Thursday Afternoon, November 3, 2011

Plasma Science and Technology Division
Room: 202 - Session PS+SS-ThA

Plasma Surface Interactions (Fundamentals & Applications) II
Moderator: A. Kumar, Case Western Reserve University

2:00pm **PS+SS-ThA1 Plasma Prize Lecture - The Role of Atomic Hydrogen on Plasma Synthesis of Carbon Nanotubes**, ***E.S. Aydil**** , University of Minnesota **INVITED**

Hydrogen containing discharges are used widely in plasma synthesis of a variety of nanustructures including nanoparticles and carbon nanotubes. We developed a method for measuring the H-atom flux at the plane of the substrate surface during H_2 plasma exposure. Our method is based on infrared measurements of the change in free-electron absorption in a polycrystalline ZnO film when this film exposed to H atoms. Hydrogen acts as an electron donor in ZnO, and thus the concentration of hydrogen-generated free carriers can be extracted from their absorption in the infrared. The change in the concentration of free carriers can in turn be related to the flux of H atoms impinging on a ZnO film placed on the substrate platen. Using this and a suite of additional plasma and material characterization techniques, including optical emission, infrared, and Raman spectroscopy and electron microscopy we systematically investigated the interrelation among plasma gas phase composition, catalysts morphology, catalyst structure, and carbon nanotube structure in plasma enhanced chemical vapor deposition of carbon nanotubes. The structures of carbon nanotubes grown from catalytic nanoparticles via PECVD in CH_4 /H_2 mixtures show a strong dependence on the H_2-to-CH_4 ratio in the feed gas. Hydrogen plays a critical role in determining the final carbon nanotube structure through its effect on the catalyst crystal structure and morphology. At low H_2-to-CH_4 ratios, iron catalyst nanoparticles are converted to Fe3C and well-graphitized nanotubes grow from elongated Fe_3C nanoparticles. High H_2-to-CH_4 ratios in the feed gas result in high atomic hydrogen concentrations in the plasma and strongly reducing conditions, which prevents conversion of Fe to Fe_3C. In the latter case, poorly-graphitized nanofibers grow from ductile bcc iron nanocrystals that are easily deformed into tapered nanocrystals that yield nanotubes with thick walls. In the limit of pure hydrogen the cylindrical graphene walls of a nanotube are etched and amorphized by the H atoms. Etching is not uniform across the length of the CNT but rather, small etch pits form at defective sites on the CNT walls along the entire nanotube length. Once an etch pit is formed, etching proceeds rapidly, and the remainder of the CNT is quickly etched away.

2:40pm **PS+SS-ThA3 CF and CF_2 Contributions to Plasma-Enhanced Chemical Vapor Deposition of Fluorocarbon Films in C_xF_y Systems**, ***M.F. Cuddy***, *E.R. Fisher*, Colorado State University

Inductively coupled fluorocarbon (FC) plasmas produced from C_xF_y ($x,y \geq 1$) precursors are widely employed in industrial processes ranging from circuitry fabrication to preparation of low-*k* optical coatings. The utility of the plasma system is largely dictated by the y/x ratio, specifically in that precursors with lower ratios tend to more efficiently deposit FC films. Film growth is thought to be related to the behavior of radical species within the plasma, such as CF and CF_2. We report here on gas-phase behavior of these radicals in FC plasma systems with precursor y/x ratios ≤ 4, including relative gas-phase concentrations and kinetics and subsequent contributions to Si wafer processing. Our imaging of radicals interacting with surfaces (IRIS) experiment reveals that the propensity for scatter of CF and CF_2 declines dramatically with decreases in precursor y/x ratio. Similarly, with decreasing y/x ratios, we observe increases in FC film surface energies, suggesting that avenues to tailor specific film properties are feasible. High-resolution x-ray photoelectron spectra and surface sum frequency vibrational spectra which corroborate the relationship between the choice of precursor and characteristics of deposited FC films will also be discussed. Ultimately, this work aims to establish a connection between species behavior near surfaces and resulting film properties during FC plasma processing.

3:00pm **PS+SS-ThA4 Polymer Surface Modification: Real-time In Situ Electron Spin Resonance Study for Plasma Processes**, ***K. Ishikawa***, *N. Sumi,* Nagoya University, Japan*, A. Kono, H. Horibe,* Kanazawa Institute of Technology, Japan*, K. Takeda, H. Kondo, M. Sekine, M. Hori*, Nagoya University, Japan

A comprehensive understanding of interaction between plasmas and soft-materials is essential for advanced plasma processing technology. Simultaneous measurements of the gas-phase ESR signals and the surface dangling bond signal [1,2], and kinetics analysis of radical formation were performed using *in situ* real-time electron spin resonance (ESR). Chemical reactions under plasma are very complicated, due to the simultaneous irradiation of electrons, ions, radicals, and photons. Therefore, the individual contributions of each of these reactive species in the plasma must be elucidated.

An ESR system was connected to a plasma discharge system (2.45 GHz, 50 W) using a quartz tube with an inner diameter of approximately 9 mm. Gas (H_2, O_2, etc.) was flowed into the quartz tube and the pressure was maintained at approximately 10 Pa in the down-flow region. ESR measurements were conducted using a standard X-band (9 GHz) spectrometer (Bruker Biospin, EMX plus) with a microwave resonator. The quartz tube and polymer (PTFE, PMMA, etc.) film sample were inserted inside the ESR cavity in the down-flow region, typically 20 cm from the plasma discharge.

Individual contributions from gaseous radicals and plasma emission light have been studied in a similar manner using pallets for plasma process evaluation (PAPE) [3].

For irradiation with both atomic H and VUV on the PTFE film, significant acceleration in the rate of C-DB formation was observed at the beginning of irradiation.

Moreover, the surface radicals produced immediately changed to peroxy-radicals when the treated PTFE films were exposed to air. This suggests high reactivity of C-DB with oxygen and the peroxy-radical species can contribute to enhancement of the surface biocompatibility.

In summary, during exposure of gaseous radicals on the polymer surface, the *in situ* real-time ESR technique was demonstrated as a new experimental approach to the microscopic understanding of chemical reactions on surfaces with gaseous radicals during plasma processes. We have successfully obtained information regarding the reaction mechanism with radicals generated by plasma induced surface interactions.

ACKNOWLEDGMENT

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REFERENCES

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[2] K. Ishikawa, *et al*., Appl. Phys. Lett. 81, 1773-1175 (2002).

[3] S. Uchida, *et al*., J. Appl. Phys. 103, 073303:1-5 (2008).

3:40pm **PS+SS-ThA6 Control of Hydrocarbon Surface Density during $H_2/D_2/Ar$ Low Temperature Plasma Interaction**, ***N. Fox-Lyon***, *G.S. Oehrlein,* University of Maryland, College Park*, N. Ning, D.B. Graves*, University of California, Berkeley

Control of surface properties of hydrocarbon materials during interaction with $H_2/D_2/Ar$ low temperature plasma has applications in diverse areas including: thin film synthesis, electronic device manufacturing, nuclear fusion reactor design, and plasma sterilization. Plasma processing/exposure of hydrocarbon materials can cause large changes to the surface chemistry and morphology due to interaction with ions, reactive neutrals, and UV/VUV photons. Hard hydrocarbon materials such as amorphous hydrocarbon (a-C:H) and diamond-like carbon (DLC), suffer a loss of density and a thick modified layer with reactive plasma etching through reactant saturation of the surface and an increase in density and formation of a thin modified layer by inert plasma etching through selective sputtering of H, whereas soft hydrocarbon materials (polymers, biomaterials) exposed to reactive and inert plasmas have been shown to increase in density and become chemically modified. In this work we have explored the plasma/surface interaction with hard/soft hydrocarbon films using different $H_2/D_2/Ar$ gas feedstock compositions along with different ion energy/fluence to the surface. The time dependent changes in optical properties and the etch yields were found using real time in-situ ellipsometry. Using multilayer films (e.g., soft a-C:H over hard a-C:H) we monitored dynamic changes in the penetration/modification depths for different plasma chemistries.

* 2009 Plasma Prize Winner

Shallow modifications by inert plasmas (such as Ar) are well understood. Ar plasma depletes H from the surface of a-C:H films through selective sputtering, scaling with ion energy. H_2 plasmas have been shown to cause deep hydrogenation of the surface not predicted with TRIM models. Mixing the processing gas (Ar/H_2) can be used to control the surface density from H depleted to H saturated. To better understand the roles of ion mass, etch rate and diffusion on the depth/degree of modification seen for H_2 plasmas, we performed comparable studies using D_2. We find that increasing the mass of the ions (by using H isotopes such as D) causes a large change in the etching and surface modification behavior. The etch rate of hard a-C:H in D_2 plasma is ~2 times the rate in H_2 plasma, and surfaces show a lower degree of modification (hydrogenation) than for H_2 plasma. In soft hydrocarbon materials exposed to D_2, H_2, and Ar plasmas (listed in order of modification, least to greatest), we find that the density increase is dependent on the ion chemistry, energy, penetration depth, and mass. The data will be compared with molecular dynamics simulation results.

4:00pm **PS+SS-ThA7 Atomic Force Microscopy Determination of the Elastic Modulus of Nanometer Thick, Ultra-Stiff Modified Layers after Plasma Etching of a Polymer Film**, ***T. Lin***, University of Maryland, College Park, *H.C. Kan,* National Chung Cheng University, Taiwan, Republic of China, *R.L. Bruce, G.S. Oehrlein, R.J. Phaneuf*, University of Maryland, College Park

We report on a determination of the elastic modulus for ultrathin (< 2nm) stiff damaged layers produced by argon plasma etching of the model photoresist polymer, polystyrene (PS). Measured force curves allow a direct determination of the effective modulus of the damaged layer plus polystyrene underlayer within a model which accounts for adhesive forces. The modulus of the modified layer is then extracted via comparison with numerical simulations for contact between a spherical AFM probe and a bilayer-structured film system in a Hertzian mechanics model. Our results show directly that an extremely stiff modified layer is formed, with the modulus increasing with Ar-ion energy during etching, in good quantitative agreement with estimations based upon measurement of the dominant corrugation wavelength and buckling theory.

4:20pm **PS+SS-ThA8 Polymer Hardening Technique for Enhancement in Etch Selectivity/Durability Using DC Superimposed Capacitively-Coupled Plasma**, ***S. Okamoto***, *A. Nakagawa, F. Inoue, H. Oka,* Tokyo Electron Miyagi Ltd., Japan, *H. Mochiki, K. Yatsuda*, Tokyo Electron Ltd., Japan

Higher aspect ratio of DRAM capacitor is required in order to maintain enough capacitance as the device structure is scaled down. The electrode of DRAM capacitor is generated in mold by metal CVD – typically TiN, and the mold is fabricated by RIE – typically dielectric. Thus, it is necessary to develop new techniques to fabricate higher aspect ratio dielectric mold for further DRAM scaling. RIE challenges for mold fabrication are high dielectric etch selectivity to mask, minimum bowing, and sustainment of enough bottom CD.

Generally speaking, mold etch process is optimized by accurate polymer control. However, conventional polymer control technique became marginal in highly scaled DRAM structure. Even slightly excessive polymer makes bottom CD smaller, and sometimes clogs the top portion of mold. On the other hand, slightly lacking polymer bridges neighboring molds at the top and/or sidewall portion due to lack of etch selectivity to mask and/or bowed etch profile.

In this paper, we suggest DC superimposed capacitively-coupled plasma (CCP) etch technique as a breakthrough of high aspect ratio dielectric etch. High energetic electrons emitted and accelerated by superimposed DC harden the polymer generated on mask and sidewall. This hardening technique works in two roles. The first role is etch selectivity enhancement of undesired etch material. Since polymer is maintained thin enough with good etch selectivity to mask, the top portion of mold is not clogged by polymer. The second role is etch durability enhancement of undesired etch portion. Normally, ultra high aspect ratio dielectric etch needs very high ion energy, which results in bowing etch profile due to incoming angular ions. But, superimposed DC hardens the sidewall polymer, and prevents etch profile from bowing. Bottom CD can be enlarged in the over etch step after etch front reaches etch stop layer. In general, bowing etch profile becomes significant during the over etch step. However, this effect can be avoided with stiff polymer enhanced by superimposed DC.

In conclusion, etch selectivity/durability of the undesired etch material/portion can be enhanced by superimposed DC as long as polymer is generated in the desired area by etch process optimization. Superimposed DC allows us to enhance etch selectivity/durability not with thickness of polymer but stiffness of polymer.

4:40pm **PS+SS-ThA9 H_2O Plasma Surface Modification of Track-Etched Polycarbonate Membranes Leading to Polar Surface Functionalization and Improved Wettability**, ***B.D. Tompkins***, *J.M. Dennison, E.R. Fisher*, Colorado State University

Plasma surface modifications have the ability to improve performance and realize new applications for polymer membranes in a variety of areas including: microfiltration, gas separation, and water treatment. Past studies in our labs have shown that although some polymer membranes can be successfully modified and are stable after treatment, many partially revert to their untreated state when aged. We are developing a technique that utilizes inductively coupled H_2O plasmas to implant polar functional groups onto the surface of track-etched polycarbonate membranes free of wetting agents. Water contact angle results on freshly treated and aged membrane samples show that the treated membranes have improved wettability compared to untreated samples and that the effects persist after treatment. Analysis of freshly treated samples using x-ray photoelectron spectroscopy (XPS) shows increases in oxygen incorporation, whereas high resolution XPS spectra of the C1s region shows that the fundamental polycarbonate structure is maintained near the surface. Treatment effectiveness under different plasma conditions, aqueous flux used to evaluate the performance of modified membranes, analysis of gas phase plasma species using optical emission spectroscopy (OES) to probe the processes that lead to surface modification, and a comparison with a similar plasma system using a mixture of O_2 and NH_3 as feedgasses will be discussed along with comparisons to other polymer membrane materials treated under similar conditions.

5:00pm **PS+SS-ThA10 Plasma Printing: A New Inline Technology for Polymers Surface Modification**, *E.A.D. Carbone, M.W.G.M. Verhoeven,* Eindhoven University of Technology, Netherlands, ***W.J.M. Brok***, *A. Stevens,* Innophysics B.V., Netherlands, *J.J.A.M. van der Mullen*, Eindhoven University of Technology, Netherlands

Fast and easy tunable patterning of surfaces has become of growing interest in the last couple of years in different fields like surface functionalization, thin film coatings and biomedical applications.

The concept of *Plasma Printing* combines the advantages given by the non-equilibrium character of pulsed corona discharges (tunability of surface chemistry), their creation and propagation along small volumes (local plasma treatment) and the mobility of the plasma source as a conventional printer (inline processing). This unique combination allows to treat (in real time) surfaces with arbitrary patterns design with limited restrictions unlike in the use of atmospheric pressure (dielectric barrier discharge) DBD for patterning of surface (also called DBD stamping).

InnoPhysics developed a proprietary Digital-on-Demand PlasmaPrint hardware solution that enables software patterned surface functionalization, etching and deposition of functional coatings on thin (plastic) substrates. A few kV sinusoidal pulse is applied on the electrode gap (pin to plate geometry configuration) in the 50-100 kHz range which generates a 1-10 µs pulsed plasma of about ~ 200 µm diameter in contact with the surface.

In order to assess the performances of the setup, a parametric study of polymers with respect to gas mixtures was performed to detect optimum of surface hydrophilization as well as selective chemistry groups grafting like OH, NH and CO.

PE, PET, FEP as well as PTFE (and PCTFE) were treated by nitrogen and different admixtures of gas/solution namely oxygen, ethanol, water and ammonia (NH_4OH solution). The surfaces were analyzed by water contact angle (WCA), X-ray photoelectron spectroscopy (XPS) and IR spectroscopy in attenuated total reflectance mode (FTIR ATR).

WCA was used to measure the surface energy of the surface and significant improvements of wetting properties were found for a few seconds of treatment time (i.e. $<30^o$ in the case of PET treated by N_2/NH_3). Grafting of N species up to a few percents was also found for various plasma compositions. The deconvolution of high resolution C1s, N1s and O1s spectra combined with the analysis of the IR spectra for the same conditions allowed eventually to get more insight in the chemical groups grafting at the surface following the plasma treatment.

5:20pm **PS+SS-ThA11 Design of a Plasma Cleaning Unit to Clean Backside Contamination on Substrates**, ***F.T. Molkenboer***, *N.B. Koster, A.J. De Jong, J.C.J. van der Donck, A.M.C.P. de Jong, O. Kievit*, TNO, Netherlands

In this presentation we will report our work on the design and experimental results of a plasma unit to clean the backside of substrates. Backside contamination of substrates can limit the quality of the front side process. Outgassing of backside contaminants can influence the front side process, or particles on the backside can influence the image quality in a wafer stepper. The complete backside cleaning unit uses three modules to remove both organic and an-organic particles as well as organic contamination

layers. This is all done in a high vacuum environment. To remove particles we will use a commercial available tacky roller. The second method to remove particles uses an UV lamp that will charge the particles on the substrate and a strong electric field to remove these charged particles from the substrate.

To remove organic contamination, for example resist residues after processing, we will use a RF plasma. The design of the RF plasma unit makes continuous cleaning over a large surface area possible. The gas in the plasma unit itself will have a pressure of 0.5 to 1 mbar. The vacuum chamber in which the complete backside cleaning unit is placed will have a pressure of around 10^{-3} mbar when the plasma unit is in use. This difference in pressure is achieved by placing the inlet of the gas in the RF plasma unit and making the outlet to the vacuum chamber very small. This design leads to a large expansion of the gas at the outlet of the RF plasma unit. The benefits of this design are that the pressure within the RF plasma unit is high enough for creating plasma and the pressure within the vacuum chamber is low enough to prevent that the whole vacuum chamber is filled with plasma.

This project focuses on backside cleaning of wafers within the "European Equipment & Materials Initiative for 450 mm" (EEMI450) under the ENIAC research program.

Within this European project, TNO is responsible for addressing contamination control issues. The concept of this backside cleaning unit can also be used to clean substrates used in roll to roll lines for solar cells or other processes that need continuous cleaning at high speed.

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