UW NSF MRSEC for Nanostructured Materials.

12:00pm **PS1+NS-WeM13 Comparison between NF_3 and CF_4 Chemistries for the Selective Etching of SiGe Sacrificial Layers in a 300mm Chemical Dry Etching Reactor**, ***S. Borel***, CEA-Leti MINATEC, France, *C. Arvet,* STMicroelectronics, *D. Watanabe*, Shibaura Mechatronics Corporation, Japan

The selective removal of a SiGe sacrificial layer is a key step in the realization of several architectures that are based on the SON technology.

Such a process has been developed and studied in 200mm, showing very good results in terms of selectivity by using CF_4 as an etching gas. This competence has been transferred in 300mm by using a new generation chemical dry etching tool that offers an additional and alternative source of fluorine which consists in NF_3. A process based on this environment-friendly molecule has been developed and compared with the CF_4 reference in terms of SiGe:Si selectivity while keeping a comparable etch rate. In that aim, a strong dilution (1:10) was necessary because of the high dissociation level of NF_3 that results in high etch rates. Morphological analyses clearly show that the selectivity obtained by using NF_3 is prohibitive for the realization of advanced devices. Indeed, the selectivity value is around 3, which means that the thinning of the Si cap is only 3 times lower than the SiGe tunnel depth whereas it needs to be higher than 30 (it reaches 70 by using CF_4). Surface analyses by XPS reveal that a Si substrate exposed to the CF_4 process presents some carbon, which suggests a passivation mechanism that may be involved in the selectivity. With the carbon-free NF_3 molecule, this phenomenon does not occur, hence the lack of selectivity we observe. As a conclusion, even if it is possible to etch SiGe faster than Si by using NF_3, the reference process made of CF_4 remains the best solution for the tunnel etching of advanced devices where a controlled etch rate is necessary and a high SiGe:Si selectivity is mandatory.

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