## Plasma Science and Technology
## Room 315 - Session PS-ThA

### Plasma Diagnostics: Mechanisms

**Moderator:** N.C.M. Fuller, IBM TJ Watson Research Center

2:00pm **PS-ThA1 In-Situ Monitoring of Unstable Neutral Molecules using Ion Attachment Mass Spectrometer*, Y. Shiokawa*,** *M. Nakamura, Y. Hirano, Y. Taneda, T. Fujii,* Anelva Corporation, Japan

Ion Attachment Mass Spectrometer (IAMS)@footnote 1@ has a unique advantage of fragment-free; mass analysis of true original molecule without dissociation, which is impossible by common methods such as electron impact. Therefore, IAMS has been expected to measure unstable neutral molecules in gas processes, and was already applied to analysis of thermal reaction by metallic-organic material for Cu-CVD and of exhaust gas from dry etching system.@footnote 2@ Although conventional IAMS used in these experiments is large and needed higher pressure than 100Pa for sampling, newly developed IAMS@footnote 3@ is compact and needs only 1Pa, so that IAMS in-situ monitor seems to be realized. Therefore we are investigating capabilities of new IAMS for in-situ monitoring of unstable neutral molecules in many processes, including tool for plasma diagnostics. In this experiment, plasma was produced by small inductively coupled source with 2Pa of c-C@sub 4@F@sub 8@ (100%), and new IAMS was put on it at a distance of 10cm apart. Neutral molecules of CF@sub 2@, C@sub 2@F@sub 4@, COF@sub 2@ by IAMS and ions of CF@sub 2@@super +@, C@sub 2@F@sub 4@@super +@, COF@sub 2@@super +@, ionized in plasma, were measured simultaneously. First, when plasma power increased from 25W to 200W, CF@sub 2@@super +@, C@sub 2@F@sub 4@@super +@ did not change largely, but CF@sub 2@ reduced to one-tenth and C@sub 2@F@sub 4@ one-hundredth at only 50W. On the other hand, both COF@sub 2@@super +@ and COF@sub 2@ did not change largely. Next, when pressure decreased from 2Pa to 0 .5Pa, CF@sub 2@@super +@ kept constant but CF@sub 2@ reduced to one-tenth. These results show that behavior of true original molecules is completely different from that of ions ionized in plasma. It is well known too that neutrals such as CF@sub 2@, C@sub 2@F@sub 4@ cannot be detected correctly by electron impact. Therefore it was confirmed that new IAMS is very useful as in-situ monitor in plasma. We would like to present some examples of c-C@sub 4@F@sub 8@ plasma in manufacturing conditions and of SiH@sub 4@ plasma throughout our talk. Precious discussions with Prof. Nakata and Prof. Takayanagi of Tokyo University of Agriculture and Technology are gratefully acknowledged. @FootnoteText@ @footnote 1@ T.Fujii, Mass Spectrometry Review 19(2000) 111, @footnote 2@ M.Nakamura et al, JVST-A 19(2001) 1105,@footnote 3@ Y.Hirano et al, AVS Int.Sympo. PS-TuP3 (2002)

2:20pm **PS-ThA2 Discharge Frequency Dependence of Plasma Parameters in Parallel-plate-electrode VHF Plasmas*, Y. Ichikawa,*** Fuji Electric Co. Ltd., Japan*; T. Sasaki,* Fuji Electric CRD, Japan*; S. Matsumura,* Musashi Institute of Technology, Japan

Recently, plasmas generated by power supplies of VHF band attract considerable interest in plasma CVD technique to increase deposition rate and to improve film properties of silicon related thin films. In this work, we have studied the effect of discharge frequency on the characteristics of plasma with a view to understanding the mechanism why VHF plasmas are more desirable than the conventional 13.56MHz plasma. We used a capacitively coupled plasma CVD apparatus with a pair of parallel plate electrodes of 160mm in diameter; the discharge frequency can be varied from 10MHz to 100MHz continuously. To measure the plasma parameters of VHF plasma precisely, we developed the following two probe diagnostic techniques: (1) A modified capacitance probe to measure the amplitude of plasma potential variation (V@sub sp-p@) at discharge frequency (2) Compensation single probe by which variation of the plasma potential is compensated and precise current voltage characteristics are measured Employing these probe techniques, we measured electron temperature, electron density, time averaged space potential, and V@sub sp-p@ in H@sub 2@ VHF plasmas. The results measured at frequencies of 13, 24.5 and 92.3MHz show that (1) the electron temperature, Te, decreases with increasing discharge frequency; (2) the electron density for 92.3Hz is about 30 times as high as that for 13MHz under the same discharge power condition. The spatial distributions of these plasma parameters and the space potential were also measured. The details of these experimental results will be presented and discussed.

2:40pm **PS-ThA3 Model-based RF Plasma Monitoring under Industrial Conditions*, M. Klick,*** ASI Advanced Semiconductor Instruments, Germany **INVITED**

The increased demand for characterization of plasmas under industrial conditions was mainly driven by the complexity of industrial plasma processes. The interaction of the plasma with the surface determines the quality and performance of the electronic devices on the substrate. Hence a good understanding of the key mechanisms of plasma excitation is required. To address the heating mechanisms of the electrons, knowledge of the electron energy distribution function (EEDF) is imperative - or at least parameters derived from its moments, as the collision rate of electrons for momentum transfer or, taking into account stochastic heating, too, the effective collision rate. Especially the last property, the thermalisation of the electric field's energy, can only be accessed by measuring the self-excited resonance of the electrons in RF plasmas(SEERS, last 's' for spectroscopy). SEERS utilizes nonlinear and resonance effects in the plasma in the sheath and the plasma body leading to a non-sinusoidal RF current. Thus SEERS uses nonlinear and RF effects which usually disturb or even avoid the application of classical methods as Langmuir probes in RF plasmas. The measurement principle is based on a passive RF current sensor and a discharge model involves the effects mentioned above and can be used in reactive plasmas without any restriction. SEERS data based of ten thousands of wafers for different processes show the high efficiency of this approach, in particular under industrial conditions as polymers on chamber wall and sensor itself and undesired effects as arcing at the chamber wall. On the other hand, basic experiments show that plasma physical mechanisms as skin effect in the plasma, ohmic and stochastic heating of electrons can be qualitatively observed in productions tools which are necessary for the understanding and development of process and new chamber types.

3:20pm **PS-ThA5 Study of Pulsed Plasma Doping System by Time-resolved Ion Mass-energy Spectrometry*, L. Godet*,** *B.-W. Koo,* VSEA, France*; G. Cartry, C. Cardinaud,* Institut des Materiaux de Nantes, France*; Z. Fang,* VSEA, France*; A. Grouillet, D. Lenoble,* STMicroelectronics, France

Pulsed PLAsma Doping (P@super 2@LAD) continues to emerge as a viable alternative technique to ion implantation for advanced semiconductor devices,@footnote 1@ since it is capable of delivering high rate dose at ultra low energy (100V to 10kV applied voltage) giving rise to ultra shallow junctions.@footnote 2@ In P@super 2@LAD, plasma is ignited and extinguished with each negative voltage pulse applied to the wafer. During the pulse, positive ions are accelerated across the sheath and implanted within the wafer. This process was studied using a Hiden EQP mass spectrometer implemented within the pulsed electrode, focussing principally on BF@sub 3@ plasma for different implant process conditions. Previous work, employing time averaged mass spectrometry,@footnote 3@ indicated that BF@sub 2@@super +@ is the dominant ion species in the BF@sub 3@ plasmas, and BF@super +@ is the second most abundant ion species. Due to the short (10 - 50µs) pulse length and low repetition rate (100 - 5000Hz) of the P@super 2@LAD process, the time between the pulses is relatively long so that a time-resolved ion mass-energy measurement is necessary to follow the process before, during and after the pulse period. Time resolved Langmuir probe measurements@footnote 4@ have shown the presence of a cold plasma during the afterglow which may be a key parameter for understanding and controlling the entire process (i.e. charge neutralization, etching, deposition). In this paper, we present time-resolved mass spectrometry data allowing a more complete understanding of BF@sub 3@ P@super 2@LAD processing including the role of negative charges during the afterglow period. @FootnoteText@@footnote 1@D.Lenoble et al., Ion Implantation Technology 2002, Taos, USA.@Footnote 2@R.B. Liebert et al., Ion Implantation Technology 2000, Alpbach, Austria.@footnote 3@B.W. Koo, Z.Fang, S.Felch, Ion Implantation Technology 2000, Alpbach, Austria@footnote 4@Z.Fang et al., Ion Implantation Technology 2002, Taos, US.

3:40pm **PS-ThA6 Gas-Phase Diagnostics and Mechanisms of Energy Transfer in O@sub 2@/NH@sub 3@ Plasmas*, K.R. Kull,*** *D.S. Wavhal, E.R. Fisher,* Colorado State University

Hydrophobic polymeric membranes are used extensively throughout a variety of industrial and biomedical processes. To improve the separation performance, hydrophilic surface modification is required. In this work, we have studied hydrophilic modification of asymmetric porous polyethersulfone membranes using N@sub 2@, NH@sub 3@ and O@sub 2@/NH@sub 3@ plasma treatments. Membrane treatments using 100%

N@sub 2@ or 100% NH@sub 3@ plasmas yielded incomplete hydrophilic treatments. In contrast, the O@sub 2@/NH@sub 3@ plasma treatment produced a hydrophilic membrane that retained its hydrophilicity over an extended period after treatment. Examination of the plasma gas-phase composition using optical emission spectroscopy and mass spectrometry revealed the NH radical is present in both the 100% NH@sub 3@ and the O@sub 2@/NH@sub 3@ systems, whereas the OH radical is only observed in the O@sub 2@/NH@sub 3@ plasma. Evidence from other plasma modification systems indicates the OH radical is critical for permanent hydrophilicity using non-polymerizing plasma treatments of polymeric membrane treatments.@footnote 1@ To better understand the chemistry that occurs during these processes, we have used our laser-induced fluorescence based imaging technique to characterize the relative densities of NH and OH and their energy partitioning in these plasmas. The relative densities of both radicals are dependent on the applied rf power (P) and feed gas composition dependent. Interestingly, the rotational temperatures of both species appear nearly independent of P. Surface interactions of NH and OH with membranes, as well as their translational temperatures in the plasma, will be presented and compared to earlier results for NH@sub 2@ radicals in NH@sub 3@ plasma.@footnote 2@ Implications for plasma modification mechanisms will also be discussed. @FootnoteText@@footnote 1@ M. L. Steen, et al., Langmuir 17, 2001, 8156.@footnote 2@ C. I. Butoi, et al.,J. Phys. Chem. B 105, 2001, 5957.

4:00pm **PS-ThA7 The Study of Ion Drift Velocities and Instabilities in Presheaths in Two Ion Species Plasmas***, **X Wang**, E. Ko, N. Hershkowitz,* University of Wisconsin, Madison

The presheath is a region of weak electric field that accelerates ions into the sheath at the plasma boundary. The experiments were performed in multi-dipole DC plasmas with He-Ar gas mixtures (P@sub total@ @>=@ 1.0mTorr, n@sub e@ @>=@ 1x10@super 9@cm@super -3@, T@sub e@ @<=@ 2eV). The concentration of ion species in the two ion species plasmas was determined by measuring ion acoustic wave phase velocity and electron temperature in the bulk region.@footnote 1@ To measure ion drift velocities in the presheath, an ion acoustic wave was launched by both a continuous sinusoidal wave and a pulse, and detected by a cylindrical probe with a boxcar averager. Ion drift velocities were measured in pure Ar plasma. Based on the dispersion relation in the presheath for multi-ion species plasma and phase velocity measurements in He-Ar plasma, the relationship between Ar and He ion drift velocities was determined. Using Ar ion drift velocities from LIF data,@footnote 2@ the He ion drift velocities were determined. In two ion species plasmas, instabilities can be excited by the two ion streams with different drifting velocities that are created in the presheath. Instabilities changing with different partial pressure, positions and discharge current were observed by using a cylindrical probe biased to collect either ion saturation current or electron saturation current and a spectrum analyzer. The frequency of instabilities is ~1.0MHz and wavelength is ~5.0mm compared to ~3.0cm of presheath length. ** Work supported by US DOE grant DE-FG02-97ER54437. @FootnoteText@@footnote 1@A. M. Hala and N. Hershkowitz, Rev. Sci. Instrum. 72, 2279 (2001).@footnote 2@G. D. Severn, Xu Wang, Eunsuk Ko and N. Hershkowitz, Phys. Rev. Lett. 90, 145001 (2003).

4:20pm **PS-ThA8 Ion Collection by a Mach Probe in Flowing Unmagnetized Plasma***, **E. Ko**, X Wang, N. Hershkowitz,* University of Wisconsin, Madison

The measurement of plasma flow along the presheath in unmagnetized plasma is performed using a spherical Mach probe. Ion flow velocity in unmagnetized plasma is examined experimentally and compared to a recent numerical simulation by Hutchinson.@footnote 1@ The spherical Mach probe, which was inspired by Hutchinson's theoretical model, consists of a conducting sphere that has two conducting probe tips, insulated from the sphere and mounted at @theta@ = 0° and 180° with respect to the flow direction. Although the simulation included T@sub i@ = 0.1T@sub e@ ~ 10T@sub e@ and flow velocity v@sub f@ = 0 ~ 3c@sub s@, where c@sub s@ is the sound speed, the laboratory plasma in the presheath was limited to T@sub i@ < 0.1T@sub e@ and v@sub f@ @<=@ 1.0 c@sub s@. The experiment is performed in a multi-dipole DC plasma with Argon pressure ranging from 0.1 to 3mTorr. The upstream and downstream probe tips and the surface of the sphere were simultaneously biased to minimize the probe edge effects, and to obtain a much closer condition to the simulation. This work also examines a previous experiment@footnote 2@ that used the Hudis and Lidsky formula,@footnote 3@ which though shown to be invalid@footnote 4@ still attained results in good agreement with the simulation. *Work Supported by US DOE grant DE-FG02-97ER 54437. @FootnoteText@ @footnote 1@ I. H. Hutchinson, Plasma Phys. Control. Fusion, 44 1953 (2002)@footnote 2@ L. Oksuz, M. A. Khedr, and N. Hershkowitz, Phys. Plasmas, 8 1729 (2001)@footnote 3@ M. Hudis and L. M. Lidsky, J. Appl. Phys., 41 5011 (1970)@footnote 4@ I. H. Hutchinson, Phys. Plasmas, 9 1832 (2002).

4:40pm **PS-ThA9 Novel Plasma Monitoring Scheme by Surface Wave Probe***, **H. Sugai**, H. Kawai,* Nagoya University, Japan*; K. Nakamura,* Chubu University, Japan

A novel and simple technique for measuring the electron density@footnote 1@ and temperature@footnote 2@ of plasma reactors using a surface wave probe (SW probe) is presented. This probe is also called plasma absorption probe as it is based on absorption of surface waves by plasma. The SW probe enables us to measure the local absolute electron density even when the probe surface is soiled with processing plasmas. The technique relies on absorption of surface waves resonantly excited around the probe head at critical frequencies which mainly depend on the electron density. The probe consists of a small antenna connected with a coaxial cable and is enclosed in a tube of dielectric constant @epsilon@@sub d@ inserted in a plasma of electron plasma frequency @omega@@sub p@. A network analyzer feeds a rf signal to the antenna and displays the frequency dependence of the power absorption. The absorption is observed at frequencies slightly above the surface wave resonance frequency, @omega@@sub p@/ (1+ @epsilon@@sub d@),@footnote 1,2@ which allows us to determine the electron density. Use of a pair of SW probes of different sizes enables measurements of both electron temperature and electron density. The measurements were made in a wide range of electron density (10@super 8@ - 10@super 13@ cm@super -3@) and gas pressure (10 mTorr -10 Torr) with high resolutions of space (@DELTA@x~2 mm) and time (@DELTA@t~1 µs). Time-variation of a few percents of electron density is detectable. @FootnoteText@ @footnote 1@H. Kokura, K. Nakamura, I. Ghanashev and H. Sugai, Jpn. J. Appl. Phys. 38, 5262 (1999)@footnote 2@K. Nakamura, M. Ohata and H. Sugai:, J. Vac. Sci. Technol. A21, 325 (2003).

5:00pm **PS-ThA10 Measurement of Absolute Radical and Metastable Species Densities in O@sub 2@ and N@sub 2@ Plasmas using Modulated Beam Appearance Ionization Mass Spectrometry***, S. Agarwal,* University of California, Santa Barbara*; G.W.W. Quax, B. Hoex, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands*; D. Madoudas,* University of Massachusetts, Amherst*; **E.S. Aydil**,* University of California, Santa Barbara

Measurement of radical densities in an electrical gas discharge is important for understanding and improving plasma etching and plasma-assisted deposition processes. We have designed, developed and demonstrated an experimental apparatus for measuring the density of the radicals and electronically excited molecular species in a plasma using modulated beam line-of-sight appearance ionization mass spectrometry (LOS-AIMS). In LOS-AIMS, the species in the plasma are sampled through an aperture on the substrate platen and detected using a quadrupole mass spectrometer (QMS) placed in line-of-sight with this aperture in a three-stage differentially pumped vacuum chamber. Although LOS-AIMS is a versatile tool for measuring absolute radical densities, we show that it requires careful vacuum design and calibration which should take into account various sources of error such as the contribution to the QMS signal from the background gases, the ion mass-to-charge ratio dependence in the sensitivity of the QMS, and space-charge limitations in the QMS ionizer. In addition, collisions within the extracted molecular beam must be taken into account for higher operating pressures in the plasma chamber. Careful consideration of these effects and modulation of the sampled radical beam with a chopper allows the determination of the absolute radical densities, parent molecule concentrations, and the neutral gas temperature near the substrate plane. Specifically, we have measured densities of O and Ar atoms and O@sub 2@ molecules in O@sub 2@/Ar plasma mixtures and N atoms and metastable N@sub 2@ molecules in N@sub 2@ plasmas. In addition, we find that at low pressures, the O@sub 2@ translational temperature is higher than that for Ar. We attribute this difference in Ar and O@sub 2@ translational temperatures to hot O@sub 2@ molecules that are created by O-O recombination reactions on the walls of the plasma chamber which do not equilibrate effectively with Ar atoms at lower pressures.

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