Real-Time Plasma Monitoring and Detection of Trace H_2O and HF Species in an Argon Based Plasma

Jian Wei
Extrel CMS, 575 Epsilon Drive, Pittsburgh, PA 15238.

(Presented at the 191st Electrochemical Society Meeting, May 4-9, 1997)

A plasma monitoring system was constructed by combining a molecular beam sampling system with a quadrupole deflector energy filter coupled to a quadrupole mass filter. The plasma is sampled via rapid pressure reduction into an intermediate chamber as a molecular beam, eliminating secondary reactions due to collisions with neutrals and other ions after sampling. Ionic species of differing energies are separated through the use of a quadrupole deflector energy filter, allowing differentiation of the source of the ionic signal (plasma versus sheath). To detect trace H_2O and HF in Ar based plasmas, the quadrupole mass spectrometer needs both high mass resolution and high abundance sensitivity. High mass resolution and high abundance sensitivity can be achieved through the operation of a quadrupole in the second Mathieu stability region. Using this high resolution mode, a quadrupole can be used to separate H_2O^+ from $^{36}Ar^{++}$ and HF^+ from and $^{40}Ar^{++}$.

I. INTRODUCTION

The chemical composition of a plasma can be complicated. The challenge in the analysis of the plasma chemistry is to measure the composition as it is in the plasma. The implementation of the molecular beam sampling scheme with a sampling skimmer and two stage differential pumping, enables the sampling of the ions, radicals and neutrals before they collide with one another or with the analyzer chamber wall. By using two distinct pumping stages, the sampling orifice can be made larger, improving sensitivity, while pumping the scattered background gases more efficiently than possible in a one stage system.

The analysis of the plasma ions may also require the sampling of ions in a certain energy range or the mapping of the ion energy distribution. For example, at a suitably high pressure, all of the ions originating directly in the plasma are at the same potential, while there is a potential gradient in the sheath that surrounds the plasma. The incorporation of an energy filter into the mass spectrometer system allows simple characterization of the energy distribution of the ion samples by sampling the plasma at high energy resolution, and varying the center-point energy of the energy filter, resulting in an energy scan. One can characterize ions with a specific energy by simply selecting the appropriate center-point energy.

Detection and monitoring of contamination species in a plasma source is a critical issue in semiconductor manufacturing processes. For example, when Ar plasma is used for the sputtering of metal films, trace water in the plasma source can cause a detrimental effect to the films. Monitoring of the plasma source with a high resolution quadrupole mass spectrometer can allow the detection and quantitation of these contaminants in real time.

The Ar plasma generates both single- and double-charged ions. With a normal residual gas analyzer (RGA), the Ar^{++} ions will cause ion interference at 18 and 20 m/z and prevent the detection of trace H_2O and HF in the Ar plasma. The difference in mass-to-charge ratio between H_2O^+ and $^{36}Ar^{++}$ is 0.0268 amu, and that between HF^+ and $^{40}Ar^{++}$ is 0.0250 amu. The detection of trace H_2O and HF in the Ar based plasma thus requires both high mass resolution and high abundance sensitivity (contribution of the intensity from a given mass at the baseline of the neighboring masses) from the quadrupole mass spectrometer. The operation of the quadrupole mass filter in the second Mathieu stability region has demonstrated a resolving power (full width at half maximum) of better than 0.001 amu at m/z 4 (1) and about 0.005 amu at m/z 28 (2). Second stability operation has also shown an enhancement of more than two orders of magnitude in abundance sensitivity over the operation in the first stability region (1). The addition of the second stability operation to the quadrupole mass spectrometer will greatly enhance its capability in product quality control and monitoring in plasma applications.

II. EXPERIMENTAL

The plasma monitoring measurements were performed on an Extrel two stage molecular beam sampling system, shown in Figure 1. A molecular beam sampling approach with two stage differential pumping is used here to avoid the collision of the ions, radicals and neutrals with one another and with the chamber walls. The floating skimmer, which separates the plasma source and the first stage chamber, provides the mechanism to sample the positive or the negative ions. The beam chopper can be utilized to perform modulated beam measurements to differentiate beam components from residual gas background (scattered species) or, via a suitable bias voltage, to exclude the ions from the plasma source when the neutrals and radicals are being analyzed. Radicals and neutrals are then ionized by the electron impact (EI) ionizer situated in the second stage chamber. The quadrupole deflector energy filter behind the EI ionizer is designed to select ions in a particular kinetic energy range or to provide an energy scan for the ions. The off-axis arrangement for the quadrupole mass filter and ion detector also reduces the background noise from photons, electrons and other high kinetic energy species originating in the plasma.

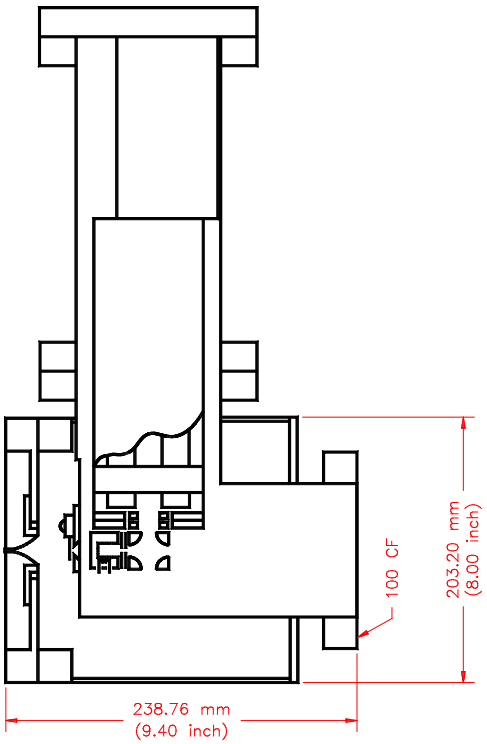

Figure 1. Schematic of the Plasmatron chamber.

The plasma source which was monitored in this work was a DC glow discharge, mounted directly to the molecular beam sampling system chamber. The schematic for the DC glow discharge is shown in Figure 2.

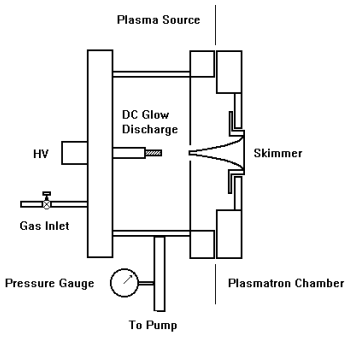

Figure 2. Schematic for DC glow discharge chamber.

The mass filter used in the plasma monitoring study was an Extrel Merlin MEXM-500 system consisting of a 19 mm diameter quadrupole operating at 1.2 MHz. Merlin control electronics were used for instrument control and data acquisition.

Three different gas mixtures were analyzed in the DC plasma. Two mixtures were maintained at 1.0 Torr: 99.99% pure Argon; and a mixture of SF_6 (1%), H_2 (3.67%), Ar (1.0%) and N_2 (balance). 'Pure' C_2H_6 was used for the appearance potential measurements, with the gas pressure maintained at 0.11 Torr.

The DC glow discharge voltage applied to the cathode was about -2kV, except for the C_2H_6 plasma where the voltage was -3.8 kV. The DC glow discharge current was maintained at a fix current ranging from 4 to 9 mA. When the ions from the plasma were analyzed, the EI filament was turned off.

For the high resolution second stability work, an Extrel Merlin MEXM-500B mass spectrometer system (9.5 mm quadrupole operated at 2.1 MHz) was used. The experiment was carried out in a vacuum chamber equipped with two variable leak valves, with ions generated from the resulting residual gasses using an axial molecular beam ionizer with a heated cathode tungsten filament. The ^{36}Ar isotope (abundance: 0.337%) from a leak of Ar gas into the chamber was used to generate the $^{36}Ar^{++}$ ions, and ionization fragments of perfluorotributylamine (PTA) was used to react with the background H_2O to provide the HF^+ ions.

Extrel CMS
575 Epsilon Drive Pittsburgh, Pennsylvania 15238-2838 USA
Tel: (412) 963-7530 FAX: (412) 963-6578 Web: www.extrel.com E-mail: info@extrel.com

III. RESULTS AND DISCUSSION

A. Plasma Monitoring with the First Mathieu Stability Region

Figure 3 shows the EI mass spectrum for the neutral plasma products from the DC glow discharge in C_2H_6. The C_2H_6 pressure in the discharge chamber was maintained at 0.11 Torr and the resulting background pressure in the ionizer chamber was 2.9×10^{-7} Torr. The DC Glow discharge voltage was kept at -3.8 kV, with the discharge current at 7.0 mA.. The ions from the plasma source were blocked off with a high positive voltage on the beam chopper. The electron impact ionizer was operated with the electron energy set at 15 eV. The ion signals at 15, 16 and 26 m/z are due to the products from the glow discharge and these product species are CH_3, CH_4 and C_2H_2 respectively. Figure 4 shows the appearance potential measurements performed on the C_2H_2 species. Estimate on the appearance potential by a linear fit to the data yields a fitted value of 12.33 eV (the true value would require a calibration of the appearance potential with a known standard compound).

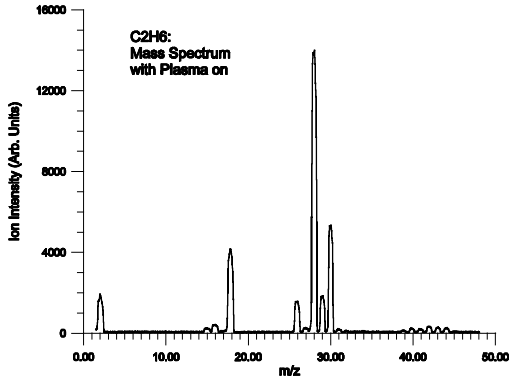

Figure 3. EI mass spectrum for neutral plasma products from C_2H_6.

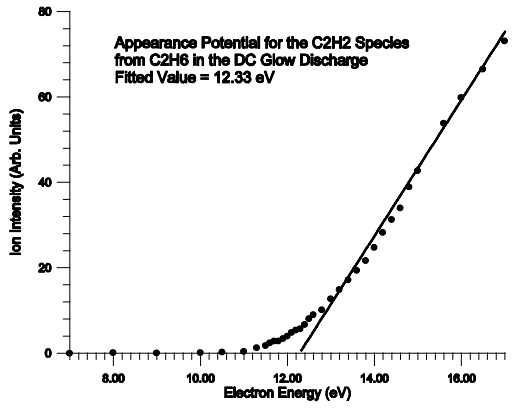

Figure 4. The appearance potential measurements for C_2H_2 Species.

Figure 5 shows the mass spectrum for the positive ions produced from the DC glow discharge in Ar. The Ar pressure in the discharge chamber was maintained at 1.0 Torr. The ions at 40 and 20 m/z are $^{40}Ar^+$ and $^{40}Ar^{++}$ respectively. The naturally occurring ^{36}Ar isotope shows up at 36 m/z and the background H_2O at 18 m/z. Due to a low concentration of doubly charged Ar^{++} ions, the contribution of $^{36}Ar^{++}$ at 18 m/z is very small. The ion energy distribution for the $^{40}Ar^+$ is shown in Figure 6. The $^{40}Ar^+$ from the plasma peaks at about 17.5 eV with a FWHM (full width at half maximum) of about 1eV. This narrow energy distribution indicates that most of the $^{40}Ar^+$ ions got to the quadrupole mass filter without a collision with other gas species. Figure 7 shows the energy scan for the $^{40}Ar^+$ ions coming from the DC glow discharge of Ar at 2.0 Torr. Other parameters were kept the same as those used for Figure 6. The broader distribution of the ion kinetic energy demonstrates that the $^{40}Ar^+$ ions experienced more gas phase collisions at a higher Ar pressure in the plasma chamber.

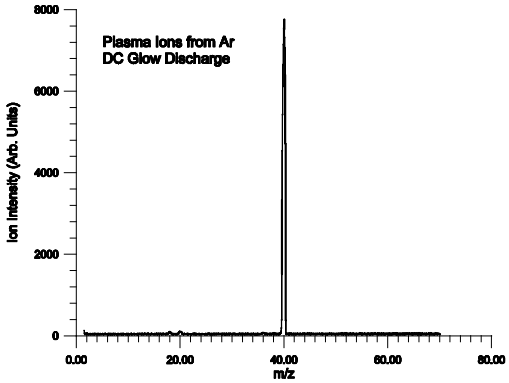

Figure 5. Positive ions from Ar DC glow discharge plasma.

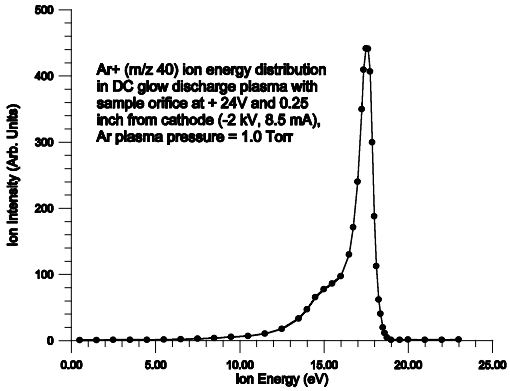

Figure 6. Ion energy scan for Ar^+ ions from the DC glow discharge at 1 Torr.

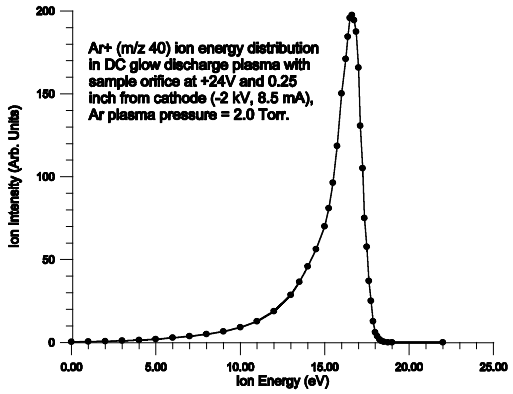

Figure 7. Ion energy scan for Ar^+ ions from the DC glow discharge at 2 Torr.

The energy scans shown in Figures 6 and 7 also demonstrate that the energy resolution of the quadrupole deflector energy analyzer is better than 1 eV.

Figure 8 shows the mass spectrum for the negative ions from the DC glow discharge in the gas mixture containing SF6. The most dominant ions are F^- at 19 m/z. The tailing for the F^- peak indicates the presence of ions with very high kinetic energy. Energy scan on the F^- ions (not shown here) demonstrated a very broad energy distribution (close to 100 eV).

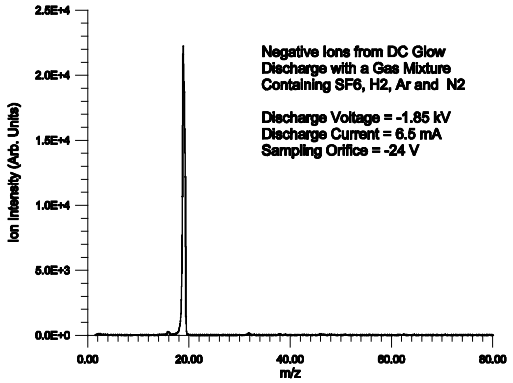

Figure 8. Negative ions from the DC glow discharge in the gas mixture with SF_6.

B. Trace H2O and HF in Ar Based Plasmas and Second Mathieu Stability Region

Figure 9 shows the separation of H_2O^+ and $^{36}Ar^{++}$ in the second stability region. The Ar pressure in the ionizer was 1.05×10^{-5} Torr, with a partial pressure of 3.5×10^{-8} Torr for the ^{36}Ar isotope. The ratio between Ar^+ and Ar^{++} was about 10%. The H_2O^+ ions were due to the residual water background in the ionizer. The FWHM of the H_2O^+ peak is about 0.008 amu. The tailing of the H_2O^+ peak into the mass position of $^{36}Ar^{++}$ is negligible and the abundance sensitivity is only limited by the signal-to-noise level on the baseline. This demonstrates the high resolving power (high mass resolution) as well as the high abundance sensitivity with the second stability operation of the quadrupole mass filter.

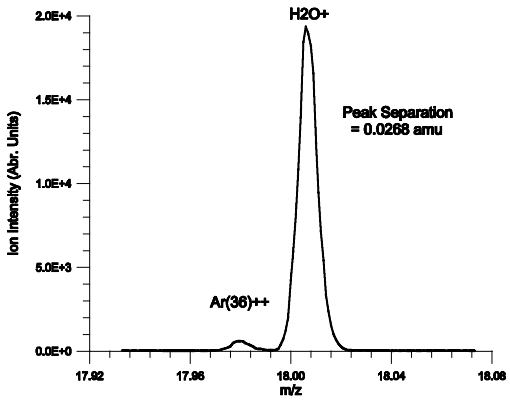

Figure 9. Separation of H_2O^+ and $^{36}Ar^{++}$ in the second stability region.

Figure 10 shows the separation of HF^+ and $^{40}Ar^{++}$ in the second stability region. The Ar pressure in the ionizer was 9.3×10^{-6} Torr. About 10% of the Ar ions produced were Ar^{++} ions and HF^+ ions were produced by the chemical reactions between the ionization fragments of perfluorotributylamine (PTA) with the background H_2O. As a comparison with the results shown in Figure 9, similar mass resolution and abundance sensitivity are shown here.

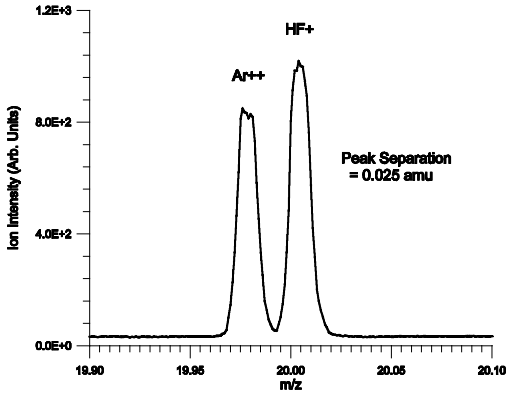

Figure 10. Separation of HF^+ and $^{40}Ar^{++}$ in the second stability region.

IV. CONCLUSIONS

The molecular beam sampling system in plasma analysis avoids the secondary reactions due to collisions with neutrals and other ions after sampling. With two distinct pumping stages, the sampling orifice can be made larger to improving sensitivity, while the scattered background gases

can be more efficiently pumped than possible in a one stage system.

The coupling of a quadrupole deflector energy analyzer with the quadrupole mass filter makes it possible to selectively sample the plasma ions at a certain kinetic energy. This energy analyzer can also provide the energy scan capability for the plasma ions.

The operation of the quadrupole mass filter in the second Mathieu stability region can be used to detect trace H_2O and HF in the Ar based plasma. The small differences in the mass-to-charge ratios between H_2O^+ and $^{36}Ar^{++}$ (0.0268 amu) and between HF^+ and $^{40}Ar^{++}$ (0.0250 amu) require the high mass resolution and high abundance sensitivity in the second Mathieu stability region.

REFERENCES

1. Randall E. Pedder and Richard A. Schaeffer, *Proceedings of the 43rd ASMS Conference on Mass Spectrometry and Allied Topics*, Atlanta, Georgia, May 21-26, 1995.

2. Randall E. Pedder and Richard A. Schaeffer, *Proceedings of the 44th ASMS Conference on Mass Spectrometry and Allied Topics*, Portland, Oregon, May 12-16, 1996.

Extrel CMS
575 Epsilon Drive Pittsburgh, Pennsylvania 15238-2838 USA
Tel: (412) 963-7530 FAX: (412) 963-6578 Web: www.extrel.com E-mail: info@extrel.com