Wednesday Morning, November 5, 2003

Plasma Science and Technology
Room 314 - Session PS1-WeM

Plasma Processing of Nanostructures and Nanomaterials

Moderator: S. Samukawa, Tohoku University, Japan

8:20am **PS1-WeM1 The Study of Plasma Etching Limits Using Nanometer-Scale Self-Assembled Arrays*, Y. Zhang*,** *T.J. Dalton,* IBM

Fine patterning of semiconductor nano-scale features at the sub-20nm region is a challenging task. Among the nanometer scale features of importance in microelectronics and bio-microelectronics applications are: (1) open standing nano-features, i.e., a Si gate, and (2) small nano holes, i.e., an array of vias with nanometer scale diameter. The rapid shrinking of conventional CMOS technology is quickly approaching a perceived scalability limit or "brick wall". Plasma etching of true nanometer scale features may also face its limits. For open standing nano-features, the main challenge (or soft limits) is CD control, e.g., line edge roughness (LER) control of sub-10nm Si gate lines. A LER tolerance of 10% for 10nm gates means controlling 1nm, which has about 1 layer of silicon atoms on each side of gates. For true nanometer scale via arrays, the diameter of the vias for sub-10nm sizes is approaching the sizes of reactive products, e.g., SiBr4, SiF4, and SiCl4. In this case, plasma etching may hit its ultimate limits ("hard" limits). In this study, self-assembled nanometer scale diblock copolymer arrays were used to generate large scale (across 200 mm wafers) sub-20 nanometer test structures. The nanometer hole arrays were used to tested plasma etching characteristics of different materials, i.e., silicon, silicon dioxide, and silicon nitride with different plasma chemistries, from fluorine, chlorine, to bromine to vary the sizes of reactive species, F, Cl, to Br, and etching byproducts, such as SiF4, SiCl4, to SiBr4, with the aim of finding the plasma etching limits. In this paper, we present our recent work on the challenges of pattering nano-features, e.g., decreasing patterning layer thickness, aspect ratio dependent etch (ARDE), selectivity, and limits for sub-10 nm scale holes. Underlying principle of the different etching chemistry and processing parameters and their advantage and drawback to etch nanometer scale features will be also discussed.

8:40am **PS1-WeM2 Insights into Nanoparticle Formation Processes in a Thermal Plasma Process*, C.R. Perrey*,** *C.B. Carter, T. Renault, A. Gidwani, R. Mukherjee, X. Wang, J. Hafiz, W.M. Mook, W.W. Gerberich, P.H. McMurry, J.V.R. Heberlein, S. Girshick,* University of Minnesota

As nanoscale metal and ceramic particles are increasingly considered for industrial applications, a fundamental understanding of the effects of processing on particle morphology is required. The size, shape, structure, chemistry, and resulting properties of nanoparticles are all potentially functions of the formation method. This study examines the structure and chemistry of both nanoparticle films and individual nanoparticles produced by hypersonic particle plasma deposition. The process utilizes a thermal plasma to generate nanoparticles which are then rapidly assembled to form nanostructured films; the mechanical properties of both the particles and the films appear to differ significantly from the bulk material of the same composition. Observations made by electron microscopy are used to analyze the materials at each stage of the process. The presence of nanoparticles with atomically flat planar defects and a spherical shape imply a rapid condensation and crystallization from the gas phase. This paper will illustrate studies involving the production of Si, SiC, and Ti nanoparticles and nanostructured films, allowing comparisons for the different materials.

9:00am **PS1-WeM3 Reactive Gas Condensation of Aluminum Nitride Nanoparticles*, C. Baker*,** *A. Ceylan, S.I. Shah,* University of Delaware

AlN nanoparticles were synthesized using Reactive Gas Condensation (RGC) technique in which a gas mixture of NH3 and N2 was used for the nitridation of aluminum vapors that were obtained by resistive evaporation of Al wire. NH3 served as the reactive gas while N2 served as both a carrier gas and a source for particle condensation. The process was carried out at a pressure range of 50 - 100 Torr in order to facilitate the condensation. X-ray diffraction (XRD) and X-ray photoelectron (XPS) analysis revealed that the samples deposited with more than 10% NH3 in N2 were composed entirely of hexagonal AlN nanoparticles. The particles were single crystal, as determined by electron diffraction in transmission electron microscopy. The particle size was controlled by varying the pressure of the gas mixture for high relative concentrations of NH3. AlN nanoparticles were dispersed in various liquids to enhance the fluid thermal conductivity. Results will be presented to show that the thermal conductivity of the liquid was considerably increased with the addition of minimal amount of AlN nanoparticles.

9:20am **PS1-WeM4 Properties of Carbon-based Nanofibers Grown by Low-pressure Plasma Enhanced Chemical Vapor Deposition*, J.B.O. Caughman*,** *L. Zhang, D.W. Austin, M.A. Guillorn, A.V. Melechko, V.I. Merkulov,* Oak Ridge National Laboratory

The role of the plasma in the growth of carbon-based nanofibers is being determined by related plasma conditions to the physical and electrical properties of the nanofibers. Forests of nanofibers, as well as single isolated nanofibers have been grown using an inductively coupled plasma source operated from 50 to 200 mTorr. The plasma is composed of hydrogen and either acetylene or methane as the carbon source, with the addition of diborane and/or nitrogen to modify the composition of the nanofibers. The plasma conditions are determined by using mass spectroscopy and optical emission spectroscopy. The electrical properties of the nanofibers are found by using a four-point probe method, where electrodes are deposited on individual nanofibers. Processing results show that acetylene utilization increases with input power and reaches values of 70 to 80 percent as the discharge transitions to the inductively coupled regime, which results in well-formed cylindrical nanofibers. Excessive carbon in the plasma results in an increase in amorphous carbon deposition on the nanofiber sidewalls. Substrate bias plays an important role in controlling the physical etching component during deposition, where a transition is made from an amorphous thin film to a cylindrical nanofiber to a damaged structure as the bias increases. The electrical characteristics of the nanofibers grown with the low pressure method are compared to those grown with a conventional DC plasma-based method, where the resistivity has been found to be nearly the same as polycrystalline graphite. Details of the effect of plasma properties and the effect of nitrogen and boron addition on the electrical/physical properties of the nanofibers will be presented.

9:40am **PS1-WeM5 Growth of Vertically Aligned Carbon Nanotubes Using a High Density Plasma CVD Process*, H.W. Wei,*** National Tsing Hua University, ROC*; K.C. Leou,* National Tsing Hua University, ROC, R.O.C*; M.T. Wei, K.J. Shen, C.H. Tsai, C. Lin,* National Tsing Hua University, ROC

Vertically aligned multiwall carbon nanotubes are grown on silicon substrates with Ni catalyst patterns using an inductively-coupled high density plasma chemical vapor deposition reactor. The plasma is produced by 13.56 MHz RF power and a feed gas of C@sub 2@H@sub 2@ and H@sub 2@ mixture at a pressure below 100 mtorr. A heated and DC biased subtrate stage is employed to allow low temperature and aligned growth of CNTs. Due to low pressure operation, the growth rate of the CNTs is relative low (50-200 nm/min.) while the diameter of the tubes ranges from 30 nm to 120 nm depending on growth conditions. Another feature of the patterned and aligned growth of the CNTs using this HDP-CVD process is that the density of CNTs is relatively low (10@super 8@ to 10@super 9@ 1/cm@super 2@) although the CNTs are directly grown on 5 µm x 5 µm catalyst patterns. This will result in a reduction of the shielding effect of electric field for field emission appication of the CNTs. Results from parametric study of CNTs properties based on Raman spectroscopy, TEM and field emission measurements with process conditions as well as measurements from a mass spectrometer and plasma emission actinometry (for H atom) will be presented. @FootnoteText@ Work supported by the NSC of the R.O.C., grant No. NSC 90-2622-E-007-004.

10:00am **PS1-WeM6 Correlation between Size of Clusters and Qualities of a-Si:H Films for SiH@sub 4@ High Frequency Discharges*, K. Koga*,** *N. Kaguchi, M. Shiratani, Y. Watanabe,* Kyushu University, Japan

Previously, we have shown that a reduction of amount of particles below 10 nm in size (clusters) formed in SiH@sub 4@ high frequency discharges is the key to deposit hydrogenated amorphous silicon (a-Si:H) films of extremely small microstructure parameter R@alpha@ < 0.01. In this work, we have studied correlation between cluster size and a-Si:H film qualities by using the cluster suppressed plasma CVD method@footnote 1@ together with newly developed downstream cluster collection (DCC) method. The following results have been obtained in our experiment: 1) the DCC method offers a quite high sensitivity deduction of size and density of clusters above 1 nm in size and 10@super 4@ cm@super -3@ in the reactor; 2) An initial fill factor (FF@sub i@) of a n@super +@Si/a-Si:H/Ni Schottky solar cell gradually increases from 0.46 for mean cluster size d@sub c@= 9.0 nm to 0.48 for d@sub c@= 3.7 nm and significantly increases to 0.53 for d@sub c@= 1.6 nm. 3) The FF@sub i@ value increases with decreasing volume fraction of clusters. Experiments for studing correlation between amount of clusters of sub nm in size and film qualities

is underway. @FootnoteText@ @footnote 1@M. Shiratani, K. Koga, M. Kai, and Y. Watanabe, Thin Solid Films 427, 1(2003).

10:20am **PS1-WeM7 Study of Plasma-Nanoporous Silica Surface Interactions in Fluorocarbon and O@sub2@ Discharges: Comparison with SiO@sub 2@ and Organosilicate Glass***, **X. Hua**, G.S. Oehrlein, R.M. Briber,* University of Maryland, College Park*; P. Lazzeri, N. Coghe, M. Anderle,* Center for Scientific and Technological Research, Italy

We have investigated plasma surface interactions of nanoporous silica (NPS) films with porosities of up to 50%, SiO@sub 2@ and organosilicate films in either C@sub 4@F@sub 8@/Ar discharges (used for plasma etching) or O@sub 2@ plasmas (used for resist mask removal). Surfaces of the various materials after the above plasma processes were studied by x-ray photoemission spectroscopy as a function of process conditions. In addition, time-of-flight secondary ion mass spectrometry (in static or dynamic mode) was used to obtain additional information on the compounds formed on the surfaces of these materials, or on variations of elemental densities as a function of depth. The plasma-surface interactions of NPS are strongly modified relative to conventional SiO@sub 2@ or OSG. Several depth scales of these alterations exist: The surface and near-surface region (down to ~10 nm), intermediate depth (~50 nm), and the complete NPS film thickness to the interface with the substrate. In the surface/near-surface region the porosity of the NPS material increases the plasma-surface interaction area, which during fluorocarbon etching leads to differences in surface fluorocarbon film coverage for NPS relative to SiO@sub 2@ and associated changes in etching behavior. The larger depth scales are especially relevant for O@sub 2@ cleaning which strongly decreases the residual carbon content of both OSG and NPS down to intermediate depths and for NPS materials of 30% and 50% porosity produces deep penetration of fluorine down to the substrate-interface.

10:40am **PS1-WeM8 High Flux and Low Energy Neutral Beam Formation Using a Low Angle Forward Reflected Neutral Beam System***, **D.H. Lee**, S.J. Jung,* Sungkyunkwan University, South Korea*; K.H. Baek,* Samsung Electronics, South Korea*; C.J. Kang,* Samsung Electronics, South Korea, Korea*; G.Y. Yeom,* Sungkyunkwan University, South Korea

Plasma etching is one of the key technologies in the fabrication of deep submicron silicon-based integrated circuits. However, plasma etching has a serious disadvantage due to the energetic charged particle such as positive ion and photons generated in the plasma. Charge-induced damage during the plasma etching is one of the serious problems that have to be solved for the deep submicron semiconductor devices as well as future nanoscale devices. To avoid the charge-related damage, several low-damage processes have been proposed and one of the techniques to avoid the problem is to use neutral beam etching. Among the techniques fabricating a neutral beam, a low angle reflection of the ion beam where ions extracted from the ion source are neutralized by a low angle reflection during the reflection has been investigated in this study. Previous studies showed that, by the reflection of the ion beam at 5 degree angle of incidence, most all of the ions could be neutralized and nearly vertical SiO2 etching could be obtained for various fluorine based gases. In this study, for the formation of high flux and low energy neutral beam, a modified neutral beam source was proposed, and Si and SiO2 etch properties such as etch rate, etch selectivity, and etch profiles with fluorine-based gases using this system have been investigated. Also, the surface damage of the etched Si surface was investigated using TEM.

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