Ion contributions to gas–surface interactions in inductively-coupled fluorocarbon plasmas

Michael F. Cuddy, Joshua M. Blechle, Ellen R. Fisher *

Colorado State University, Department of Chemistry, Fort Collins, CO 80523-1872, United States

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ABSTRACT

The role of plasma-generated ions for plasma processing of substrates was investigated to develop a deeper understanding of the phenomena which occur at plasma–surface interfaces. Energy analyses were performed for nascent ions for a range of fluorocarbon (FC) plasma source gases, including CF_4, C_2F_6, C_3F_8, C_3F_6, and hexafluoropropylene oxide (HFPO). Mean ion energies ($<E_i>_{total}$) for all observed nascent ions in a given plasma system are strongly correlated with applied rf plasma power, with total average energies ranging from 15 to 90 eV. Notably, $<E_i>_{total}$ values also influence surface scatter of CF_x radicals from deposited FC films, determined from imaging of radicals interacting with surfaces (IRIS) experiments. In ion-limited IRIS studies, scatter coefficients for CF_x species decrease considerably relative to ion-rich systems under all conditions, suggesting that ion-mediated processes are crucial for determining CF_x behavior at the gas–surface interface. Mass spectrometric techniques were used to determine the relative gas-phase proportions of oligomeric film precursors. The amount of oligomeric species relative to CF_3 in all systems influences film deposition significantly, substantiating the concept that oligomers contribute to FC film growth. Speculations on the role of low-energy ions in the plasma systems are presented for their expected contributions to FC film propagation.

1. Introduction

Plasma ions are significant driving forces for plasma chemistry, often controlling both surface and gas-phase reactions. Indeed, ion–surface interactions are a central aspect of many plasma-based modification techniques as ions can assume dual roles as contributors to film growth for plasma deposition of films or as etchants for removal of material. To this end, the mechanisms of ion–surface interactions in plasma systems are of significant interest and have been studied extensively in both experiment and simulation [1–3]. Energetic ions may be employed to create active sites (broken chemical bonds) at a surface through ion bombardment, thereby promoting "ion-induced" film growth [4]. Concurrently, these ions may also remove material from a surface via chemical and/or physical sputtering [5]. The propensity for ions to experience highly exothermic gas-phase recombination reactions is also significant; neutral radicals formed by such processes can produce aggregates through a cascade of additional gas-phase reactions [6]. As such, it is imperative to consider the contributions of ions to plasma processing of materials for any materials application.

In the late 1980s, Armentrout and coworkers began studying gas-phase ion–molecule reactions related to Si-based plasma processing [7–15]. Over a period of ~15 years, they investigated the kinetic energy dependence of a number of fundamental ion–molecule reactions relevant to plasma chemistry using guided ion beam mass spectrometry (GIBMS) [7]. The primary goals of this work were to provide energy-dependent cross sectional data for ion–molecule reactions occurring in a range of plasma systems along with accurate thermochemical data for both ionic and neutral plasma species. Interestingly, one of the notable findings from this work was a distinct coupling between translational and electronic energy during ion–molecule reactions involving rare gas ions and molecules such as SiH_4 and CF_4 [9,11,16]. Thus, this pioneering GIBMS work on ion–molecule reactions of interest to the semiconductor industry revealed substantial fundamental thermochemical and kinetic data. Moreover, it afforded significant insight into the underlying chemical mechanisms in a range of plasma systems.

One specific category of plasma systems that continues to realize significant interest from the plasma community is fluorocarbon (FC) plasmas. In particular, FC systems are widely employed in both deposition and etching regimes for applications ranging from fabrication of microelectronic devices to the development of novel materials with specific surface properties [17–24]. Plasma-enhanced chemical vapor deposition (PECVD) of FC films is a complex process, often involving the interaction of a multitude of gas-phase neutrals, radicals, excited species, and ions at a surface [25–27]. Ions are integral to FC plasma processes, including selective etching in the case of high-energy ions [28,29], and film

deposition in the case of low-energy ions [30,31]. FC plasma-related GIBMS work in the Armentrout group focused on the reactions of rare gas ions, O^+, and O_2^+ with CF_4 and C_2F_6 [16,32,33]. This work elucidated the kinetic energy-dependent rate constants for dissociative reactions of C_xF_y species and rare gas ions so vital for accurate modeling of plasma systems. In the O_2^+ and O^+ systems, they found that the reactions of O^+ with C_xF_y precursors led to reactive etchants such as F atoms. In all of these systems, CF_3^+ was a dominant product ion, with $C_2F_5^+$ also a strong constituent in the C_2F_6 systems. Su and coworkers conducted similar studies for CF_3^+ reactions with hexafluoropropylene oxide (HFPO) using selected ion flow tube (SIFT) mass spectrometry and determined that the only product of this reaction is $C_3F_7^+$ [34]. Notably, in both the GIBMS and SIFT studies, data were collected under single collision conditions, whereas in plasmas, multiple gas-phase and gas-wall collisions can occur, potentially significantly altering both the energetics and composition of the plasma.

Our laboratory has previously demonstrated that ions have a significant influence over the behavior of CF_2 species at the plasma–surface interface [35,36]. Specifically, mean ion energies for CF_2^+ correlate linearly with scatter coefficients observed for CF_2 in FC systems. Despite this body of work, a comprehensive analysis of ions in FC plasmas and their behaviors at the gas–surface interface does not exist. Thus, we aim to explicate here the mechanisms by which ions influence CF_x scatter from surfaces during plasma processing and the contributions of gas-phase FC species to film deposition by PECVD.

Characterization of the types of ions present in a FC plasma and the energies of those ions is important both for plasma modeling and for understanding the key reactions that ultimately lead to surface modification. For instance, in other polymerizing plasma systems, such as allylamine, the interactions of gas-phase ions and molecules lead to the formation of oligomeric species [37]. Indeed, oligomeric gas-phase fluorocarbon species are thought to be chief contributors to polymerization and film initiation [38]. Models developed by Zhang and Kushner demonstrated the profound effect of increasing ion energies on CF_2 loss mechanisms at surfaces. They showed that the net loss of $CF_{2(s)}$ increased dramatically over $CF_{2(g)}$ sticking when the plasma sheath voltage potential exceeded 78 V [39]. CF_x ($x = 1–3$) species are of particular interest in these systems because of their dichotomous and dynamic roles as etch products or deposition precursors [40].

Here, we have employed mass spectrometric measurements via a high-energy mass spectrometer to not only identify nascent gas-phase ions and oligomers directly from the plasma source, but also to analyze the energies of those species. The energy analysis capability of our instrument allows for measurement of ion energy distributions (IEDs) over a broad energy range (1000 eV) with the ionizer off to sample only ions produced by the plasma itself. The mean ion energy, $<E_i>$, can be calculated from an IED via Eq. (1), where E represents the ion energy in eV for a particular nascent ion in the plasma [41]. The instrument can also be operated in

$$< E_i > = \frac{\int f(E)E \, dE}{\int f(E) \, dE} \tag{1}$$

residual gas analysis (RGA) mode with its ionization source on to observe all the gas-phase plasma species present, including oligomers formed through recombination reactions. The fundamental understanding of the behavior of gas-phase ions, coupled with the knowledge concerning the constituents of the plasma bulk, allow us to develop plasma processing mechanisms based upon complementary gas–surface interface data.

We have previously examined the surface reactivity of CF_x species using our imaging of radicals interacting with surfaces (IRIS) technique [35,36,40,42–45]. Generally, a significant decrease in the

observed surface scatter coefficient of CF_2, $S(CF_2)$, is commensurate with the removal of ions from the system, either through implementation of a grounded mesh or via application of a substrate bias. We have not, however, expressly developed a complete body of work regarding the effect of ions on CF and CF_2 surface reactivity over a broad range of plasma parameters, such as applied rf power (P) and choice of plasma precursor. The effect of ions on the observed scatter coefficient for CF_x radicals can be gauged by determining $\Delta S(CF_x)$, defined as the difference between the ion-rich case and the ion-limited case, Eq. (2):

$$\Delta S(CF_x) = S(CF_x)_{ions} - S(CF_x)_{ion\text{-}limited} \tag{2}$$

In the present studies, the ion-limited case was achieved by biasing the substrate exposed to the plasma molecular beam with a +200 V direct current to repel positively charged species [46]. Mitigating ion flux to the surface allows for examination of the processes which occur exclusive of ion influence. Thus, $\Delta S(CF_x)$ values provide an avenue for inferring the role of ions as they dictate CF_x behavior at the gas–surface interface. Ultimately, the correlation between plasma properties and the phenomena occurring at the plasma–surface interface can be used to more fully understand the effect of ion contributions in FC systems.

2. Materials and methods

Inductively-coupled plasmas were generated in glass tubular reactors, described previously [47–50], by coupling 13.56 MHz rf frequency through an eight turn Ni-plated copper coil. Individual plasma precursors used in this work included CF_4, C_2F_6, C_3F_8, C_3F_6 (all Airgas, >95%), and HFPO (Aldrich, 98%). Precursor flow rates ranged from 4 to 6 sccm, resulting in total system pressures of ∼50 mTorr above base, as measured by a capacitance manometer. Applied powers (P) ranged from 50 to 200 W. The reactors could be interfaced to either a mass spectrometer or the IRIS apparatus to sample species of interest and perform relevant experiments.

Mass spectra and energy scans were acquired for nascent ions produced in the plasma using a Hiden PSM003 mass spectrometer described elsewhere [51]. Briefly, the instrument consists of an ion extractor, electron-impact ionization source, a ±1000 V Bessel box energy filter, and a triple-filter quadrupole with secondary electron multiplier detection. For detection of nascent ions, the ionization filament was turned off. Species generated in the plasma entered the probe through a 600 μm sampling orifice located 5 cm from the exit orifice of the plasma reactor. The base pressure of the apparatus was maintained at ∼10^{-8} Torr through use of a 60 l/s turbomolecular pump backed by a 400 l/min mechanical pump. The operating pressure of the instrument during plasma sampling was typically ∼10^{-5} Torr, such that the mean free path of plasma species (>50 cm) exiting the reactor was significantly greater than the distance traversed en route to the sampling orifice. IEDs were acquired for all major nascent ions identified in the mass spectrum of each plasma feed gas by selectively filtering appropriate mass-to-charge ratios and scanning a 150 eV energy range. Oligomeric species, including gas-phase plasma recombination products, were monitored in RGA mode, with the ionization source on (with ionization energy of 70 eV). The relative intensities of oligomeric species were gauged by comparison to the CF_3^+ ion signal intensity, as CF_3^+ was the most abundant species observed in each of the plasma systems discussed here and its intensity (i.e., counts) did not change appreciably over the course of experiments for a given FC plasma system, thereby acting like an actinometer does in optical emission experiments. Thus, comparison of signal intensities to CF_3^+ is a useful way to gauge variations in species quantity under changing plasma conditions.