Collisional and Spectroscopic Data Relevant to the Fundamental Processes in Plasmas Containing Si-Organic Admixtures

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1 Introduction

Silicon-organic molecules are used in various plasma-assisted deposition and polymerization applications [1,2]. The most commonly employed monomers [3-7] include tetraethoxysilane (TEOS), $Si(O-CH_2-CH_3)_4$, tetramethylsilane (TMS), $Si(CH_3)_4$, and hexamethyldisiloxane (HMDSO), $(CH_3)_3$-Si-O-Si-$(CH_3)_3$. TMS is among the simplest Si-organic compounds, whereas HMDSO is the simplest of the siloxane compounds, which are characterized by a -Si-O-Si- bridge in their molecular structure. In spite of the practical importance of plasma-assisted material processing using discharge mixtures containing Si-organic admixtures, little is known about the fundamental physical and chemical processes in these plasmas and about the collision-induced decomposition of these molecules in the plasma. Ionization studies under single collision conditions combined with mass spectrometric studies in the actual plasma have shed some light on the processes in TMS-containing plasmas [8,9] and similar studies are currently underway for TEOS and HMDSO [10]. In addition to mass spectrometry, optical plasma diagnostics methods can also shed light on the fundamental plasma processes [11]. Optical emissions from plasmas containing Si-organic molecules have been studied to some extent [12]. Optical emissions in the visible and near-ultraviolet region of the electromagnetic spectrum produced by controlled electron-impact under single collision conditions on TMS, TEOS, and HMDSO have been studied recently in our group [13,14].

Researchers at the Institut für Niedertemperatur-Plasmaphysik (INP) in Greifswald, Germany have been engaged in a comprehensive series of experimental studies aimed at (i) the measurement of absolute partial ionization cross sections for various Si-organics under controlled single collision conditions, (ii) in-situ studies of the behavior and properties of the neutral and ionic components in realistic deposition plasmas containing Si-organic admixtures, and (iii) correlating the single collision observations with the plasma observations. This effort is complemented by studies of the visible, near-ultraviolet, and vacuum ultraviolet emissions produced by controlled electron impact on these Si-organic cmpounds carried out at the Stevens Institute of Technology in Hoboken, NJ, USA.

2 Experimental Details

The experimental apparatus and the data acquisition and analysis procedures for the photoemission studies employs a crossed beam arrangement where the interaction region is defined by the intersection of the electron beam and the gas beam. A five-element electron gun

produces a spatially well defined electron beam with a current of typically 80 μA at 100 eV. The energy of the electron beam can be varied over the range of 5 - 200 eV with an energy spread of about 0.8 eV (full width at half maximum) at an energy of 100 eV. A multicapillary array produces the gas beam which crosses the electron beam at right angles. The estimated gas density in the interaction region is of the order of 10^{12} molecules/cm^3. A precision leak valve controls the backing pressure in the gas line to the multicapillary array. This pressure was monitored by a Baratron capacitance manometer. The analysis/detection system for the vacuum ultraviolet (VUV) emissions is positioned mutually perpendicular to both the gas beam and the electron beam. The VUV emissions are spectrally analyzed using a Minuteman model 302-VM 0.2m vacuum monochromator of the Seya-Namioka design and the VUV photons are subsequently detected with by a channel electron multiplier (CEM). The output signal of the CEM is fed into a standard circuit for single photon counting. The monochromator is equipped with a holographic grating for the wavelength range from 50 to 250 nm. The monochromator and detector are evacuated to a pressure of 5×10^{-7} Torr under operating conditions. The main vacuum chamber which houses the crossed-beam set-up is evacuated to a pressure in the low 10^{-7} Torr range without gas load which rises to about $2\text{-}5 \times 10^{-5}$ Torr under operating conditions.

At the INP, Dr. Schmidt and his co-workers have a high-resolution (m/Δm = 40 000) double focusing sector field mass spectrometer MCH 1310 with a Nier-type electron-impact ion source [15,16]. The target gas pressure in the ion source, which is typically in the range 0.1 to 1 mPa compared to a background pressure of 0.001 mPa, is measured with a spinning rotor viscosity gauge. The electron gun is operated with a stabilized electron beam current of 10 •A emitted from a directly heated tungsten band cathode. The impact energy can varied from 5 eV to 100 eV. The energy spread of the electron beam, which is collimated by a weak longitudinal magnetic field of 200 G, is about 0.5 eV (FWHM). The ions are extracted from the ionization region by a penetrating electric field. The acceleration voltage between the ion source and the entrance slit of the mass spectrometer is 5 kV. Argon, which is used as reference gas, is always added to the target gas under study for calibration purposes. The ion efficiency curves (relative ionization cross sections) are measured simultaneously for Ar and the target gas in a well-defined mixture in an effort to ensure equal operating conditions for the detection of all ions. The measured relative partial ionization cross sections are put on an absolute scale by normalizing the total single ionization cross section for a given species relative to the total Argon ionization cross section of 2.77 x 10^{-16} cm^2 at 70 eV.

Recently, the ion optics for the extraction, acceleration and deflection of the product ions was rebuilt based on ion trajectory simulations [16] in conjunction with in-situ experimental studies in an effort to minimize and/or quantify the discrimination of energetic fragment ions. The modified mass spectrometer can now be operated either in a high mass resolution mode (with significant discrimination effects present) or in a high extraction efficiency mode (by partially sacrificing the high mass resolution capability). All measurements routinely employ a sweep of the ion beam across the entrance slit of the mass spectrometer and absolute cross sections are obtained by integrating the ion signal over the complete ion beam profile. The advantage of the INP instrument is its superior mass resolution and a very large dynamic range which allows very small ionization cross sections (down to 1 x 10^{-20} cm^2) to be measured with high precision. On the other hand, even with the new ion extraction optics, the instrument has a limited capability of extracting and detecting energetic fragment ions and, of course, it can only investigate stable targets.

Very recently, a second apparatus has become available at the INP, a time-of-flight mass spectrometer, which will be operational by the end of this year. The new instrument combines the

capability to extract and detect very efficiently energetic fragment ions with a large dynamic range, but its use is still limited to stable targets and has a much reduced mass resolution compared to the high-resolution instrument.

The in-situ plasma measurements are carried out in a 13.56 MHz rf capacitively coupled discharge reactor. The two electrodes, which have a diameter of 12.8 cm each, are separated by a gap of 4 cm. Typical rf powers are from 15 to 150 W. The pressure in the reactor ranges from 1-20 Pa and typical gas flow rates are 10 sccm of the carrier gas (Ar) and 0.1 – 0.2 sccm of the Si-organic admixture. The reactor is coupled to a VG SXP 300H plasma monitor (mass spectrometer) which is also equipped with an ion energy analyzer in order to determine the kinetic energy distribution of the various ions in the plasma. The plasma monitor, whose mass dependent detection sensitivity has been carefully calibrated, can be used to probe either the neutral or the ionic plasma component.

3   Some Selected Results

The ionization cross section measurements for TMS have been completed. It was found that by far the most dominant channel is the formation of the $Si(CH_3)_3^+$ fragment ion with a maximum cross section value of about 1×10^{-15} cm^2 which accounts for about 50% of the total TMS ionization cross section. The maximum TMS parent ionization cross section is less than 2% of that value. Based on our measured partial ionization cross sections for more than 20 fragment ions and on their measured appearance energies we proposed a collision-induced decomposition scheme for the TMS molecule in low-temperature plasmas. Three major decomposition routes were identified which all involve the total or partial removal of a CH_3 methyl group.

Ionization cross section studies for the other two Si-organics have also been completed and the results are in many respects similar to what was found for TMS, viz. very small parent ionization cross sections, a dominance of dissociative ionization processes, a small number of fragment ions with comparatively large ionization cross sections. In contrast to TMS, the ionization data for TEOS and HMDSO are more difficult to interpret on account of the much more complicated cracking pattern and the much larger number of fragment ions with appreciable cross sections for their formation.

Detailed in-situ studies in realistic deposition plasmas containing Ar as the carrier gas and small (1-2%) admixtures of TEOS and HMDSO revealed a variety of noteworthy findings: whereas the ionic plasma component in both cases still reflected to some extent the cracking pattern of the parent molecule, there was little evidence of the parent cracking pattern in the neutral component. A common feature was the significant increase (in some cases by 2-4 orders of magnitude) of certain small fragment ions in the plasma compared to calculated ion abundances using the single collision ionization cross sections. Furthermore, we found ample evidence of the formation of "new" ions in the plasma by various plasma chemical reactions. This indicates that secondary processes such as dissociation into neutral ground-state fragments followed by subsequent electron collisions and ion-molecule reactions play a very important role in the plasma chemistry of deposition plasma containing Si-organic admixtures.

The comparatively large values of the ionization cross sections for TMS, TEOS, and HMDSO (relative to e.g. Ar) and the relatively low appearance energies of many fragment ions (7-10 eV compared to 15 eV for Ar) explain why a small TEOS admixture of 2% to an Ar plasma leads to a situation where the ionization balance in the plasma is completely determined by the Si-organic admixture.

The photoemission studies involving TMS, HMDSO, and TEOS in the various spectral regions (vacuum ultraviolet, near-ultraviolet, and visible) revealed several common features:

(1) the vacuum ultraviolet spectra are completely dominated by the H Lyman series
(2) the Lyman-α and Lyman-β lines are heavily influenced by cascading from higher H states
(3) the measured appearance energies indicate that partial fragmentation processes are the dominant break-up mechanisms leading to the formation of excited H fragment atoms
(4) the near-ultraviolet and visible spectra contain mostly the hydrogen Balmer series and emissions from the excited CH radical
(5) the TMS and HMDSO emission spectra show also the presence of atomic Si emissions
(6) in general, the measured emission cross sections are comparatively small

Future work will focus on a continuation of the work in TEOS and HMDSO and will eventually also involve other Si-organics, e.g. dimethylsilane, $(CH_3)_2SiH_2$, which is used in processing applications which require environmentally "green" processing gases.

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