Wednesday Morning, November 6, 2002

Plasma Science
Room: C-103 - Session PS+NT-WeM

Plasma Science and Technology for Nanostructures
Moderator: V.I. Merkulov, Oak Ridge National Laboratory

8:20am **PS+NT-WeM1 Plasma Enhanced Chemical Vapor Deposition of a Dense SiO_2 Cap Layer on Low-k Nanostructured Porous Silica**, ***Y.B. Jiang***, *N. Liu, C.J. Brinker, J.L. Cecchi*, University of New Mexico

Surfactant-templated self-assembled nanostructured porous silica is a promising material for low-k interlevel dielectrics (ILDs) in integrated circuits. With mono-dispersed pore sizes as small as 2 nm and an ordered pore structure, nanoporous silica has excellent mechanical and thermal properties, even at porosities high enough for k values of 2 and below. For ILD applications, the pores must be capped to prevent adsorption on pore surfaces during subsequent processing, such as the deposition of a copper diffusion barrier. In this work, we report on a process for capping nanoporous silica with a dense-but-thin SiO_2 layer that acts as a diffusion barrier without significantly increasing the overall dielectric constant of the ILD. Nanoporous silica was deposited on a silicon wafer by spin coating with a sol-gel solution. After spin coating, the films were solidified by heating. The pore surfaces were rendered hydrophobic by soaking the films in a 6% HMDS solution, which terminated the pore surfaces with methyl groups. An SiO_2 cap layer was deposited by plasma-enhanced chemical vapor deposition (PECVD) in an inductively-coupled plasma reactor, using a SiH_4/O_2/Ar gas feed mixture. RF power, total pressure, gas composition, and flow rate were varied systematically to produce a high-density film with low surface roughness. The corresponding deposition rate resulted in 50 nm-thick films in approximately 15 minutes. N_2 absorption measurements performed with a surface acoustic wave (SAW) technique indicate a reduction of more 10 between the capped and the uncapped nanoporous film. X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements both confirm that the pore structure in the nanoporous silica is unchanged by the capping process. Fourier transform infrared (FTIR) detection of methyl groups shows that the hydrophobicity of the nanoporous silica remains after the dense SiO_2 cap layer is deposited.

8:40am **PS+NT-WeM2 RIE processes of Formation of Nanometer-Scale Dot Arrays**, ***Y. Zhang***, *K.W. Guarini, E. Sikorski, C.T. Black, T.J. Dalton*, IBM T.J. Watson Research Center

Nanometer scale structures are increasingly merging into microelectronics and other applications. One of the challenges of fabricating nanometer scale structures is the simultaneous scaling of vertical and horizontal features. As the horizontal feature scale shrinks down to nanometer sizes, the vertical scale often shrinks at a faster rate. When using these materials for masking layers, this leads to new challenges in fabricating multi-layer nanometer scale structures for a variety of microelectronics applications. In this paper, we explore the challenges of plasma RIE processing to fabricate densely-spaced, uniformly-sized nanometer-scale dot arrays over large wafer areas based on self-organizing diblock copolymers. High selectivties among variety materials, precise CD control, real time process monitoring, and flexible and uniform plasma processing conditions are necessary for fabricating nano-scale structures with high aspect ratios (AR), e.g., ~ 20nm polysilicon hole or column arrays with AR > 15:1. The results show the versatility of RIE process techniques through examples of dot arrays formed of conducting, insulating, and polymeric materials. These fabrication processes vary in complexity, utility, and degree of optimization, and we discuss the relative merits of each. The ability to create uniform nanoscale features below lithographic resolution limits may enable key applications in fields such as magnetic recording and microelectronics.

9:00am **PS+NT-WeM3 Efficient Production of Single-Wall Carbon Nanotubes by Means of the Gravity-free Gas Arc Dischargee**, ***T. Mieno***, Shizuoka University, Japan, *M. Kanai*, University of London, UK, *H. Shinohara*, Nagoya University, Japan **INVITED**

Single-wall carbon-nanotube (SWNT) are attracting much attention by their unique structures and properties, and applications of nanotubes are demonstrated as a cold electron emitter, strong wire, electronic devices and hydrogen absorber. The SWNT are produced by the gas-arc method as same as the fullerene production method. A carbon anode mixed with metal catalyst is arc sublimated in He gas (p> 40 kPa), and high density carbon particles deposit on metal particles in hot gas atmosphere making nano-pipe structures, diameter of which is about 1 nm. As these nanotubes, metal particles and another carbon clusters are flown up by the heat convection, the reaction time is limited by this heat convection. If the heat convection is suppressed by the gravity-free condition, diffusion speed of these particles is suppressed and longer reaction time can be expected.[1] In order to examine this gravity effect, the 12m-high vertical swing tower[1] is used and the carbon nanotubes are produced in the gravity-free condition.[2] Integrated gravity-free sublimation time is about 14 min. After the discharge, the carbon soot is collected and its weight is measured. As a result, production rate of the carbon soot including SWNT about 7 times increase in the gravity-free condition compared with that of the normal gravity condition. By the TEM (microscope method) their morphology is observed and more (about 2 times) dense bundle of SWNT is confirmed in the gravity-free condition. Thickness of the produced nanotube is measured by the Raman scattering method, and fatter nanotube (mainly d= 1.4 nm) is produced in the gravity-free condition compared with the normal-gravity case.

[1] T. Mieno, Jpn. J. Appl. Phys. 37 (1998) L761.
[2] M. Kanai, T. Mieno, H. Shinohara et al, Appl. Phys. Lett. 79 (2001) 2967.

9:40am **PS+NT-WeM5 Patterned Growth of Vertically Aligned Carbon Nanofibers using a High Density Plasma Enhanced Chemical Vapor Deposition Process**, ***J.B.O. Caughman***, *L.R. Baylor, M.A. Guillorn, V.I. Merkulov, D.H. Lowndes*, Oak Ridge National Laboratory

Patterned arrays of vertically aligned carbon nanofibers (VACNFs) have been grown using a high density plasma enhanced chemical vapor deposition process. The nanofibers are grown from a nickel catalyst that can be patterned to form arrays of individual isolated electron emitters. Forests of nanofibers, as well as single isolated nanofibers have been grown. An inductively coupled plasma source is used to grow the fibers. The plasma source operates at 13.56 MHz and couples power via a flat spiral coil. The plasma is composed of hydrogen and either acetylene or methane. The VACNFs are grown on a heated substrate located downstream from the ionization zone. Typical growth temperature is 700 degrees C. The energy of the ions impacting the growth surface is controlled by radio frequency bias, with typical self-bias voltages of between -50 and -300 volts. Plasma conditions are related to growth results by comparing optical emission from the plasma to the physical structure and electron emission from the nanofibers. For example, as the acetylene flow increases, the optical emission from the plasma indicates a decrease in atomic hydrogen production and an increase in molecular carbon production. The decrease in atomic hydrogen production results in a decrease in the chemical etching component during nanofiber growth. Plasmas that contain a high hydrogen to carbon ratio result in fairly narrow nanofibers, while plasmas with a high carbon to hydrogen ratio result in nanofibers with a broader base with more of a cone-like structure. The threshold electric field from isolated emitters has been measured and is typically 30-50 volts/micron and can vary with growth conditions. The relationship between plasma conditions and growth results/performance will be presented.[1]

[1]Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Dept. of Energy under contract DE-AC05-00OR22725.

10:00am **PS+NT-WeM6 Carbon Nanotubes by ICP-CVD: Growth, Characterization, Plasma Diagnostics, and Modeling**, ***D.B. Hash***, *L. Delzeit, K. Matthews*, NASA Ames Research Center, *B.A. Cruden*, Eloret Corporation, *M. Meyyappan*, NASA Ames Research Center

Applications in field emitter devices, electrode and sensor development require a very high degree of vertical orientation of carbon nanotubes (CNTs) on the substrate. This is not possible using thermal CVD. The inherent electric field in a direction normal to the substrate in a plasma process enables achievement of vertical orientation of the nanotubes. We have built an ICP reactor and grown multiwalled carbon nanotubes (MWNTs) from hydrocarbon feedstock (CH_4, C_2H_2, and C_2H_4) diluted with hydrogen. The MWNTs have been characterized using SEM, HRTEM, and Raman scattering. The MWNTs are highly aligned and suitable for the applications mentioned above. Results as a function of pressure, substrate power, and temperature will be discussed. To understand the effects of process parameters on growth as well as mechanisms - including identification of species responsible for nanotube growth, we have undertaken a 2-D plasma modeling of the process. Modeling results are compared with plasma diagnostics using optical emission spectroscopy, UV Absorption, and Residual Gas Analysis (RGA).

10:20am **PS+NT-WeM7 Zinc Oxide Nanowires Grown by Plasma Assisted Chemical Vapor Deposition**, ***J.B. Baxter***, *E.S. Aydil*, University of California, Santa Barbara

Zinc Oxide is a wide band gap semiconductor (Eg=3.37eV) that can exhibit visible and UV luminescence, piezoelectricity, and high conductivity. ZnO nanowires and hexagonal columns have been grown using plasma assisted chemical vapor deposition, using either metallic zinc or metalorganic

precursors. Nanowire growth is catalyzed by monodisperse gold nanoparticles (20 nm diameter) dispersed on a substrate from a colloidal solution. Transmission electron microscopy and electron diffraction show that single crystal ZnO nanowires grow from the gold particles in the <0001> direction. The nanowires have monodisperse diameters determined by the diameter of the gold particles (~ 20nm), and can grow to several microns in length. Energy dispersive x-ray spectroscopy confirms that the wires have a Zn:O ratio of 1:1. ZnO columns were formed by subliming metallic zinc in oxygen plasma, with the columns growing in the <0001> direction from the zinc surface. The columns are several 100 nm in diameter and are hexagonally faceted. Cathodoluminescence results show that both wires and columns emit photons upon excitation by electrons, with the columns emitting most light through the top face. This suggests that ZnO nanowires act as light pipes by internally reflecting the emitted light, making them good candidates for UV lasing. Because the gold particles from which the wires grow can be closely packed, the wires can be grown on a substrate in very dense, high surface area arrays. This property suggests that ZnO nanowires are also ideally suited toward application as the mesoporous semiconductor in dye sensitized (Gratzel) solar cells.

Authors Index

Bold page numbers indicate the presenter