Electron-surface Interactions

Electron-stimulated desorption from the products of chemisorption of trifluorochloroethene on silicon

Gregory D. Cooper[a], Jason E. Sanabia[b], Jon Orloff[c], John H. Moore[d],*

[a]*Department of Physics,* [b]*Chemical Physics Program,* [c]*Department of Electrical and Computer Engineering and* [d]*Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA*

Abstract

Electron-stimulated desorption of F^+, F^-, Cl^+ and Cl^- from Si(100) exposed to $F_2C=CFCl$ has been observed as a function of electron energy and surface temperature. $F_2C=CFCl$ dissociates on the silicon surface. Fluorine ions desorb from chemisorbed molecular species. Chlorine ions similarly originate from molecular species as well as from atomic chlorine on the surface. Negative ions are the result of dipolar dissociation. (Int J Mass Spectrom 205 (2001) 293–298) © 2001 Elsevier Science B.V.

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1. Introduction

Under appropriate conditions low-energy electrons are effective probes of the chemical nature of molecules on surfaces as, for example, in the case of various electron spectroscopies. Under other conditions, low-energy electrons may be responsible for significant modification of the chemical state of adsorbates on surfaces; plasma processing of semiconductor materials and electron beam deposition are examples. In the work reported here, we have investigated the electron-stimulated desorption of both positive and negative ions from a surface adsorbate resulting from chemisorption of trifluorochloroethene, $F_2C=CFCl$, on Si(100) as functions of both temperature and electron energy. Although chemical changes induced by electron bombardment have been demonstrated [1], the experiments reported here involve electron beams of sufficiently low intensity that ion desorption reflects the state of the adsorbate without inducing gross changes in its chemical composition [2,3].

2. Apparatus

The apparatus is illustrated in Fig. 1. The major components include a substrate holder on a rotatable stage, an electron gun, a quadrupole mass spectrometer and a gas-inlet system. The gas-inlet system

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* Corresponding author. E-mail: jm89@umail.umd.edu

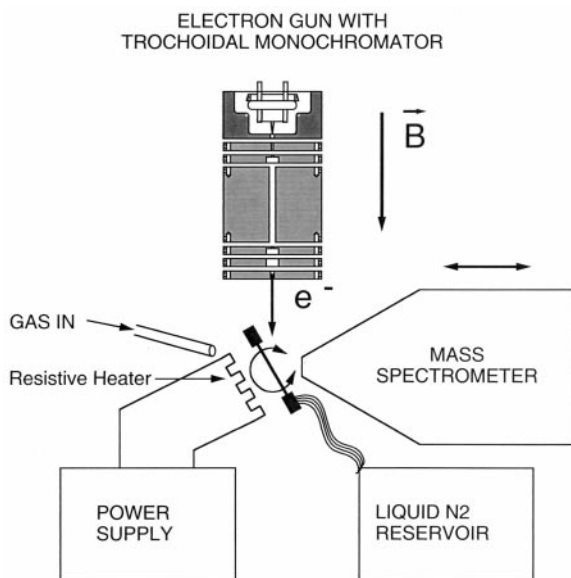Dedicated to Professor Aleksandar Stamatovic on the occasion of his 60th birthday.

Fig. 1. Schematic of experimental apparatus.

admits a measured dose directed at the sample through a nozzle 2 cm away.

The sample wafer is held in a molybdenum fixture. This fixture and the sample are cooled by conduction through a copper braid attached to a liquid-nitrogen dewar and heated by radiation from a resistive heater beneath the sample. The temperature of the molybdenum fixture is measured with an attached type-K thermocouple and the temperature of the silicon is calibrated (±15K) to that of the fixture. With this arrangement the substrate temperature can be varied from 130K to 970K under computer control. In addition the substrate can be heated to much higher temperatures by passing current directly through the sample, once again under computer control. The experiment is contained in a small ultrahigh vacuum (UHV) system pumped by a turbomolecular pump to a base pressure of 2×10^{-10} torr.

The electron gun incorporates a trochoidal monochromator. A magnetic field is required to collimate the electron beam and energetically disperse the electrons in the monochromator. As a consequence, the entire experiment is immersed in a field of about 70 gauss. The electron gun can provide 100 nA into 1

mm^2 at energies from 0 eV to 100 eV with a resolution of 0.2 eV.

The mass spectrometer covers a range up to 300 amu with 1 amu resolution and is computer controlled. A standard electron-impact ionization source in the spectrometer housing permits the detection of neutral species. The sensitivity to $F_2C=CFCl$ is calibrated by the admission of a measured dose of gas into the vacuum system. This calibration subsequently permits the determination of the quantity of gas desorbed from a substrate. With the spectrometer ion source off, both positive and negative ions generated at the substrate can be detected. The mass spectrometer housing is mounted on a translational stage to permit the spectrometer to be moved away from the rotating stage. A snout affixed to the front of the spectrometer housing shields the stage and the electron beam from fields associated with the spectrometer electrodes. Ions that drift into the snout are electrostatically focused on the spectrometer entrance aperture.

3. Experiment

Before each experiment a standard heat treatment cycle is applied to the silicon to remove passivating adsorbates [4]. Heating is accomplished by passing current through the silicon. The temperature is determined from the resistance of the sample and the current is controlled accordingly. The silicon is maintained at 920K for 20 min to outgas; then rapidly heated to 1440K and held there for 40 s; then cooled to 1070K and held for 120 s; and finally cooled at a rate of 1.5K/s to 700K. At 700K the temperature is no longer controlled, and the silicon is cooled conductively through the copper braid and reaches 170K in 20 min.

Our dosing procedure was to admit a dose of 1.1×10^{16} molecules directed at the silicon surface at 170K. The dewar was then emptied and warmed to room temperature to preclude subsequent outgassing from the sample mount and copper braid during succeeding measurements. As the substrate warms, a relatively large amount of physisorbed $F_2C=CFCl$ is desorbed in

the 200–240K range. The dewar was then refilled to cool the substrate and begin an experiment.

Experiments performed included conventional temperature-programmed desorption (TPD), wherein multiple mass peaks were monitored as the temperature was ramped from 170–950K at 1K/s using the radiative heater. The TPD experiments are complicated by the fragmentation pattern of $F_2C=CFCl$, however, knowing the intensity of each fragment peak relative to the parent peaks at 116 and 118 amu made it possible to assess the contribution of molecular $F_2C=CFCl$ to each of the peaks observed during the TPD. The sensitivity of the mass spectrometer to a measured quantity of gas-phase $F_2C=CFCl$ was also measured, thus allowing the determination of upper limits for the quantity of $F_2C=CFCl$ that desorbed from the silicon substrate and the quantity of $F_2C=CFCl$ that dissociated during TPD (assuming the same sensitivity for both the desorbed $F_2C=CFCl$ and the $F_2C=CFCl$ admitted through the gas inlet).

Similar experiments were performed in which positive- or negative-ion desorption for 100-eV electron impact was observed as a function of temperature. In addition, ion desorption as a function of incident-electron energy was recorded at selected temperatures. For the ion desorption experiments, a 100 nA beam was used, corresponding to an electron dose of approximately 10^{15} electrons/mm^2 for the ion desorption versus temperature experiments and approximately 10^{14} electrons/mm^2 for the ion desorption versus electron energy.

4. Results and Discussion

The TPD spectra display only very broad features. Molecular desorption of $F_2C=CFCl$ is observed in the range from 200K to 500K. Beyond this temperature range, smaller fluorochlorocarbons, chlorine and fluorine are desorbed. At the highest temperatures, above 850K, intense desorption of many fragments is observed. With increasing temperature, we note in particular that the mass 85 and 87 peaks do not maintain the expected 3:1 intensity ratio. This ratio
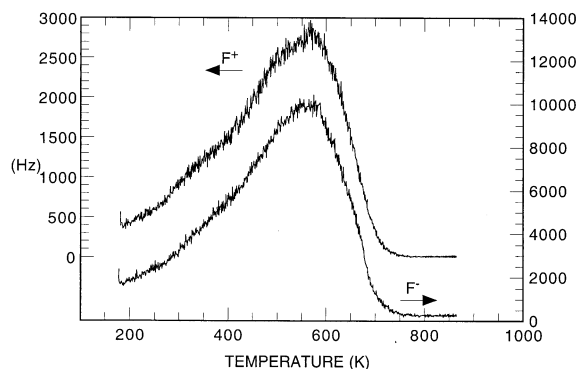

Fig. 2. Intensity of the F^+ and F^- emission for 100-eV electron bombardment of a dosed silicon surface as a function of surface temperature.

approaches 10, suggesting a significant contribution from SiF_3 at mass 85.

Following the initial warming and cooling cycle, a significant fraction of the remaining $F_2C=CFCl$ is chemically bound to the surface. Integration of parent peak intensity at 116 amu during TPD implies that the surface coverage of intact molecular $F_2C=CFCl$ is less than 3×10^{12} cm^{-2}. Integration of the 116 amu intensity during dosing and then during the warming, cooling and TPD cycle leaves a decrement equivalent to a surface coverage of dissociated parent of as much as 9×10^{14} cm^{-2}.

Bombardment with 100-eV electrons induces the desorption of Cl^+, F^+, Cl^-, and F^-. No molecular ions were observed. Ion emission as a function of temperature is shown in Figs. 2 and 3. Pulsing the electron beam to reduce the electron dose by a factor of 10 results in no change in the shape of the emission functions. We therefore conclude that the observed features are due solely to temperature effects, and not to the electron-induced chemical changes in the surface. There are three particularly interesting aspects of these data. Firstly, we note that the ion signals increase in intensity as the temperature increases from the lowest temperature. Bearing in mind that these signals reflect the concentration of emitting species on the surface, not the rate of desorption as in the case of TPD, the implication is that the signals at low temperature do not originate from molecular (i.e., phy-
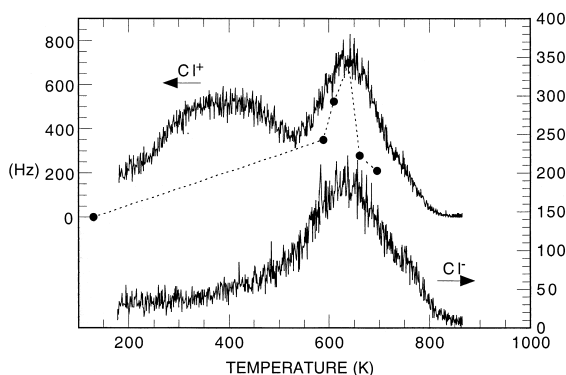
Fig. 3. Intensity of the Cl$^+$ and Cl$^-$ emission for 100-eV electron bombardment of a dosed silicon surface as a function of surface temperature. The data from Bennett et al. [5] are also shown.

sisorbed) F$_2$C=CFCl whose concentration certainly does not increase with increasing temperature. Secondly, we note that the ion emission essentially ceases above 830K for Cl and above 700K for F (although very weak F$^+$ intensity persists to higher temperatures). Finally, there are striking similarities between the positive and negative ion curves. The Cl$^+$ and Cl$^-$ curves are very similar in shape above 550K. It is especially remarkable that the shapes of the F$^+$ and F$^-$ emission functions are nearly identical. The subtle shoulder at 300K and the double peak at 500K are reproducible features.

The desorbing fluorine ions appear to originate from some molecular fragment on the surface. Bennett et al. [5] have observed electron-stimulated-desorption-ion-angular distributions of F$^+$ from F adsorbed on Si(100). They conclude that F remains stable on the silicon surface up to 1000K. Qualitatively speaking, the structured F$^+$ and F$^-$ emission functions observed here in the 200–700K range appear to be more intense than that from F$^+$ desorbing from the silicon surface as observed by Bennett et al. The implication is that the F ions observed here originate from F bound to C on the surface. The nearly complete disappearance of the F-ion signals above 770K would be due to desorption of the emitting fluorochlorocarbon species or the migration of F to the silicon surface. The weak F$^+$ intensity at higher temperature would correspond to the desorp-

tion of F atoms bound to the surface. Finally, the probability of F$^+$ formation via electron impact is expected to change with the chemical state of F; the same is true for F$^-$. Unless the ratio of these probabilities remains unaffected by a change in the chemical state of F, the ratio of F$^+$ to F$^-$ signals could not be independent of the F chemical state. The constancy of this ratio observed in Fig. 2 implies that F$^+$ and F$^-$ originate from the same chemical species throughout the temperature range. The variation of ion desorption with temperature reflects the changing concentration of a carbon-containing species and orientation of that species on the surface, since it is unlikely that the mechanisms for creating positive and negative ions have the same temperature dependence.

Our electron-stimulated Cl emission functions are compared in Fig. 3 to the observation of Bennett et al. [5] for emission of Cl$^+$ from Cl on Si(100). The 640K peak in both the Cl$^+$ and Cl$^-$ emission functions may be attributed to surface-bound Cl. We further surmise that the intensity in the broad lower-temperature peak arises from desorption from the rupture of C—Cl bonds in chemisorbed fluorochlorocarbon species. These conclusions are consistent with a study of CCl$_4$ on Si(100) conducted by Junker et al., [6]. In that work, chemisorbed CCl$_x$ species, as well as atomic chlorine, were found on the surface up to at least 700K, but were entirely absent at 1045K.

Figure 4 plots ion emission as a function of electron energy for the freshly dosed surface (170K), the room-temperature surface after the physisorbed layer is desorbed (300K) and the high-temperature surface (700K). Enlargements of the threshold region are shown. We note that the emission intensity for the freshly dosed surface is quite weak, consistent with the conclusion that molecular F$_2$C=CFCl does not contribute to the ion emission. It is also noteworthy that the emission threshold for the freshly dosed surface is shifted to higher energies. With increasing temperature, the thresholds move to lower energies, presumably a consequence of the evolution of dissociative chemisorption. With the exception of Cl$^+$, the thresholds are all in excess of 20 eV. For Cl$^+$ at 300K, two thresholds are apparent. Guo, et al. [7] observed similar threshold behavior and assigned the lower
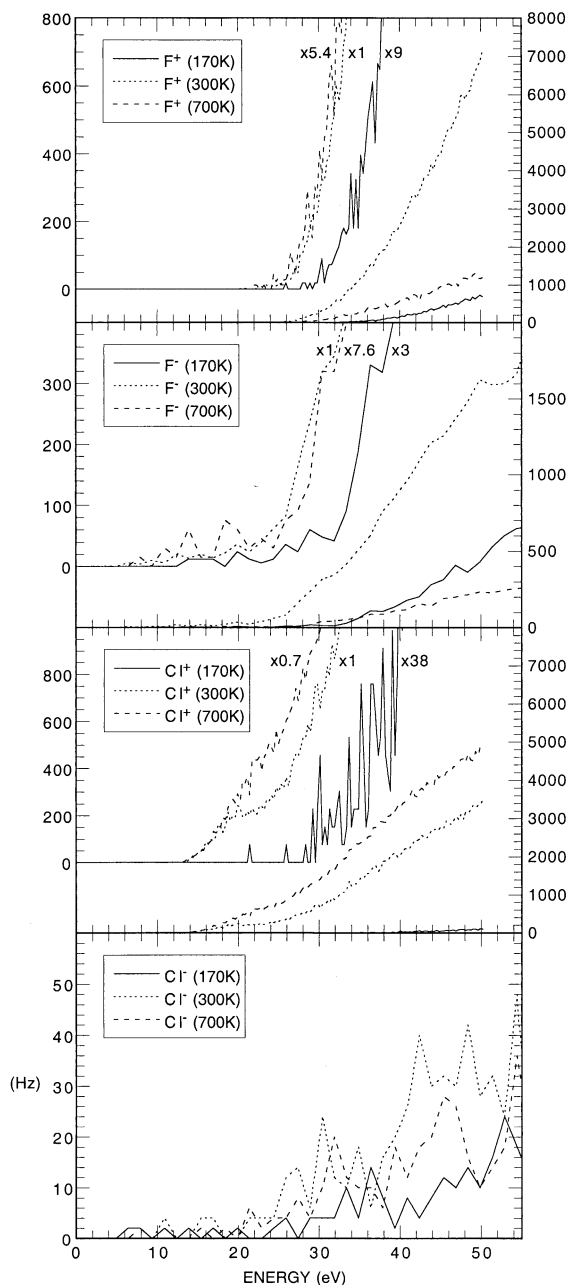
Fig. 4. Intensity of the F^+, F^-, Cl^+ and Cl^- signal as a function of incident electron energy for: a freshly dosed surface at 170K; after heating to 300K; and after heating to 700K.

threshold to direct ionization and the upper to an Auger process. The fact that the thresholds for F^+ and F^- do not change as the temperature of the surface

changes supports the conclusion that the F-ion signals come from one chemical species. An inspection of the 0–15 eV portion of the electron-induced ion yield did not reveal any resonant emission, as might have been expected since gas-phase $F_2C=CFCl$ exhibits dissociative electron attachment in this energy range [9]. In view of the high energy of the observed thresholds and the lack of any resonant emission, we conclude that negative-ion desorption is the result of dipolar dissociation and not dissociative electron attachment [8]. It should be noted that Weik and Illenberger [10] observed no resonant F^- emission for submonolayer quantities of $F_2C=CF_2$ on 10 monolayers of Kr, even though F^- desorption is more probable in this case because of the reduced image charge resulting from the dielectric layer.

Clearly, electron-induced ion emission is sensitive to the chemical nature of Cl and F on the surface. Determining factors include the electronic excitation leading to dissociative ionization, the ion kinetic energy, and the energy required to overcome the image-charge potential. Dissociative ionization of $F_2C=CFCl$ at low temperature (200–500K) would not be observed because (1) the molecule likely lies flat on the surface thus placing the halogens close to the surface with a concomitantly large image potential; (2) the carbon-halogen bond is parallel to the surface so the normal component of the kinetic energy of dissociation would be small; and (3) the concentration of $F_2C=CFCl$ on the surface may be too small. Electron-stimulated desorption at intermediate temperatures from the products of dissociative chemisorption, such as CF_2Cl, would be favored since the halogens are elevated above the surface. At the highest temperatures the attenuation of ion-desorption signals would be consistent with a surface state in which the halogens exist primarily as atomic species directly bonded to surface silicon atoms.

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