Plasma Science and Technology
Room 311 - Session PS2-TuA

Plasma Diagnostics I

Moderator: T. Tatsumi, Association of Super-Advanced Electronics Technologies (ASET)

2:00pm **PS2-TuA1 Effect of Xenon Dilution on Fluorocarbon Plasma Chemistry and Electron Distribution Function**, ***H. Sugai***, *T. Ishijima, M. Ikeda,* Nagoya University, Japan

Two types of unmagnetized high-density fluorocarbon plasmas, ICP (inductively coupled plasma, 13.56 MHz) and SWP (surface wave plasma, 2.45 GHz), are produced and compared in an identical vessel under the same gas conditions (10 % C@sub 4@F@sub 8@ + 90 % Ar, total pressure 20 mTorr). The ion and radical compositions are measured by a quadrupole mass spectrometer. The measurements at the same electron density of 2.5 x 10@super 11@ cm@super -3@ reveal that the ICP is more strongly dissociated than the SWP, with the smaller ratio of CF@sub x@ radical density to F radical density. Such different plasma chemistry between the two plasmas is attributed to the difference in the electron distribution functions (EDFs) observed in the experiment. Namely, the ICP has the EDF close to Maxwellian with higher electron temperature while the SWP has a bi-Maxwellian type of EDF composed of a cold electron group (lower temperature T@sub ec@) and a hot electron group (higher temperature T@sub eh@). The bi-Maxwellian EDF might be formed by stochastic heating at the plasma resonance layer in the SWP. Furthermore, replacement of the argon buffer gas with xenon gives rise to dramatic changes in plasma properties as follows. First, the xenon dilution makes it possible to obtain the same electron density by a factor of five less discharge power. Second, the radical density ratio of CF@sub x@ to F is increased by an order of magnitude in the Xe dilution, compared with the Ar dilution. Thirdly, the EDF measurement showed the value of T@sub ec@ lower by a factor of 2/3 in case of the Xe dilution. Finally, a global model of particle balance based on the measured EDFs supports these observations.

2:20pm **PS2-TuA2 Comprehensive Measurements of Neutral and Ion Number Densities, Neutral Temperature, and EEDF in a CF@sub 4@ ICP**, ***H. Singh***, *J.W. Coburn, D.B. Graves,* University of California at Berkeley

We present comprehensive measurements of the neutral number densities, ion number densities, neutral temperature, and the electron energy distribution function in a CF4 inductively coupled plasma at pressures between 1 and 30 mTorr, and deposited powers between 150 and 550 W. High degrees of dissociation are observed at the lower pressures. We believe this is a result of the large electron temperature (5-9 eV) at the lower pressures. The measurements of all the dominant radical and stable neutral species using appearance potential mass spectrometry allows the estimation of the neutral temperature at the neutral sampling aperture. The neutral temperature is also estimated from the change in the number density of a trace amount of argon added to CF4 when the plasma is turned on. Neutral temperatures up to 925 K are measured at the sampling aperture. The increase in neutral temperature with power at a constant pressure results in a decrease in the total neutral number density at a constant pressure. The electron temperature is sensitive to the neutral number density, especially at low densities. This leads to a significant increase in the electron temperature with power, resulting in the higher degrees of dissociation observed at low pressures. The number densities of radicals and their corresponding ions are generally strongly correlated in the plasma. We show evidence for a large surface loss coefficients for C and CF radicals.

2:40pm **PS2-TuA3 Planar Laser-Induced Fluorescence Investigation of Fluorocarbon Plasmas**, ***K.L. Steffens***, *M.A. Sobolewski,* National Institute of Standards and Technology **INVITED**

Fluorocarbon plasmas are extensively used in the semiconductor industry for etching and chamber-cleaning applications. The etching process involves a competition between substrate removal and deposition of a fluorocarbon polymer layer on the wafer surface. The CF@sub 2@ radical is thought to be a major participant in the formation of this polymer layer either directly or by forming gas phase precursors which deposit to form the layer. Thus, measurements of the CF@sub 2@ radical are crucial to the understanding of etching chemistries. In this work, the planar laser-induced fluorescence (PLIF) technique was used to measure two-dimensional images of CF@sub 2@ density in CF@sub 4@ and C@sub 2@F@sub 6@ plasmas in the capacitively-coupled Gaseous Electronics Conference rf Reference Cell. Measurements were made at 200 mTorr with power deposited in the plasma ranging from 30 to 150 W, both without a substrate and with a Si wafer present, in pure fluorocarbon and in oxygen/fluorocarbon mixtures. In addition to the PLIF images, we obtained broadband emission images, which indicate the regions where reactive species are formed in the gas phase, and measurements of the rf current and voltage at the electrodes. The spatial distribution of CF@sub 2@ is observed to go through a transition as power is increased, becoming more radially-uniform at higher powers. In addition, the presence of the wafer was found to have a strong effect on the CF@sub 2@ by both increasing the CF@sub 2@ density and affecting the spatial distribution. The addition of O@sub 2@ decreases the CF@sub 2@ density even in the presence of a wafer. Comparisons will also be made with previous studies in 100 - 1000 mTorr O@sub 2@/C@sub 2@F@sub 6@ and O@sub 2@/CF@sub 4@ chamber-cleaning plasmas. The results of this study will help to elucidate the role of CF@sub 2@ in fluorocarbon plasmas as well as provide data for development and validation of plasma simulations.

3:20pm **PS2-TuA5 Determination of Electron Temperature, Fluorine Concentration, and Gas Temperature in Fluorocarbon/Argon Plasmas using Optical Emission Spectroscopy**, ***M. Schabel***, *V.M. Donnelly, A. Kornblit, W. Tai, F. Klemens,* Lucent Technologies, Bell Laboratories

Recent advances in the interpretation of optical emission spectra from plasmas has made it possible to measure parameters such as electron temperature (T@sub e@), relative electron density, and gas temperature (T@sub g@) with this nonintrusive technique. This allows for the characterization and real-time monitoring of plasmas under conditions where the use of Langmuir probes is difficult (i.e. deposition plasmas or in manufacturing). Here we discuss the application of several advanced optical emission techniques to characterize fluorocarbon/Ar plasmas in an Applied Materials IPS inductively-coupled reactor. We have employed trace rare gas optical emission spectroscopy (TRG-OES), optical actinometry, and N2 vibrational spectroscopy to determine T@sub e@, fluorine atom concentration, and T@sub g@ respectively. Two etching processes, containing mixtures of Ar, C@sub 2@F@sub 6@, and C@sub 4@F@sub 8@, were evaluated as a function of pressure (5-90 mTorr). In the case of TRG-OES and optical actinometry, a mixture containing equal parts of He, Ne, Ar, Kr, and Xe (~1% ea.) was added. Large partial pressures of Ar prevent its use in TRG-OES because of radiation trapping effects (only the Kr and Xe lines were used to determine T@sub e@). Above 40 mTorr, T@sub e@ is insensitive to variations in pressure, and is ~2.5 eV. Below 40 mTorr, T@sub e@ increases with a decrease in pressure to 7 eV at 5 mTorr. The relative fluorine concentration increases with pressure and with the fraction of fluorocarbon species in the gas. At 5 mTorr, T@sub g@ is ~1010 K. Finally, we evaluated the effect of replacing Ar in the process gas with He or Ne, thereby allowing for the emission of the added Ar to be included with the Kr and Xe lines for determining T@sub e@. The resulting change in the accuracy of T@sub e@ measured by TRG-OES will be discussed in addition to how the use of He or Ne affects T@sub e@ and the relative electron density.

3:40pm **PS2-TuA6 Time-Resolved Measurements of Fluorocarbon Radical Concentrations during Pulsed Oxide Etching Plasmas**, ***T.M. Bauer***, *X. Wu,* University of New Mexico*; J.L. Cecchi,* University of New Mexico, US

We have measured the time evolution of the concentrations of the fluorocarbon radical precursors, CF@sub 2@ and CF, in pulsed plasmas using oxide etching chemistries. These measurements were performed in an inductively coupled plasma (ICP) reactor with a CHF3/Ar feedstock. We have explored a range of ICP powers of 300 to 900 W and a range of total pressure from 10 to 30 mTorr. The concentrations of CF@sub 2@ and CF, were measured with a wavelength-modulated diode laser spectroscopy system, modified to provide data with a time resolution of less than 0.3 ms. The pulse repetition rate and duty factor were varied to explore the full range of CF@sub 2@ CF and kinetics. Following the initiation of the plasma, [CF] increases in a nearly first-order manner. The behavior of [CF@sub 2@] is more complicated. Under pulsing conditions where [CF@sub 2@] remains nonzero for the entire period, there is an initial, very rapid (< 3 ms) decrease in [CF@sub 2@], indicating an enhanced loss, followed by a slower rise to equilibrium. After the termination of the plasma, [CF@sub 2@] shows a rapid increase, followed by an exponential decay. [CF] shows only an exponential decrease. The time constant for [CF@sub 2@] decay is in the range of 0.08-0.20 s, while the time constants for [CF] are more than a factor of ten smaller. Both time constants decrease with increasing pressure, and show a much smaller dependence on ICP power. We interpret our measurements with simple kinetic models and have extracted

kinetic parameters during both the plasma pulse and after plasma termination.

4:00pm **PS2-TuA7 Development of an Instrument: Resonantly Enhanced Multiphoton Ionization of Radicals Detected Using Time of Flight Mass Spectrometry**, ***W.C. Flory***, *K.L. Williams, E.R. Fisher,* Colorado State University

Plasma deposition and etching mechanisms have been studied extensively in recent years due to the technological utility of low-temperature plasmas. Much remains to be done on a molecular level, however, before a complete understanding of the underlying chemistry is gained. To this end, we have designed and constructed a molecular beam apparatus employing resonantly enhanced multiphoton ionization (REMPI) to examine the production and reactivity of radical species in low temperature plasmas. This newly constructed plasma molecular beam apparatus builds on our past experiments employing laser-induced fluorescence (LIF) to study the surface reactivity of plasma radicals. The REMPI instrument has been employed to study SiF radicals produced in a SiF@sub 4@ plasma. The SiF radicals are detected using [2+1] REMPI combined with time of flight mass spectrometry (TOFMS). The absorption band from the (1,0) C@super"2@@SIGMA@@super+@ <-- X@super2@@PI@@sub1/2@ transition of the SiF molecule was monitored. Production of SiF in the plasma has been measured as a function of plasma parameters, including addition of H@sub2@ and O@sub2@, and applied rf power. In addition to results for SiF, comparisons will be made to fluorocarbon radicals (CF, CF@sub3@) and to other silicon-containing species (e.g. SiH@sub2@, SiH@sub3@). Preliminary results from these systems will be presented.

4:20pm **PS2-TuA8 Temperature and Distance Dependencies of Fluorocarbon Species Desorbed from Polymer Deposited Metal Surface in C@sub 4@F@sub 8@ Inductively Coupled Plasma**, ***H.-H. Doh***, University of Tokyo, Japan*; T. Ichiki,* Toyo University, Japan*; Y. Tezuka, Y. Horiike,* University of Tokyo, Japan

To investigate the interaction between chamber wall and fluorocarbon plasmas, various fluorocarbon species such as CF@sub x@ (x=1-3) and C@sub 2@F@sub 4@, C@sub 3@F@sub 5@ emitted from the polymer coated copper stage has been measured by in-situ in C@sub 4@F@sub 8@ inductively coupled plasma using quadrupole mass analyzer (QMA) for the temperature of the stage, the distance between the QMA orifice and the stage. The QMA and hot stage are installed around the center of the chamber and the temperature of chamber wall can be controlled with water cooling system. The copper stage is equipped with heating rod, externally forced nitrogen blowing and can be movable with the radial direction. When we measured the radical density at the distance between hot stage and the orifice over 10 mm at 10 mT of pressure and 500 W of RF power, the results did not show any effect from hot stage and the densities of CF, CF@sub 2@, CF@sub 3@ have an order of 10@super 13@/cm@super 3@, 10@super 13@/cm@super 3@, 10@super 12@/cm@super 3@ respectively. At the distance below 10 mm, however, all radical densities increase and the behavior of CF@sub 3@ radical shows the biggest change with the decrease of the distance. Next, at the distance of 3 mm, the change of radical density with the surface temperature from 50 to 300 ° C was investigated. The density of CF@sub 2@ and CF@sub 3@ decrease slightly up to 100 ° C and 170 ° C, respectively then increase continuously to 300 ° C. The CF@sub 3@ radical density changed also dramatically with the temperature. It goes up to 7x10@super 14@/cm@super 3@ at the surface temperature of 300 ° C. It suggests that the pressure or the number of density around the hot wall is high locally. The increased number of density is due to the emitted species from the hot wall and consists of CF@sub 3@ mostly. It is considered that the surface plays both roles of sink and source of radicals for its temperature and CF@sub 3@ radical is the dominant species emitted from the hot wall inferred from the results measured at 3 mm of the distance with the variation of the surface temperature.

4:40pm **PS2-TuA9 C@sub x@H@sub y@ Radical Measurements using Cavity Ring Down Spectroscopy in a Remote Ar/C@sub 2@H@sub 2@ Plasma**, ***M.C.M. van de Sanden***, Eindhoven University of Technology, The Netherlands*; K.Y. Letourneur,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.G.H. Boogaarts,* Eindhoven University of Technology, The Netherlands*; D.C. Schram,* Eindhoven University of Technology, The Netherlands, Netherlands

The ground state densities of C@sub x@H@sub y@ (x = 1,2, y = 0, 1) radicals in a remote Ar-C@sub 2@H@sub 2@ plasma used for high rate deposition of hard hydrogenated amorphous carbon films (a-C:H, rates up to 500 Å/s) have been investigated in detail by cavity ring down absorption spectroscopy (CRDS). Both C@sub 2@ and CH could be spectroscopically identified and measured as function of C@sub 2@H@sub 2@ gas flow admixture. From previous studies we deduced that the main dissociation products of C@sub 2@H@sub 2@ dissociation in our remote plasma is C@sub 2@H and H. In an attempt to measure the ground state density of C@sub 2@H we looked for a spectroscopic signature in the 260-280 nm region where Laser Induced Fluorescence measurements of ground state C@sub 2@H have been reported. No clear spectroscopic fingerprint of C@sub 2@H@sub 2@ could be measured although a clear broadband absorption is observed. The absence of a fingerprint of the C@sub 2@H radical could be due to the limited spectral resolution (0.7 cm@sup -1@) of the laser system used. Another plausible reason could be the hostile plasma environment (including formation of clusters) which influences the formation process of C@sub 2@H to such an extend (in terms of excitation of rovibrational and electronic states) that broadband absorption results. However, the broadband absorption measured as function of the C@sub 2@H@sub 2@ gas flow admixture shows trends we expect from the C@sub 2@H radical. In an attempt to resolve the problems faced we have designed an experiment in which we measure the C@sub 2@H radical using simultaneously threshold ionization mass spectrometry and cavity ring down spectroscopy. First results of these experiments will be presented.

5:00pm **PS2-TuA10 Electron Energy Control in Large-Diameter Inductively Coupled Plasma for High Performance of Etching**, ***T. Urayama***, *T. Tsurumi,* Tokai University, Japan*; Y. Horiike,* The University of Tokyo, Japan*; S. Fujii,* ADTEC Co., Ltd., Japan*; H. Shindo,* Tokai University, Japan

A method of electron energy control was studied in an inductively coupled plasma of a large diameter employing the multimode antenna, for high performance in device fabrication etching plasma processes. In etching plasmas, the electrons are prone to be excessively energetic in high density plasmas generated at low pressures. In SiO2/Si selective etching, for example, the high etching selectivity has been hardly realized under high etch rate, and this is understood as the radical density is too much low compared with the ion density. This happens eventually because the electron energy becomes too high at low pressures. The experiment was carried out in an inductively coupled plasma which was produced in a stainless-steel chamber of 350 mm in diameter by supplying the RF power of 13.56 MHz through the quartz window at one end. The electron energy could be reduced by changing the azimuthal mode of one-turn antenna from m=0 to m=2 with no notable change in electron density. The electron energy reduction was found higher in the higher mode and essential at low pressures by Langmuir probe measurement. These behaviors were also confirmed by optical emission spectroscopy. The method was extended to two-loop antenna with different diameters which enabled us to make the radial mode as well as the azimuthal mode. It was verified that these two-loop antenna with the modes could imporove the radial uniformity as well as the electron energy reduction, and a physical sputter etch rate of Si showed 5% radial uniformity in 12 ich area. It was concluded that the electron free path divided by the induction field reverse distance was the essential parameter in electron energy control.

Author Index

Bold page numbers indicate presenter