Plasma Science and Technology
Room: 210A - Session PS-MoA

Plasma Diagnostics, Sensors and Control I
Moderator: Erik Johnson, LPICM-CNRS, Ecole Polytechnique, France, Jeffrey Shearer, IBM Research Division, Albany, NY

2:20pm **PS-MoA1 Submillimeter Studies of Molecular Plasmas: Applications to Semiconductor Plasma Processing**, ***Frank De Lucia***, Ohio State University **INVITED**

The use of submillimeter (smm) absorption spectroscopy to study molecular plasmas is well established. This has been driven by a number of applications including the molecular astrophysics of free radicals and ions, diagnostics of excitation and energy transfer in laser plasmas, and fundamental physical chemistry.

Attributes of smm spectroscopy of plasmas include: (1) They are transparent and essentially noise free in the smm, (2) Very high resolution leads to essentially 'absolute' specificity and low clutter backgrounds, (3) It is a non-invasive probe with straightforward sampling, (4) Calibration free measurement of absolute concentrations can be obtained from first principles, (5) The spectra provide measurements of the rotational/translational temperatures, (6) The technique can probe 'dark' chambers, and (7) Measurements can be 'real time.

Limitations include: (1) The molecules require a dipole moment, (2) The technique is more challenging as pressure is raised above 1 Torr, and (3) Because of diffraction, it requires a larger probe beam.

In this talk we will first discuss the basic physics and chemistry that underlies the smm spectroscopy of low-pressure plasmas. We will then describe results initially obtained on a test reactor at OSU provided by Applied Materials, followed by results obtained on production and research reactors at Applied Materials. This will include measurements of concentrations and temperatures of plasma constituents as a function input flows, discharge power, and time.

3:00pm **PS-MoA3 Using Broadband Absorption Spectroscopy to Elucidate Energy Partitioning and its Impact on Surface Reactivity**, ***Joshua Blechle***, *A.R. Hanna, E.R. Fisher*, Colorado State University

The partitioning of energy within plasma systems is of vital importance to plasma chemistry as it provides insight into reactivity via possible species formation and decomposition mechanisms as well as its significant contribution to surface reactivity of individual plasma species. Here, such investigations are used to determine the internal and kinetic energies of species within a variety of inductively coupled plasma systems. To obtain this information, broadband absorption spectroscopy (BAS) and the imaging of radicals interacting with surfaces (IRIS) technique were utilized to determine species energetics (vibrational, rotational, and translational temperatures). In particular, the vibrational and rotational temperatures of NO, N_2, OH, and O_2 in various gas mixtures are measured, indicating significantly higher vibrational temperatures (i.e. >3000K) than rotational temperatures (i.e. <1000K) are obtained. One focus of this work is the development of a BAS system and the impact of various methods of data collection on determined temperatures evaluated using different computational models. These data are also used to demonstrate the relationship between internal energetic and observed surface scatter coefficients (*S*) for NO, OH, and other plasma species, which is directly related to surface reactivity (*R*). Such observations allow for unique insight into these plasma systems and the integral role energy partitioning plays in the assessment and understanding of complex plasma chemistry.

3:20pm **PS-MoA4 CF_3^+ Fragmentation by Electron Impact Ionization of Perfluoro-Vinyl-Ethers**, ***Yusuke Kondo***, *K. Ishikawa, T. Hayashi, Y. Miyawaki, K. Takeda, H. Kondo, M. Sekine, M. Hori*, Nagoya University, Japan

In plasma etching processes, the densities of chemically reactive species have attracted attention. A higher etch yield for SiO_2 at lower ion impact energies was reported when using CF_3^+ ions.[1] Perfluoro-vinyl-ether forming selectively CF_3^+ ions were reported.[2] Here we extensively studied in details the gas phase fragmentations of perfluoro-vinyl-ether.

A quadrupole mass spectrometer (QMS; Hiden Analytical, EQP) was installed in the chamber wall of the commercial plasma etching reactor. PPVE (CF_3-CF_2-CF_2-O-CF=CF_2, $C_5F_{10}O$) or PMVE (CF_3-O-CF=CF_2, C_3F_6O) was introduced into the chamber and maintained at a pressure of 1.0 Pa.

Dissociative ionization caused by impact with 20 eV electrons provided positive ion fragmentation pattern to three peaks for PMVE: CF_3^+, $C_2F_2O^+$ and $C_3F_6O^+$, and five peaks for PPVE: CF_3^+, $C_2F_2O^+$, $C_2F_5^+$, $C_3F_7^+$ and $C_5F_{10}O^+$. Figure 1 shows comparison of the ion efficiency for CF_3^+ between (a) PPVE and (b) an isomer of PMVE. The large ionization efficiency of CF_3^+ was experimentally observed significantly as the leading cause of large cross-sections for dissociative ionization of CF_3^+ ions. For comparison, the CF_3^+ ion density fragmented from perfluoro-alkanes is only 30 to 40%. By the energetic electron impact on the perfluoro-vinyl-ethers, excess energy is distributed among internal energies at the vinyl-ether bond, due to polarization of the charge on the bridging oxygen atom. The fragmentation via direct bond rupture into smaller product ions occurs more favorably than the rearrangement or cleavage into molecules with large mass.

[1] K. Karahashi *et al*. J. Vac. Sci. Technol. A **22** 1166 (2004). [2] M. Nagai *et al.*, Jpn. J. Appl. Phys. **45** 7100 (2006); Y. Morikawa *et al*., Jpn. J. Appl. Phys., **42**, 1429 (2003).

3:40pm **PS-MoA5 A Comprehensive Quantitative Study of Low Pressure Inductively-Coupled Plasmas in Cl_2, O_2 and Mixtures**, *M. Foucher, D. Marinov, P. Chabert*, LPP-CNRS, Ecole Polytechnique, France, *A. Agarwal, S. Rauf*, Applied Materials Inc., ***Jean-Paul Booth***, LPP-CNRS, Ecole Polytechnique, France

Inductively-coupled plasmas in diatomic electronegative gases such as Cl_2 and O_2 are widely used in semi-conductor fabrication for gate etching and photo-resist stripping. Moreover they are an archetype for plasmas in simple electronegative gases with the advantage that techniques exist to measure the densities of nearly all their stable and reactive species. They provide an opportunity to benchmark models such as the Hybrid Plasma Equipment Model. We are then undertaking a comprehensive set of measurements in the pure gases and their mixtures.

The plasma is sustained in a cylindrical chamber (55 cm diameter,10 cm height) by a 4-turn planar coil excited at 13.56 MHz above a dielectric window. Pure gases (Cl_2 and O_2) were studied over a range of pressure [5-80 mTorr] and RF power [50-550 W]. The effect of O_2 addition (0-100%) to Cl_2 plasmas was studied at 10 mTorr 500W. The electron density was determined by hairpin resonator probe. The Cl and O atom absolute densities and surface reaction coefficients were obtained by Two-Photon Absorption Laser-Induced Fluorescence. A novel ultra-broadband high sensitivity absorption bench was used to measure ground state and vibrationally excited Cl_2 and vibrationally excited O_2, as well as OCl, OClO and Cl^- ions.

In all gas mixtures, the electron density was observed to increase initially with gas pressure, pass through a maximum and then decrease at higher pressure. In O_2 a broad maximum is observed around 40 mTorr, whereas for Cl_2 the electron density peaks at 10 mTorr before dropping sharply. This difference can be attributed to rapid dissociative attachment of electrons in the case of Cl_2. In all cases the electron density increases with RF power. In O_2, highly vibrationally excited molecules $O_2(v)$ were observed (with v up to 18), and analysis of the rotational structure of the O_2 Schumann-Runge bands showed rotational temperatures (=translational temperatures) ranging from 400 K (10mTorr 100W) to 900 K (80 mTorr 500W). The non-equilibrium vibrational distribution may be attributed to electron impact excitation combined with low rates of V-T energy transfer processes in O_2. In contrast, in pure Cl_2 the vibrational temperature is equal to the gas translational temperature, (~1000K) due to efficient V-T transfers between Cl_2 and Cl atoms. In Cl_2/O_2 mixtures the densities of electrons and Cl and O atoms all decreased when O_2 or Cl_2 is added to the pure gas (Cl_2 or O_2). This coincides with the formation of ClO and OClO, which consumes the atoms which are easier to ionize than molecules.

We are currently working on modeling of these results to obtain a deeper understanding of the kinetics of Cl_2/O_2 plasmas.

4:00pm **PS-MoA6 Optical Emission Diagnostics for Detection of High Energy Electrons in Argon Plasmas**, ***Shicong Wang***, *J. Boffard, C.C. Lin, A.E. Wendt*, University of Wisconsin - Madison

The electron energy distribution function (EEDF) is one of the most important and fundamental parameters in low temperature plasmas. The high-energy range of the EEDF in particular is responsible for ionization, excitation and gas phase chemistry, which are critical for many industrial applications. Non-invasive OES diagnostics provide an attractive means to measure EEDFs, using emissions from argon states excited by electron collisions [1,2]. Emission lines dominated by excitation of ground state argon atoms are particularly sensitive to the population of high energy (>13

eV) electrons. We report on optical emission diagnostics for detection of energetic electrons in argon plasmas. The OES diagnostic makes use of an emission model based on measured argon excitation cross sections that computes the relative emission intensities at a selected set of wavelengths, with a trial EEDF as input. The trial EEDF that produces the best fit to the spectrum measured in the experiment is determined after a search in which the shape and average energy of the trial EEDF is varied. In both pulsed argon inductively coupled plasmas (ICPs) and capacitively coupled plasmas (CCPs), a high electron temperature has been previously observed at the beginning of the pulse period in time-resolved OES measurements. Meanwhile, the relative argon emission intensities between emissions originating from upper levels populated primarily by high energy and low energy electrons , respectively, (i.e., 420.07/419.83 nm line ratio) imply the existence of a `hot tail' of energetic electrons, as compared to a Maxwellian distribution. In addition, the OES method of detecting high energy electrons is explored in the presence of a supplemental source of energetic electrons. A biased auxiliary set of heated filaments will be used to inject high energy electrons into an argon inductively coupled plasma. The filament bias voltage will be varied to control the energy of emitted electrons, and the filament heater current will be controlled separately to vary the emitted electron flux. The OES diagnostic is used to observe the changes in emission spectra and extracted EEDF caused by the supplemental energetic electrons. The OES method will be examined and compared to Langmuir probe measurements of EEDF as the energy and current of the supplemental electron population are systematically varied.

The authors acknowledge support from NSF grant PHY-1068670.

[1] Wang et al., JVSTA 31, (2013) 021303.

[2] Boffard et al., Plasma Sources Sci. Tech. 19 (2010) 065001.

4:20pm **PS-MoA7 Plasma Characteristics in a Dual-Frequency Inductively Coupled Plasma Source for the Etch Tool**, ***Vladimir Nagorny***, Mattson Technology, *V. Godyak*, RF Plasma Consulting

It is always desirable to have more than one antenna in ICP plasma source for etch for better both radial uniformity control and process window. So, configurations with two antennas are being used in ICP for quite a while. However, there is always a question about their interference.

Recently Mattson Technology introduced an etch tool with a dual frequency ICP plasma source [1]. The logic behind complementing a standard 13.56MHz antenna with a 2MHz antenna with ferrite core was quite simple - no interference between antennas, high efficiency 2MHz design [1–3] of the second antenna and respectively low additional cost. This source demonstrated large operating window, high plasma stability in both electro-positive and electro-negative gases, good process control. With this source design it is possible to tune process uniformity (Max-Min) down to 1% and better on a blanket wafer.

Energizing plasma with different frequencies put a reasonable question, if the two essentially different frequencies create similar processing plasmas comparing to a 13.56MHz drive or not. To answer this question, a comprehensive study of the electron energy probability functions, EEPF have been measured in Ar and in real processing plasmas, including gas mixtures that generate depositing plasma. The measurements performed in a wide range of processing condition with different power ratio at 13.56 and 2 MHz have demonstrated independence of the measured EEDFs on frequency, but only on the total absorbed power, gas composition and its pressure. These results are in agreement with earlier observation in different reactors [4] and with analysis of ionization and electron energy balances in gas discharge plasma [5].

[1] V. Nagorny, D. Lee and A. Kadavanich, *US PTO Publication* US20140197136, *patent pending*

[2] V.A. Godyak, *US Patent* 8920600.

[3] V.A. Godyak, C. Crapuchette, V. Nagorny, *US PTO Publication patent pending.*

[4] N. Hershkowitz, J. Ding, R.A. Breun, R.T.S. Chen, J. Mayer, and A.K. Quick 1996 *Phys.Plasmas* **3** 2197

[5] V.A. Godyak 2006 *IEEE Trans. Plasma Sci.* **34** 755

4:40pm **PS-MoA8 Spatial Oscillations and Frequency Shifts in Pulsed Capacitively Coupled Plasmas**, ***John Poulose***, *L.J. Overzet*, The University of Texas at Dallas, *S. Shannon*, North Carolina State University, *D. Coumou*, MKS Instruments, *M.J. Goeckner*, The 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 spectral lines from pulsed plasmas through Ar, O_2, N_2, CF_4 gases and CF_4/O_2/Ar gas mixtures have been collected. The OEIs measured from CF_4/O_2/Ar gas mixtures show an axial oscillation of intensity with an approximate speed of 10^6 cm per second. This oscillation starts at the plasma strike and dampens to the background during the first 10 µs in 1 kHz pulse frequencies or lower. Radio frequency voltage and current measurements show changes over similar time periods. The transient reactance has been observed to correspond to the sheath formation in the OEI studies. Measured current and voltage frequencies have been observed to shift/pull by as much as 400 kHz during the initial turn on phase. The amount of the frequency pull is dependent on gas composition, electrode gap, pressure, and pulse properties. This shift occurs as a reaction to the plasma formation, specifically, the sheath development. We will present these results and the effects of other parameters on the transitory behavior of pulsed discharges.

5:00pm **PS-MoA9 Curling Probe Measurement of Electron Density in Pulse-Modulated Plasma at High Frequency**, ***Anil Pandey***, Chubu University, Japan, *W. Sakakibara*, DOWA Thermotech, Japan, *H. Matsuoka*, DOWA Thermotech, *K. Nakamura*, *H. Sugai*, Chubu University, Japan

Curling probe (CP), a modified form of microwave resonator probe has recently been proposed [1] which enables the local electron density measurement even in reactive plasma for non-conducting film deposition. The electron density is obtained from a shift of ¼ wavelength-resonance frequency of the spiral slot antenna in discharge ON and OFF monitored by a network analyzer (NWA). CP is a compact monitoring tool (minimum diameter 6 mm) coated with alumina or yttria for applications to semiconductor plasma processing. A variant of CP installed with an optical fiber, called *opto-curling probe* (OCP) has also been developed which enables simultaneous monitoring of electron density and optical emissions from plasma [2]. In this paper we demonstrate that CP can be applied not only to a constant density plasma but also to a plasma pulse-modulated at high frequency such as several tens of kHz. In case of pulse-modulated discharge, synchronization of discharge pulse with frequency sweep of NWA must be established [3]. Such CP measurement was performed in a pulsed glow discharge plasma primarily used for metal-nitridation. A CP of 16-mm diameter was inserted in a cylindrical chamber of 60 cm in diameter and 50 cm in length. A negative high-voltage pulse of -1.0 to -2.0 kV was applied to a cathode, which generates a pulsed glow plasma in different discharge gas at varying pressures. The pulse frequency was changed from 0.4 to 25 kHz with various duty cycle ratios. The NWA (Agilent E5071C) was externally triggered using *on point* mode and the electron density in glow phase and afterglow phase was measured in time-resolved manner in argon, nitrogen and hydrogen discharges. At higher pulse frequencies (>5 kHz), the electron density was found to be time-modulated and didn’t decay completely to zero. Also, a minimum time resolution of 2 µs was attained. Thus, CP is concluded to be a powerful tool for the time-resolved electron density monitoring in pulse-modulated plasma often used in industrial materials processing.

[1] I. Liang, K. Nakamura, and H. Sugai, Appl. Phys. Express 4, 066101 (2011).

[2] A. Pandey, K. Nakamura, and H. Sugai, Appl. Phys. Express 6, 056202 (2013).

[3] A. Pandey, W. Sakakibara, H. Matsuoka, K. Nakamura, and H. Sugai, Appl. Phys. Lett. 104 (2014) 024111.

5:20pm **PS-MoA10 Detection of Biomedically Relevant Reactive Oxygen Species in Atmospheric Pressure Plasmas**, ***Sandra Schröter****, *J. Bredin*, *K. Niemi*, *J.P. Dedrick*, University of York, UK, *M. Foucher*, Ecole Polytechnique, France, *N. de Oliveira*, *D. Joyeux*, *L. Nahon*, Synchrotron Soleil, France, *J.-P. Booth*, Ecole Polytechnique, France, *E. Wagenaars*, *T. Gans*, *D. O'Connell*, University of York, UK

Cold atmospheric pressure plasmas (APP) are known to be sources for reactive oxygen species (ROS) [1,2], which makes them potentially well suited for biomedical applications. Examples of ROS of interest are atomic oxygen (O) and hydroxyl radicals (OH) because of their high reactivity and as potential precursors for longer lived reactive species. In order for APPs to achieve widespread usage in therapeutic applications, controlled production of the species of interest and hence their quantification is essential. However, at atmospheric pressure this is particularly challenging due to the short lifetimes of excited states as a result of their rapid de-excitation by collision induced quenching. Additionally, determination of the exact gas composition in APPs is difficult, especially in the jet region, where a gradual transition from the feed gas to the ambient air occurs.

*** Coburn & Winters Student Award Finalist**

In order to overcome these challenges, we will present three advanced diagnostic techniques used to quantify absolute densities of reactive species in helium RF APPJs with molecular admixtures, namely picosecond Two-photon Absorption Laser Induced Fluorescence (ps-TALIF) [3], high-resolution Fourier-transform synchrotron VUV absorption [4,5] and UV-Broad-Band Absorption Spectroscopy (UV-BBAS). Under a variation of the water content in the gas phase, absolute densities of OH and O were determined in the plasma core to be in the order of 10^{20} m^{-3} and 10^{19} m^{-3} respectively. The densities were found to increase with increasing water admixture. Additional insight was gained about the air diffusion into the plasma effluent by mapping the lifetimes of the excited atomic oxygen in the axial and radial directions. Typical lifetimes in the order of a few nanoseconds were decreasing away from the nozzle and radial centre of the plasma jet due to diffusion of air from the ambient environment into the jet region.

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[1] M. G. Kong et al., New J. Phys. **11** (2009) 115012

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[3] J. Bredin et al., "Picosecond-TALIF measurements of atomic oxygen in RF driven atmospheric pressure plasma jets", 67th Gaseous Electronics Conference, Raleigh, NC (Nov 2014)

[4] K. Niemi et al., Appl. Phys. Lett. **103** (2013) 034102

[5] L. Nahon et al., *J. Synchrotron Rad.*, **19**, 508 (2012)

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