Plasma Science and Technology
Room: Hall D - Session PS-TuP

Plasma Science and Technology Poster Session

PS-TuP3 Optical Emission Spectroscopy of CH_3F/CO_2 Plasmas and Etching of SiN_x and p-Si, ***Qiaowei Lou***, *S. Kaler, D.J. Economou, V.M. Donnelly*, University of Houston

CH_3F plasmas are widely used in selective SiN_x etching over Si or SiO_2 with additives like O_2 or CO_2. In this work, inductively coupled CH_3F/CO_2 discharges were studied by optical emission spectroscopy (OES), with rare gas actinometry, as a function of feed gas composition and power (5–400 W), at a constant pressure of 10 mTorr. SiN_x(300 nm on Si) and Si (10 nm on Ge) etching was also studied in "plasma beams" created from both CH_3F/CO_2 and CH_3F/O_2 feed gases. Surfaces and film thicknesses were characterized *in situ* by vacuum-transfer XPS, and *ex situ* by spectroscopic ellipsometry. An abrupt transition in H, F, and O number densities was observed when the CO_2 feed gas was increased above 74-80 vol. %, similar to the enhancement in the number densities of these species above 48% O_2 in CH_3F/O_2 plasmas. These step changes were ascribed to the transition from polymer-covered to polymer-free reactor walls as increasing O_2 or CO_2 additions cause the film etching rate to exceed the deposition rate. Absolute H, F, and O number densities increased with power in CH_3F/CO_2 (20%/80%) plasmas, reaching 0.24, 0.81 and 1.92 $x10^{13}/cm^3$, respectively, at 300W. This gas composition results in polymer-free wall conditions. Compared with CH_3F/O_2 (50%/50%) plasmas, the F and H number densities were lower and the O number density was higher in CH_3F/CO_2 plasmas. A maximum SiN_x etching rate (no bias) of 75 Å/min was observed using a plasma beam effusing from a 50%/50% CH_3F/O_2 compact ICP. A lower maximum SiN_x etching rate of 34 Å/min was found for CH_3F/CO_2 at 25%/75% composition.

PS-TuP5 Simulation and Diagnostic Study on the Large Area Magnetized Inductively Coupled $Ar/O_2/CF_4$ Plasma, ***Ho-Jun Lee***, *E.-J. Son, Y.-G. Kim*, Pusan National University, Republic of Korea

Scaling up of inductively coupled plasma (ICP) and capacitively couple plasma (CCP) is important and urgent task for future 450 mm semiconductor wafer processing. A weakly magnetized inductively coupled plasma (MICP) have been introduced as an effort to improve efficiency, stability of low pressure operation and density uniformity of ICP. MICP is a source utilizing cavity mode of low frequency branch of right hand circularly polarized wave.(1) In the previous study, results on the simulation and optical multi-port diagnostics of Ar MICP have been presented.(2) In this study we present simulation and experimental results on the properties of ICP and MICP with Ar/CF_4, $Ar/O_2/CF_4$ chemistry. Flow field calculation of feed gas was included in the self-consistent plasma simulation. Electron density and energy was measured with tuned langmuir probes. Spatially resolved emission spectra were taken with a home-made, wafer type multi-channel optical emission measurement system. In 5 mtorr, Ar/CF_4(5~20%) discharge condition, electron density uniformity of MICP was improved about factor of two compared with that of ICP. Electron density of MICP in Ar/CF4 discharge was increased by 40 % due to improved power transfer efficient. However electron temperature became more non-uniform in MICP. Simulation results showed that density distribution of neutral species such as CF, CF_2, CF_3 were primarily affected by flow field. Highest density was observed on the top of electrode where the flow velocity was lowest.

PS-TuP6 Molecular Dynamics Simulation Study on Polymer Formation during Silicon Oxide (SiO_2) and Silicon Nitride (SiN) Etching by Fluoro/Hydrofluorocarbon Plasmas, ***Satoshi Hamaguchi***, *M. Isobe, K. Miyake, K. Karahashi*, Osaka University, Japan, *M. Fukasawa, K. Nagahata, T. Tatsumi*, Sony Corporation, Japan

For the past several years we have been working on molecular dynamics (MD) simulation on silicon dioxide (SiO_2) and silicon nitride (SiN) etching by fluorocarbon (FC) or hydrofluorocarbon (HFC) ion beams such as CF_x^+ or $CF_xH_y^+$ in order to understand surface reactions and mechanisms of selective etching processes of SiO_2 and SiN by FC/HFC plasmas [1]. In our study, the sputtering yields and surface chemical compositions after etching obtained from MD simulations are compared with those obtained from beam experiments. Recently we have improved the predictive capability of our simulation code and successfully obtained sputtering yields from MD simulation that are in reasonable agreement with those observed in the corresponding beam experiments. In this presentation, we shall discuss what aspects of MD simulation techniques need to be most carefully designed in order for the simulator to reproduce realistic beam-surface interactions.

Selective etching of SiN over SiO_2 or vice versa is widely used in the microelectronics industry. It has been known that, at relatively low incident energy, FC or HFC ions such as CF_x^+ or $CF_xH_y^+$ incident upon a SiO_2 or SiN surface from the plasma can etch the material surface while forming a thin polymer film on it. The thickness and chemical compositions of such a polymer film sensitively affect the etch rate (i.e., sputtering yield) of the material underneath. Therefore, for an MD simulation to represent beam-surface interactions with high accuracy, the simulation needs to correctly reproduce physical processes of polymer formation. It has been demonstrated that highly accurate carbon (C)-fluorine (F) interatomic potential models including electronegativity of F and an efficient thermostat algorithm to remove excess heat from incident ions are the key for better representation of ion-surface interactions by MD simulation.

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PS-TuP7 Development of a Compact Microwave Plasma Density Sensor for Processing Plasma Monitoring, ***JinSheng Chiou***, *W.C. Chen, C.H. Hsieh, K.C. Leou*, National Tsing Hua University, Taiwan, Republic of China

Plasma density is a key parameter that control the property of processing plasmas and hence the processing results. It is thus of great interest to develop a sensor not only for characterization of the plasmas but also for monitoring of the plasma based processes1. In this study, a compact microwave plasma density probe was developed and the effect of plasma sheath and pre-sheath was also investigated. The principle of the probe is based on the resonant absorption of microwave of a coaxial antenna immersed in the plasma. In this study, the probe has a outer diameter 0.9 mm, designed to minimize the perturbation to the plasma. It consists of a monopole antenna formed by a short section of the center conductor of a semi-rigid coaxial cable and a glass enclosure. Experimental measurements were carried out in an inductively coupled plasma and the results show that the resonance frequency increase linearly with the source rf power, as expected. The results are also consistent with that from measurements by a Langmuir probe. The compact probe was also investigated numerically by employing a full wave electromagnetic simulation using a finite element code (COMSOL). In the simulation analysis, a coaxial line was attached to the probe head and the "driven mode" was adopted, i.e., the wave was fed into the coaxial line and the absorption spectrum, reflection coefficient vs frequency, was then analyzed. The plasma surrounding the probe was characterized by the collisional electromagnetic plasma permittivity, determined by plasma density, wave frequency and momentum transfer collisional frequency. The simulation results show that the absorption spectrum exhibits a resonance, occurring between the plasma frequency and the surface plasma wave resonance frequency [1]. The effect of plasma sheath and presheath was also studied by the numerical simulation where the sheath (floating) was modeled by an air gap of thickness twice the Debye length while a linear plasma density distribution was assumed for the presheath region. The resonance frequency was also found to be dependent of the probe diameter and antenna length. These results are consistent with the results obtained by experimental measurements. This indicates that one can use the result from numerical simulation as a calibration for the plasma resonance probe measurement.

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PS-TuP8 Impact of Magnetic Neutral-Loop Discharge Plasma on Low-k Dielectrics, ***Weiyi Li***, *S-H. Kim, J. Blatz,* University of Wisconsin-Madison, *B.H. Moon, Y.M. Sung,* Kyungsung University (Korea), *S. Banna,* AMAT, *Y. Nishi,* Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

The magnetic neutral-loop discharge (NLD) plasma was proposed by Uchida in 1994. We developed an NLD plasma reactor using a stainless-steel chamber, instead of commonly used quartz chamber in previous work. In order to examine the usefulness of this NLD reactor, low-k dielectric films are exposed to the NLD plasma under various conditions.

The structure of the NLD plasma reactor is described as follows. A cylindrical chamber lies in the middle of three sets of magnetic coils. With DC currents flowing in opposite direction in the middle set against side sets of coils, a circle on which magnetic field is zero, *i.e.* neutral loop(NL), can be produced in the middle of the chamber. In order to generate plasma, 13.56 MHz RF is inductively coupled into the chamber with a spiral antenna, through a quartz window on one end of the chamber. The reactor can be operated at two modes, NLD mode when there are opposite direction DC currents in the magnetic coils, or ICP mode when there are no DC

currents or same direction DC currents in the magnetic coils. In NLD mode, the plasma was observed to be brighter near the NL than in the center. This difference was further confirmed with a measurement of optical spectrum using an OceanOptics spectrometer, which shows the relative plasma glow brightness at the NL is as twice high as near the center of the chamber, and about 10% higher than a non-NLD ICP plasma.

By adjusting the ratio of the DC currents running in the magnetic coils, the position of the NL can be changed. Both experiment and simulation show that the glow follows the change of NL, especially at low pressure (<1 mTorr), due to much less collision.

Low-k dielectrics are widely used in modern back-end processing, in order to reduce the R-C delay in interconnection. During processing, low-k dielectrics are often subjected to plasma exposure. The consequent damage to low-k dielectric films is presented and compared with other types of plasma reactors.

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PS-TuP9 Characterization and Simulation of a VHF Remote Plasma Source, ***Scott Polak***, *D. Carter*, Advanced Energy Industries, *A. Bhoj*, *A. Roy*, ESI US R&D Inc.

This paper describes a novel, remote source technology using capacitively coupled, VHF energy to produce a flexible and unique plasma generator. The electrode design and internal construction are compatible with most processing chemistries, allowing generation of very low to very high plasma densities across extensive flow and pressure regimes. Furthermore, Langmuir and IEDF probe measurements have illustrated a competency of the remote source to deliver plasma well beyond the output of the apparatus, into large downstream chambers. This ability makes both neutral-radical and downstream ion enhanced processing possible. Due to the enhanced efficacy of this remote plasma source, optimization and characterization across the wide operating range becomes challenging. To facilitate characterization of the remote source and to augment empirical testing, plasma simulation techniques are employed. Commercially available, multi-physics code, CFD-ACE+, is used to simultaneously solve for the electromagnetics, fluid flow, heat transfer, species chemistry and transport equations for non-equilibrium discharges. A summary of the important remote source design elements will be reviewed along with a comparison of actual and simulated results, illustrating details of the plasma generation and distribution from this new technology.

PS-TuP10 Temporally and Spatially Resolved Optical Emission Spectroscopy of Capacitively Coupled Pulsed Plasmas, ***John Poulose***, *L.J. Overzet*, *M.J. Goeckner*, University of Texas at Dallas

Pulsed plasma provides a method to 'independently' control ion and neutral fluxes. Temporal and spatial evolutions of the pulsed plasmas have been studied to provide a better understanding of transitory behavior in such systems. The optical emission intensities (OEIs) of various lines (atomic and molecular) from pulsed plasmas through Ar, O2, and N2 gases have been collected. The RF power was turned on and off at frequencies of 1, 10 and 100 kHz with a 50% duty cycle. The OEIs measured from argon plasma have shown a longer turn on/off time than those measured from O2 or N2 pulsed plasmas. Specifically, the OEIs measured from pulsed argon plasmas are still rising at the end of the on-time and do not completely extinguish at the end of the off-time at 100 kHz. This is in comparison to pulsed plasmas through both O2 and N2 in which the OEIs completely extinguish during the off-time and reach an apparent steady state level during the on-time. Additionally, the OEIs contract radially just after the start of the on-time for pulsed plasmas through argon, but a similar radial contraction phase is not found in the other gases. The radial extent of the OEIs in O2 and N2 remains essentially constant. We will present these results and the effects of other parameter and gases on the transitory behavior of pulsed discharges.

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PS-TuP11 Laser-induced Incandescence Diagnostic for *In Situ* Monitoring of Synhtesis of Nanoparticles in Plasma, ***James Mitrani***, *B. Stratton*, *Y. Raitses*, Princeton Plasma Physics Laboratory

A DC arc discharge with a consumed graphite, anode electrode is commonly used for synthesis of carbon nanoparticles, including buckyballs, nanofibers, and nanotubes [1-3]. The graphite electrode is vaporized, leading to nanoparticle synthesis in a low temperature (0.1 – 1 eV), atmospheric pressure plasma. The formation of nanoparticles in this plasma is poorly understood. For example, it is not clear where nanoparticles nucleate and grow in the arc discharge. To tackle this problem, a laser-induced incandescence (LII) diagnostic for in situ monitoring of the nanoparticles' spatial distribution in the plasma is currently being constructed. The LII diagnostic involves heating the particles with a short-pulsed laser, and measuring the resulting spatial and temporal incandescence profiles on longer timescales [4]. By appropriately modeling the spatiotemporal incandescence profiles, one can measure the particle diameters and volume fraction. LII diagnostics have been extensively used to study soot particles in various backgrounds, including laboratory flames, smokestacks, and engines. However, LII has only recently been applied to study engineered nanoparticles, and has never been applied in a strongly coupled plasma background, such as a carbon arc discharge. Even though the spatial scale-lengths for soot and nanoparticles are similar (10-100 nm), great care is needed in developing an LII diagnostic for monitoring nanoparticles in an atmospheric pressure plasma. Therefore, we will initially calibrate our LII diagnostic by measuring spatiotemporal incandescence profiles of known, research grade carbon particles, including soot and nanoparticles. Preliminary results of this study will be discussed.
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PS-TuP12 Influence of Porosity on Electrical Properties of Low-k Dielectrics Irradiated with Vacuum Ultraviolet Radiation, *F.A. Choudhury*, University of Wisconsin-Madison, *J.-F. de Marneffe*, *M. Baklanov*, IMEC, KU Leuven Belgium, *Y. Nishi*, Stanford University, ***Leon Shohet***, University of Wisconsin-Madison

During plasma processing, low-k dielectric films are exposed to high levels of vacuum ultraviolet (VUV) radiation emitted from the plasma. To reduce the dielectric constant of organosilicate (OSG) low-k materials, porosities (up to 50%) are introduced in the dielectric layer. The porous structure of these materials makes them even more sensitive to VUV modification due to their low density and deep penetration of photons into the film[1]. The effects of VUV photons on the chemical modification of OSG low-k materials as a function of porosity has been reported recently[1] and showed that OSG films having high porosities undergo higher Si-CH_3 depletion and severe chemical degradation. In this work, we investigate the changes to the electrical properties of porous low-k dielectrics as a function of porosity after VUV irradiation. VUV irradiation introduces defect states and generates trapped charges within the dielectric that can degrade the electrical properties of the film[2]. In order to investigate the influence of the porosity on the electrical properties after VUV exposure, organic low-k films of porosities between 15 and 50% were exposed to synchrotron VUV radiation of energies ranging from 6 to 15 eV and fluences up to 5 x 10^{14} photons/cm^2 to find the most damaging photon energies. CV measurements showed an increase in the dielectric constant along with a flat-band voltage shift and the presence of hysteresis after VUV irradiation. Initial IV and TDDB measurements indicate an increase in leakage currents along with lower breakdown fields after VUV irradiation. It is likely that these effects will be a function of VUV photon energy.[3]

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References:

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PS-TuP13 Ink Cap to Preserve Nanostructure during Sample Preparation for Electron Microscopy, ***Brian Krist***, *J.S. Chawla*, *M. Chandhok*, *S.R. Cook*, *H.J. Yoo*, Intel Corporation

Transmission electron microscopy (TEM) imaging of narrow critical dimension (CD) features patterned in low-k materials is critical for functional validation of the patterning process steps. For interconnect applications in particular, low-k porous dielectrics can be mechanically weak and suffer structural damage from plasma processing due to higher carbon content.

Cross-section TEM sample lamellae prepared by focused ion beam (FIB) milling using conventional in-situ protective cap materials like insulator deposition (IDep, eg. TEOS), Pt, and W alter the low-k material line width, edge/surface roughness, and profile due to stress and high energy secondary electron interaction during localized capping. In addition, the conventional cap materials cannot gap fill features trenches that are less than 20 nm wide. Gapfill defects can cause poor mechanical stability during TEM sample

preparation and imaging. These defects can also lead to ion beam damage during TEM sample preparation.

In this paper, we investigate the ability of the ex-situ liquid inks as cap material for TEM cross-section sample lamellae to replace conventional in-situ cap materials. The use of ink fill protects the surface from the secondary electron beam damage that occurs using conventional in-situ FIB dual beam capping methods. Ink fill capped samples have undistorted ILD patterns that hold to zone axis. The ink to Pt FIB mill is matched unlike high dense high stress IDep so both sample thickness and stress are more consistent. Several inks where reviewed and down selected for lack of high aspect ratio fill, or inability to cure out solvents in ink. Cross-section images in this work use either hand dispensed *BIC Mark it,* or automate dispensed using *GenesisEcono-Jet* printer 3440BK INK.

We also demonstrate how ink fill capping enables imaging of the smallest features in interconnect process technology having low-k ILD.

PS-TuP15 Surface Modification to Improve Chemical Resistance of Coatings, ***Gregory Peterson***, *W.O. Gordon,* Edgewood Chemical Biological Center*, E.M. Durke*, Excet, Inc.

Coatings are required to demonstrate chemical resistance in order to protect material, vehicles, and personnel. In addition, numerous other requirements for the development of new coatings often involve substantial reformulation efforts in order to adapt to changing conditions and applications. One method to improve chemical resistance of coatings is to modify the surface of the paint to reduce surface energy without changing the bulk; ensuring any bulk properties remain unaltered. Plasma-based chemical vapor deposition (PCVD) of perfluorinated compounds has been used for years to improve resistance of fabrics and materials to water and other chemicals. For example, there are several reports in the literature of superhydrophobic fabrics developed using PCVD. Here we report the application of a PCVD method that not only induces superhydrophobicity to a real world coating, but dramatically improves the resistance of the coating to the spreading and absorption of the chemical warfare agents, HD and VX. Over the 30 min age time, droplets remained pinned and are therefore more easily decontaminated or removed physically. Surface analysis confirms modification of the surface with fluorinated species and also shows etching of the organic components of the paint. This treatment suggests that surface modification strategies may be effective in improving chemical resistivity, without changing the bulk properties, or requiring a significant reformulation effort.

PS-TuP16 The Effect of Electron-Molecule Collision Cross Sections on Plasma Models, ***Sebastian Mohr***, Quantemol Ltd, UK*, J.R. Hamilton, A. Asokan, J.C. Tennyson*, University College London, UK

Discharges in reactive gases such as SF6 and C4F8 are commonly used for industrial etching and deposition processes. The necessary surface reactions are induced by the free radicals in these discharges which are created by electron impact and heavy particle collisions. The process speed is thus usually determined by the densities of the free radicals, a prior knowledge of these densities and their dependence on parameters such as the pressure, input power or the gas composition is desired.

Numerical simulations of reactive gas discharges are employed to systematically study the chemical reaction rates and particle densities as functions of the aforementioned parameters. Furthermore, a reliable set of rate coefficients or cross sections for the included reactions are needed.

Quantemol-N, which provides full accessibility to the well-known UK molecular R-matrix codes [1], is used to model electron polyatomic molecule interactions including those with radicals. A wide range of cross-sections, otherwise not available experimentally are calculated for the required plasma chemistries. An expert system, Quantemol-VT, based on the Hybrid Plasma Equipment Model (HPEM) [2] is then used to model plasma tool on a reactor scale.

We provide results of a systematic study of an C4F8 discharge which is commonly used for deposition during the Bosch process. This study further compares the effect of including cross sections calculated with Quantemol-N against use of datasets comprising only known and commonly used cross sections taken from experimental studies. A plasma model of the discharge in a GEC cell is provided for a plasma chemistry containing CxFy radical reactions (calculated with Q-N) and without. The two models are compared and the role of CxF y radicals in plasma processing is highlighted.

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PS-TuP17 Development of Microwave-driven 1- and 2-Dimensional Microplasma Arrays and Tests of Atmospheric-Pressure Film Deposition, ***Alan Hoskinson***, *H.C. Thejaswini, J. Hopwood*, Tufts University

Microwave-driven microplasmas allow for the generation of cold atmospheric-pressure plasmas at higher time-averaged electron densities ($\sim 10^{14}$ cm^{-3}) than most other techniques. These high densities may open unique regimes for high-pressure materials processing. The low ion energies (due to the short mean free paths at atmospheric pressure) may be partially compensated for by extremely large fluxes of ions and energetic metastable species while maintaining low gas temperatures. We present data from exploratory experiments showing rapid deposition of diamond-like carbon films at atmospheric pressure using a single microplasma. The development of one- and two-dimensional arrays of such microplasmas demonstrates a path towards film deposition on moderate-area substrates.

This work was partially supported by the DARPA Microscale Plasma Devices program (Dr. Dan Purdy, Program Manager) under awards FA9550-12-1-0006, managed by Dr. John Luginsland through AFOSR, and N00014-13-1-0619 managed by Stephen Pappert through ONR.

PS-TuP18 Mechanical Property of Polyurethane Nanocomposite Film with Carbon Nanotubes Functionalized by Atmospheric Dielectric Barrier Discharge, *D. Ogawa,* ***Keiji Nakamura***, Chubu University, Japan

Polymers composited with carbonanotubes (CNTs) have been researched for many years to modify their material properties. This is because a polymer is mechanically soft and electrically insulated. The mix of CNTs is a good idea because CNTs can compensate the weakness of the polymer by making composites.

The functionalization of CNTs is a common technique for their applications due to chemical inertness of CNTs. This is why CNTs are generally difficult to disperse well in a liquid, while CNTs can disperse well after a functionalization. Nitric acid (HNO3) is commonly used to functionalize carboxyl group on CNTs. The functional group is modified to the functional group to fit one's application. It is reported that plasma can also functionalize CNTs without using the acid by making reactive species generated in plasma.[1]

We want to enhance the mechanical property of polyurethane (PU) film (approximately 100um thickness) through functionalized multi-wall CNTs (MWCNTs). In order to achieve our goal, we created a dielectric barrier discharge (DBD) above the CNTs that is located at the bottom of a quartz test tube. The discharge was created with the peak-to-peak voltage at 9 kV, the frequency at 10 kHz, and the discharge pressure at atmospheric pressure. Our process gas was made with a certain combination among argon, nitrogen, hydrogen, and oxygen gas depending on the functionalized group we want to attach on the CNTs. Here, Fourier transform infrared (FTIR) spectrometer was used to identify the functional groups attached by plasma discharge. After the plasma treatment, the CNTs were dispersed into a tetrahydrofuran (THF) solvent. The solvent is so versatile because the solvent is miscible to water and dissolvable even to non-polar solution. Some parts of the CNTs were dispersed in a THF solvent so that the concentration of the CNTs in the solvent was found from the transmission of the light at 600 nm. The PU film formed after drying out the mixture of the solvent and the PU solution over night.

In order to evaluate the strength of the PU film, the PU film was rubbed with a sand paper for hours. Here, we compared the wearing rate of the PU film that is defined by dividing the film thickness over the time when the PU film was completely rubbed out. The mechanically stronger the PU polymer is, the more wearing rate was observed.

In the presentation, we will show our recent progresses of the PU film that contains the CNTs functionalized with atmospheric DBD plasma .

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PS-TuP20 Development of a Low Cost and Portable Needle Type DBD Jet Operated under Atmospheric Pressure, ***Chieh-Wen Chen***, *Y.J. Yang, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

A low cost and portable needle-type DBD jet operated under atmospheric pressure is developed. The plasma jet is comprised of an inner grounding electrode made of stainless steel rod, a quartz tube serving as the dielectric layer, and an outer powered ring electrode that is attached to the outer surface of the quartz tube. The quartz tube is 6-cm long with inner and outer diameters of 6 and 8 mm, respectively. A needle (25G) is attached to one side of the quartz tube that serves as the exit nozzle. This jet is powered by a low cost portable power that is commercially available (PVM 12, Information Unlimited, USA). Helium with a flow rate below 2 slm is used as the plasma gas. With this arrangement, a jet approximately 2 mm long can be extended out of the needle tip. The key features of this jet are (i) low

cost: less than USD$100 per system, (ii) portable, and (iii) equipped with a robust needle. Diagnostic studies of this plasma jet and using it for materials processing with a spatial resolution down to 1 mm will be presented.

PS-TuP21 Development of Low Cost and Flexible Microplasma Generation Devices Operated under Atmospheric Pressure, ***Chih-Ming Wang***, *T.H. Lin, Y.J. Yang, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

Microplasmas are plasmas with geometric dimension less than 1 mm. Due to its miniature size, fabrication of microplasma generation devices frequently involves high cost materials and/or processes, such semi-conductor manufacturing processes. In this work, we present the development of two types of low-cost flexible microplasma generation devices: devices made on paper substrates and on flexible printed circuit board (PCB). The former is made of paper, conductive carbon paste, and tape, while the latter is fabricated using commercially available process that makes printed circuit board. We exam the stability of the discharge and the lifetime of the devices. When the paper-based device is assembled as a dielectric barrier discharge (DBD)-type device, stable array of discharges can be sustained for tens of minutes. When it is assembled as a micro-hollow cathode discharge (MHCD)-type system, no array of discharge can be obtained and the device lifetime is no longer than 3 min. For the PCB-based device, stable array of discharges can be sustained for longer than one hour. The use of the PCB-based device to perform gas conversion is also demonstrated. CO_2 decomposition forming CO and O_2 is chosen as the system to test. It is shown that the power efficiency above 7% can be obtained under selected conditions.

PS-TuP22 A Low Cost and Flexible Microplasma Generation Device to Create Hydrophobic/Hydrophilic Contrast on Nonflat Surfaces, ***Yao-Jhen Yang***, *C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

This work presents a cost-effective (less than a quarter per device) and easy-to-fabricate dielectric-barrier-discharge-type (DBD-type) microplasma generation device for maskless surface patterning. This device was made of double-side copper laminate. A process to define circuit patterns on printed circuit board was utilized to define the electrodes required for the microplasma generation device. This device was then utilized for maskless surface patterning, either creating hydrophobic patterns on hydrophilic surfaces or hydrophilic patterns on hydrophobic surfaces. The former patterns were obtained by plasma polymerization of c-C_4F_8 precursor under He atmosphere to form fluorocarbon on designated regions on glass surfaces. The optical emission spectrum shows the CF_2 emission (250 nm-380 nm), suggesting the dissociation of precursor molecules. The FTIR spectrum of the deposited film shows strong CF_2 absorption peak at 1250 cm^{-1}. The contact angle of the film ranges from 102 to 105 degree. The hydrophilic patterns on hydrophobic surfaces were obtained by treating a fluorocarbon-coated surface using this plasma-generation device under ambient air. Non-flat surface patterning using this device will be demonstrated. (This work was supported by National Science Council of Taiwan, the Republic of China 101-2221-E-002-163-MY2)

PS-TuP23 Control of Plasma in Solution Using Bipolar Pulsed Voltage, ***Fei-Hung Huang***, *C.Y. Chou, H.W. Chang, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

This work presents control of plasmas in saline solution using bipolar pulsed DC power. It is known that plasma of such a type generates inside the gas-phase that composes of water vapor, oxygen, and hydrogen through joule heating and/or electrolysis. We use a 1-ms-wide positive pulse of 550 V to ignite the plasma. Prior to this positive pulse, a 10-ms-wide pre-pulse is applied to generate electrolytic gas. By changing polarity the pre-pulse, namely positive pre-pulse (mode++), negative pre-pulse (mode-+), or without the pre-pulse (mode0+), the gas composition can be tailored. Optical emission spectroscopy shows OH, H, and O emissions, which implies that the plasma generates hydroxyl, H, and O radicals. We used a chemical probe, disodium salt of terephthalic acid, to quantify the formation rate of OH radicals using photoluminescence spectroscopy. To assess how the power type influences the efficiency in organic degradation, acid orange 7 (AO7) was chosen as the model organic materials. AO7 decolorization was quantified using ultraviolet-visible adsorption spectroscopy. AO7 degradation kinetics was fitted using 1st order kinetics. It is shown that mode-+ has a higher AO7 degradation rate constant as well as higher OH radical formation rate.

PS-TuP24 The Effect of the Electrode Diameter on the Behavior of Plasmas in Saline Solution, ***Shen-Chieh Lin***, *C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

In this presentation, the effects of the electrode diameter on the discharge behavior of plasmas in saline solution are studied. The plasma is driven by a bi-polar DC pulse power source with an applied voltage up to 700V and a pulse width above 0.05 ms. The driving electrode is a platinum wire covered by a glass tube to precisely define the area exposed to the solution. Platinum wires of four different diameters, namely 0.1 mm, 0.3 mm, 0.5 mm, and 1 mm, were used. The grounding electrode is a bare platinum wire 0.5 mm in diameter and it is immersed in 0.1 M NaCl solution. Current and voltage probes are used to monitor the current and voltage waveforms across the electrode surface. A high speed camera is used to capture the bubble behavior and plasma appearance. An optical emission spectrometer is used to analyze plasma emission light. It is found that the breakdown voltage decreases with the electrode diameter. At a given applied voltage, the current peak value and the emission time delay upon the onset of the voltage pulse both increase with the electrode diameter, while the power density increases with the decrease in the electrode diameter.

PS-TuP25 Surface Treatment Using Portable Dielectric Barrier Discharge Device, ***Yao-Yi Kuo***, *W.S. Zseng, C.M. Wang, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

A portable dielectric barrier discharge device operated under one atmosphere is developed and the use of this device for surface treatment is performed. This device consists of a powered electrode made of a copper plate, a ground electrode made of stainless steel woven wire mesh, and a quartz plate 1 mm in thickness that serves as dielectric barrier between powered and ground electrode. This device is driven by a portable power source that is commercially available. This power source supplies voltages up to 20 kV with a frequency of 20-50 kHz. This plasma system is compact and low cost. Surface treatment under air, argon, and nitrogen atmosphere on PET, glass, and PTFE substrates to enhance hydrophilicity is performed. It is found that the water contact angle of the glass surface decreases from 40° to below 10° after treated using this device for 5 min operated in air and argon. For PET surface treatment under argon atmosphere, the contact angle decreases from 70° to 20° after 5 min of treatment. Due to its low cost and compact size, this portable DBD device shows great potential in various applications where portable devices are desired.

PS-TuP27 ***RF Pulsing Technology on Commercial CCP(Capacitively Coupled Plasma) Dielectric Etcher and ICP(Inductively Coupled Plasma) Conductor Etcher.***, ***Taeho Shin***, SEMES, Republic of Korea

RF pulsing technology in dry etcher had been developed about 20 years ago. But recently as the device node falls below 20nm (pitch size) many etch problems such as profile distortion, poor uniformity control, etc. become critical issue to be cleared. Many commercial dry etchers are currently introducing various pulsing technologies on their process chamber to overcome those process issues. They have claimed many process merits with RF pulsing. However one of the main problems in RF pulsing in mass production fabs lies in slower etch rate and unstable plasma. We also have developed RF pulsing technology on our CCP type dielectric etcher and ICP type conductor etcher. We have tested and optimized many different RF configurations such as RF frequencies pulsing, DC(Direct Current) pulsing and secondary electrode pulsing. One of tested configurations, we have found that secondary electrode DC pulsing with 3 different RF frequencies biased wafer electrode showing higher etch rate with improved mask selectivity as well as controlled bottom CD(critical dimension). Those results might be due to the fact that higher density plasma with higher ion energy is generated by enhanced electron energy distribution function(EEDF) and narrowed high energy ion density with DC pulsing.

PS-TuP28 Plasma Damage Characterization in Backbone Carbon Organosilicate Glass Low-k Films - with Backbone Chains (-Si-R-R-Si-) and (-Si-R-Si-), ***Haseeb Kazi***, *R. James, S. Gaddam, J.A. Kelber*, University of North Texas

X-ray photoelectron spectroscopy (XPS) and FTIR data indicate that organosilicate glass (OSG) films with backbone carbon (-Si-$(CH_2)_x$-Si-) exhibit significantly enhanced resistance to carbon loss upon exposure to O_2 plasma, atomic oxygen ($O(^3P)$) and vacuum ultraviolet photons (VUV+O_2) at 10^{-4} Torr O_2 compared to films with terminal methyl groups (Si-CH_3). Two different low-k films with backbone structures (-Si-$(CH_2)_2$-Si-) and (-Si-CH_2-Si-) were investigated separately. Films incorporating backbone ethyl groups (-Si-$(CH_2)_2$-Si-) were deposited from 1,2 bis (triethoxysilyl) ethane (BTESE) precursor by ebeam or plasma cross-linking with achievable dielectric constant (k) ~3.00. XPS spectra for PECVD and ebeam cross-linked films are similar. The effects of ($O(^3P)$) on ebeam cross-linked film indicates negligible carbon loss or Si oxidation, combined with C-O bond formation, under conditions where OSG films with terminal methyl groups exhibit > 80% carbon loss within the surface region of the film. C-O bond formation is never observed for terminal CH_3 groups. Further, backbone carbon (-Si-$(CH_2)_2$-Si-) films exposed to VUV+O_2 exhibit self-limiting, minimal net carbon loss and formation of C-O bonds within the surface region. In separate experiments, low-k films with methylene bridging unit (-Si-CH_2-Si-) were investigated which contains a

mixture of (-Si-CH_2-Si-) and (-Si-CH_3) bonding environments in the final deposited film (k=2.55). Data indicate these backbone carbon (-Si-CH_2-Si-) films when exposed to O_2 plasma exhibit higher carbon removal rate for terminal groups (-Si-CH_3) whereas carbon in the linking chain (-Si-CH_2-Si-) undergo relatively slower removal rate, with Si-O, C-O bond formation. This indicates that O_2 plasma-induced Si-C bond rupture still occurs in the linking unit, but with a low probability of simultaneous rupture of both Si-C bonds required for abstraction of an in-line methylene bridging group. The data thus demonstrate that OSG films containing backbone carbon groups exhibit greatly reduced rates of carbon loss in the presence of O_2 plasma, atomic O or VUV+O_2 compared to films with terminal carbon groups due to fundamentally different patterns of Si-C bond scission. The results reported here demonstrate the potential for OSG films with backbone carbon to resist O_2 plasma damage.

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PS-TuP29 A Continuous Plasma-Liquid Interface formed by a Laminar Flow Liquid Water Jet and Atmospheric-pressure Microplasma, ***BrittanyPaige Bishop***, *S. Ghosh, I. Morrison, D. Scherson, R. Akolkar, R.M. Sankaran*, Case Western Reserve University

Reactions at the interface of a plasma and a liquid surface have recently become important for applications in wastewater treatment, materials synthesis, and therapy. These experiments are typically carried out between an atmospheric-pressure plasma jet and a static liquid surface (i.e. liquid bath or film). Here, we present a continuous plasma-liquid interface formed by an atmospheric-pressure microplasma and an open air, laminar flow liquid water jet.

A vertically falling water jet is formed in open air by pumping liquid water through a microcapillary. The stability of the water jet is explained by the Plateau-Rayleigh instability. At low flow rates, surface tension leads to the breakup of the jet into droplets. At high flow rates, the jet becomes turbulent and again breaks up. The water jet is found to be highly stable at intermediate flow rates where the water jet is laminar, with a relatively constant diameter of 500 μm over lengths of more than 30 mm. This allows the microplasma to be stably formed at the surface of the water jet and current to flow across the plasma-liquid interface to a counter electrode. The system is characterized with the microplasma operating by current-voltage measurements. We find that the overall resistance is strongly influenced by the inter-electrode distance and the ion concentration in solution, suggesting that solution conductivity dominates the electrical conductivity of our system. This is explained by a simple model based on a geometrical approximation for the water jet which shows that the resistance of the water jet is large because of the confined volume.

We have applied this newly developed system to the synthesis of metal nanoparticles. Aqueous solutions of silver nitrate are formed as a liquid water jet and pumped through the plasma-liquid interface. A distinct color change is observed as the silver nitrate is reduced by the microplasma to silver nanoparticles. The solutions are characterized by ultraviolet-visible (UV-vis) absorbance spectroscopy and transmission electron microscopy (TEM) which confirm crystalline, nanometer-sized silver particles. We find that the particle production rate depends on the plasma current and the liquid water jet flow rate, the latter of which is consistent with a space time approximation for the reactor.

PS-TuP30 Anomalous Electron Cross-Field Transport in a Low Pressure Magnetized Plasma For Material Processing Applications, ***Yevgeny Raitses***, Princeton Plasma Physics Laboratory

The application of the magnetic field in a low pressure plasma can cause a spatial separation of cold and hot electron groups. This so-called magnetic filter effect is used for many plasma applications, including ion and neutral beam sources, plasma processing of semiconductors and nanomaterials, and plasma thrusters. In spite of successful practical applications, the magnetic filter effect is not well understood. In this work, we explore this effect by characterizing the electron and ion energy distribution functions in a plasma column with crossed electric and magnetic fields. Experimental results revealed a strong dependence of spatial variations of the plasma properties across the magnetic field on the gas pressure. In particular, the results showed the existence of the gas pressure threshold below which the increase of the magnetic field leads to a more uniform profile of the electron temperature. This surprising result is due to anomalously high electron cross-field transport that causes mixing of hot and cold electrons. For xenon and argon gases, this threshold is ~ 1 motrr. At higher gas pressures, a stronger separation of cold and hot electrons, which is favorable for the above applications, was observed.

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