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Low-energy collisions of CF_3^+ ions with a hydrocarbon covered surface: Scattering, chemical sputtering, and reactive collisions

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Abstract

The interaction of CF_3^+ ions with a stainless steel surface covered with hydrocarbons has been studied with a recently constructed BESTOF tandem mass spectrometer as a function of the collision energy from about 0 up to 60 eV. Whereas the efficient reflection of projectile ions at low collision energy and the efficient ejection of chemically sputtered ions at higher collision energies found here are in semiquantitative agreement with a previous report, results obtained here also demonstrate that reactive ion surface collisions are an important feature of CF_3^+ impact on the hydrocarbon-covered surface leading to the formation of various fluorohydrocarbon ions such as CH_2F^+, CH_2CF^+, and CHF_2^+. (Int J Mass Spectrom 177 (1998) 105–110) © 1998 Elsevier Science B.V.

Keywords: Tandem mass spectrometry; Ion-surface reactions, CF_3^+; Chemical sputtering

Introduction

Dielectric etching using fluorocarbon plasmas is a major tool in the integrated circuit (IC) manufacturing industry. Models of low-temperature, nonequilibrium plasmas, in particular for the description of the physical phenomena, have developed rapidly [1]. However, lack of fundamental data for the most important species is the single largest factor limiting the successful application of such models to emerging problems of industrial interest [1]. Heterogeneous (surface) reactions are at the heart of plasma materials processing techniques, but unfortunately in many instances these plasma/wall processes are less well understood than are gas phase processes. Even for some of the key species, such as SiH_4 and CF_4, the knowledge on surface reactions is sketchy at best. A similar situation exists for data concerning plasma wall interactions of relevance to the plasma edge of fusion tokamaks [2,3].

Clearly, identifying and studying specific plasma-surface reactions in the complex plasma environment is extremely difficult. Nevertheless, because of the urgent need for these data [1] we have recently started a series of measurements under the simplified laboratory conditions where the interaction of mass selected ions with a surface can be studied in the range of tens of eV laboratory energy [4–6]. When low energy polyatomic ions interact with surfaces, a variety of processes may occur [7], including elastic scattering, inelastic scattering [possibly followed by dissociation, a process known as surface induced dissociation

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(SID)], charge exchange, particle deposition, and chemical reactions (sometimes summarizes as surface induced reactions (SIR) including chemical sputtering, abstraction reactions, etc.). The extent to which a specific process occurs obviously will depend on several factors, among which the chemical nature of the projectile ion and the surface are particularly important.

In a recent study by Cooks and co-workers [8] interaction of CF_3^+ ions with a hydrocarbon covered stainless steel surface resulted in a surprising observation: at lower collision energy the major secondary ion is the intact CF_3^+ projectile ion, at higher energies ions are present in the secondary spectrum in large abundance which appear to be due to ionization of hydrocarbons at the surface of the stainless steel. Cooks and co-workers [8] therefore stated that there is no evidence at any kinetic energy studied for dissociation of the projectile ion and they did also not report the occurrence of other types of ion/surface reactions. In the present study we have repeated these measurements with our recently constructed BESTOF (consisting of a *B*-sector field, *E*-sector field, *S*urface and *T*ime *O*f *F*light mass spectrometer) apparatus [4–6] which allows the investigation of ion/surface reactions with high mass and energy resolution. Whereas the efficient reflection of projectile ions at low collision energy and the efficient ejection of chemically sputtered ions at higher collision energies found here are in semiquantitative agreement with the previous report of Vincenti and Cooks [8], results obtained here also demonstrate that reactive collisions are an important feature of CF_3^+ impact on hydrocarbon-covered surfaces leading to the formation of various fluorohydrocarbon ions.

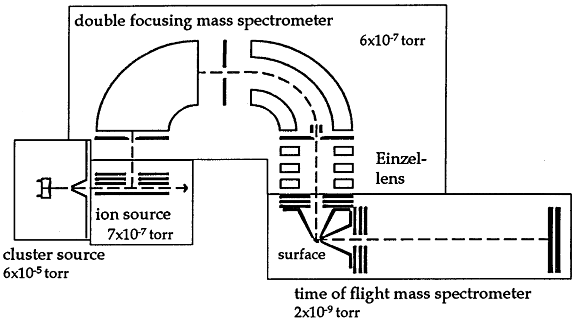

Fig. 1. Schematic view of the experimental apparatus BESTOF.

Experiment

Fig. 1 is a schematic view of the experimental set-up described in more detail in [9] (see also [4–6]). In the present experiments CF_4 was directly introduced into a Nier-type ion source and ionized by electron impact of 80 eV electrons. The ions are extracted from the source region and accelerated to 2930 V for mass- and energy-analysis by a double-focusing two-sector-field mass spectrometer. After passing the exit slit of the mass spectrometer ions are refocused by an Einzel lens and deceleration optics positioned in front of the surface. The collision energy of ions impacting on the surface is defined by the potential difference between the ion source and the surface. The potential difference (hence, the collision energy) can be varied from zero to about 2 keV with a resolution better than 0.2 eV. We have determined the energy spread of the primary beam by using the surface as a retarding potential and measuring the total ion signal as a function of the surface potential. The energy spread (as low as 100 meV) is given by the FWHM of the first derivative of the total ion signal (for details see [10]). Field penetration effects are minimized by shielding the surface by conical shield plates. A fraction of the secondary ions formed at the surface exit the shielded chamber through a 1 mm diameter orifice and are extracted and accelerated into the analyzer mass spectrometer, which is a linear time-of-flight mass selector with a flight tube about 80 cm in length. The mass selected ions are detected by a channelplate which is connected to a pulse counting unit and a laboratory computer. Background gas pressure in the target region is in the 10^{-9} Torr range, consequently the stainless steel target is covered by several monolayers of hydrocarbons originating primarily from pump oils.

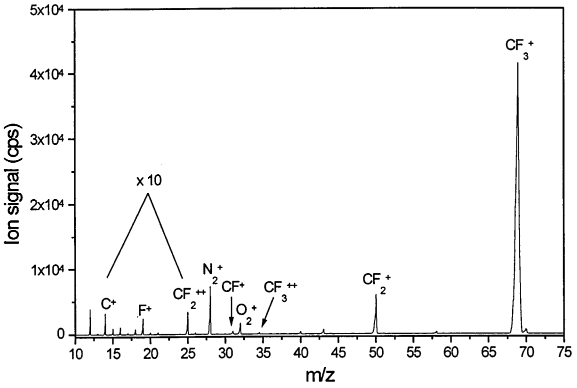

Fig. 2. Primary ion mass spectrum after ionization of CF_4 with an 80 eV electron beam.

Results and discussion

The primary positive ion mass spectrum after ionization of CF_4 by 80 eV electrons shown in Fig. 2 is dominated by CF_3^+ at $m/z = 69$. The molecular ion CF_4^+ is metastable and not observed in Fig. 2. Other fragment ions much less abundant than CF_3^+ include CF_2^+ ($m/z = 50$), CF^+ ($m/z = 31$), F^+ ($m/z = 19$), C^+ ($m/z = 12$) and weak abundances of doubly charged ions CF_3^{2+} ($m/z = 34.5$) and CF_2^{2+} ($m/z = 25$). The ion signals N_2^+ and O_2^+ result from traces of air in the gas inlet.

The intensity of CF_2^+ was insufficient for surface impact studies and only CF_3^+ was investigated. The secondary ion mass spectra after surface impact of CF_3^+ at collision energies of 20, 25, 30, 40, 50, and 60 eV are shown in Figs. 3 and 4. The most abundant ion at 20 eV is the undissociated scattered projectile ion. The secondary ion signal after surface impact was very low, at least three orders of magnitude smaller than the primary ion signal reflected from (i.e. not colliding with) the target at zero collision energy. This is evidence for efficient neutralization of the incoming projectile ions. The possibility that negative ions are formed by electron attachment along with or subsequent to CF_3^+ neutralization has not been investigated in the present study (for previous studies of the dissociation of this ion in the 100 to 600 eV range including the formation of negative ions see Koppers et al. [11]). When the collision energy is increased above 25 eV chemically sputtered hydrocarbons become the most abundant ions in the spectrum. Consistent with the previous study of Cooks and coworkers [8] relatively smaller abundances of secondary ions at $m/z = 33$, 45, and 51 are readily observable. These ions cannot be interpreted as chemically sputtered hydrocarbon adsorbates (with the exception of $m/z = 51$ which could be written as $C_4H_3^+$; this ion has however not been observed in our previous studies as a chemically sputtered ion) or as fragments of the projectile ion. Rather they result from reactive collisions of CF_3^+ with the surface adsorbates to generate the reaction products CH_2F^+, CH_2CF^+, and CHF_2^+.

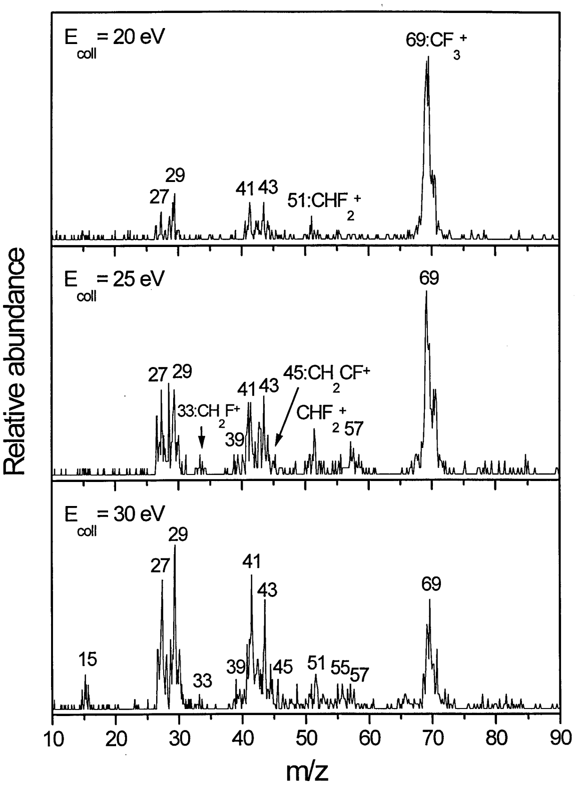

Fig. 3. Secondary ion mass spectra after surface impact of CF_3^+ at collision energies of 20, 25, and 30 eV.

Two mechanisms may be suggested to rationalize the occurrence of ion surface reactions. First, the incoming CF_3^+ may react with alkyl radicals (or molecules) with exchange of fluorine atoms for hy-

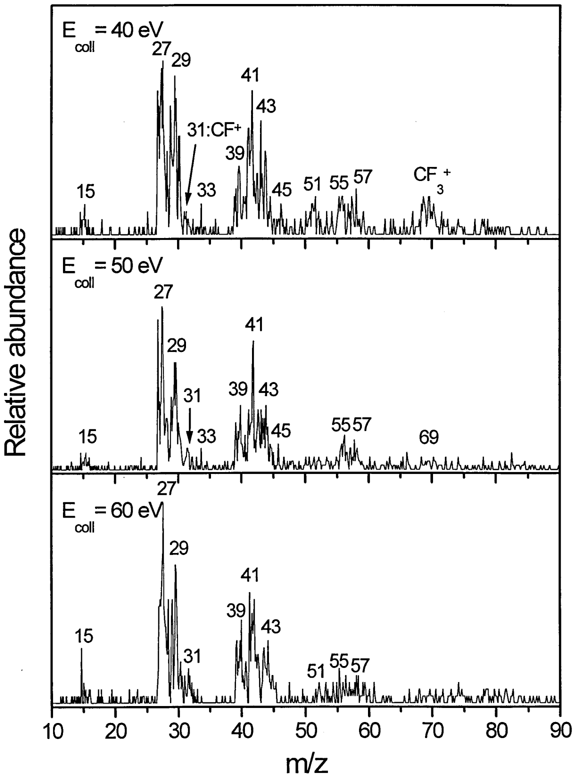

Fig. 4. Secondary ion mass spectra after surface impact of CF_3^+ at collision energies of 40, 50, and 60 eV.

drogen or methylene groups. A possible set of reactions is

$$CF_3^+ + RH \rightarrow CHF_2^+ + RF \tag{1}$$

$$CF_3^+ + RCH_3 \rightarrow [CF_3CH_3]^+ + R \tag{2}$$

$$[CF_3CH_3]^{+*} \rightarrow CH_2F^+ + CHF_2 \tag{2a}$$

$$[CF_3CH_3]^{+*} \rightarrow CH_2CF^+ + HF + F \tag{2b}$$

An alternative reaction mechanism favored by previous researchers is dissociative charge transfer with hydrocarbon adsorbate molecules. The neutralized primary ion undergoes an ion molecule reaction on the surface and an even-electron cation is released, shown schematically as follows:

$$CF_3 + CH_3^+ \rightarrow CH_2F^+ + CHF_2 \tag{3}$$

$$CF_3 + CH_3^+ \rightarrow CH_2CF^+ + HF + F \tag{4}$$

$$CF_3 + H^+ \rightarrow CHF_2^+ + F \tag{5}$$

Both reaction schemes are speculative, with the major uncertainty being lack of any information on the nature of the hydrocarbon adsorbate molecules.

At higher collision energies an additional peak is visible in the spectra, CF^+ ($m/z = 31$), first detected at 40 eV collision energy. This peak might plausibly be attributed to surface induced dissociation (SID) of the primary ion CF_3^+. However, if the origin of CF^+ is SID of CF_3^+, one would expect to observe CF_2^+ at a slightly lower collision energy. The lowest energy SID product is CF_2^+ (+F), which requires only 6 eV, whereas the reaction

$$CF_3^+ \xrightarrow{\text{SID}} CF^+ + F_2 \tag{6}$$

is endothermic by 7.6 eV [12]. Thus the absence of CF_2^+ in our spectra supports the prior suggestion by Cooks and co-workers that SID is not observed for CF_3^+ impact on hydrocarbon films [8]. A more plausible explanation for the origin of CF^+ is further dissociation of one of the reaction products, probably the dissociation

$$CHF_3^+ \rightarrow CF^+ + HF + F \tag{7}$$

As noted earlier, the major secondary ions are alkyl radical cations sputtered from the surface (chemical sputtering). By analogy to gas phase hydride transfer reactions we may write the generic dissociative charge exchange reaction

$$CF_3^+ + C_iH_j \rightarrow C_iH_{j-1}^+ + CHF_3 \tag{8}$$

Charge transfer reactions with ion-impact-generated radicals could also be written for these reaction products. The particularly stable, even-electron methyl, ethyl, propyl, and butyl ions are prominent, accompanied by the corresponding unsaturated ions, which have lost H_2 or alkene molecules in higher energy sputtering reactions. The product ion spectra shown in Figs. 3 and 4 show a monotonic shift in relative intensities of sputtered ions to the dehydrogenated ions in each correlated pair and to smaller carbon numbers as collision energy increases.

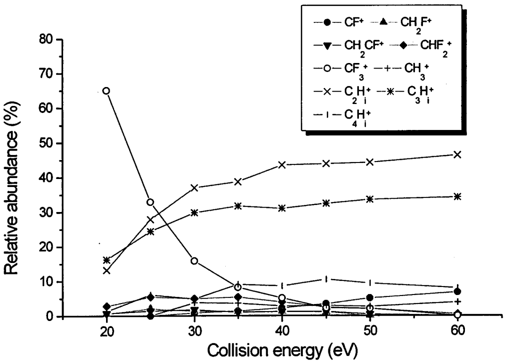

Fig. 5. Collision energy dependence of secondary ions.

The collision energy dependence of all product ions is summarized in Figs. 5 and 6. The dominance of chemically sputtered hydrocarbons is clearly demonstrated in Fig. 5. The strong decline in primary ion intensity at about 25 eV in Fig. 5, accompanied by an increase in the sputtered ion signal, is evidence for a threshold energy for opening the sputter ion channel. In contrast with previous work, we point out the clear evidence for surface reactions in our experiments. The total relative abundance of fluorine-containing ion-surface reaction products is of the order of 10% of the sputtered organic ion yield over the energy range investigated. To further illustrate this point, the fluorine-containing reaction product relative abundances are presented in an enlarged scale in Fig. 6. The carbon pickup fragment, $C_2H_2F^+$, is a minor component at all energies and declines with increasing collision energy. With increasing energy CF^+ becomes the dominant product channel.

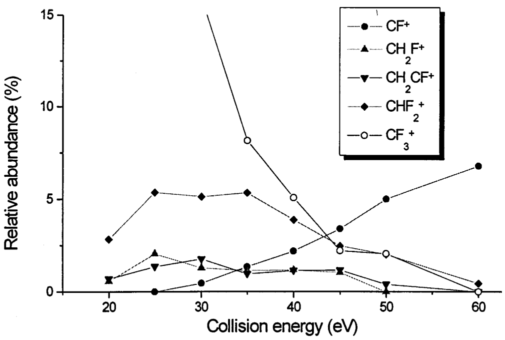

Fig. 6. Collision energy dependence of secondary ions (data of Fig. 5 in enlarged scale).

Conclusions

The identities, relative abundances, and energy dependence of formation of secondary ions resulting from the collision of CF_3^+ with a stainless steel surface covered with polylayers of adsorbed hydrocarbons reported here are in semiquantitative agreement with the previous report of Vincenti and Cooks [8]. In particular the efficient reflection of primary ions from the surface at collision energies below a certain threshold value and the efficient ejection of a readily characterized mixture of sputtered even-electron hydrocarbon ions above this threshold are the most distinctive features of both experiments. In our experiments the threshold for sputtering of organic cations is about 10 eV lower than reported in their paper. This may be related to the different scattering experimental conditions, for instance the angles utilized in the two experiments are different (i.e. the mean impact angle 45 and 60 degrees and the detection at the specular angle). Recent experiments have demonstrated a strong dependence on scattering angle of elastic, inelastic, and reactive scattering from the same type of surface [13]. In addition, Fig. 6 demonstrates that reactive collisions are an important feature of CF_3^+ impact on hydrocarbon-coated surfaces. The previous report [8] did not consider the low abundance of fluorine-containing ions significant and concluded that the only secondary ions were sputtered hydrocarbon ions. Nevertheless, the relative intensities of fluorohydrocarbon ions found in our experiments are similar to the intensities reported in their Table 1 [8], confirming that reactive collisions are part of the surface reactivity of perfluoromethyl cations.

Acknowledgements

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