Energy-selective reaction of the hydrogen-passivated Si surface with carbon tetrafluoride via dissociative electron attachment

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(Received 12 June 1995)

We report the partial fluorination of a H-passivated, sputtered Si(111) surface at 35 K induced by irradiating a physisorbed carbon tetrafluoride overlayer with 2–13 eV electrons. The reaction cross section depends strongly on the energy of incoming electrons with a threshold at 4.0 eV and a clear resonance peak at 6.0 eV having a maximum value of 4.8×10^{-17} cm^2, which is attributed to dissociative electron attachment (DEA) to CF_4. Our study demonstrates the energetic selectivity of DEA for chemically modifying a semiconductor surface.

I. INTRODUCTION

Recent studies have shown several examples of the modification of surface composition and structure of metals and semiconductors through dissociation of adsorbates by low-energy electron irradiation.[1–6] Electron-induced dissociation (EID) also provides one of the mechanisms for photon-induced surface reactions via the interaction of secondary electrons photogenerated in the substrates.[7–10] At low electron energies, an efficient channel for inducing molecular dissociation is dissociative electron attachment (DEA),[11,12] in which an electron first attaches to a molecule to form a transient negative anion, which subsequently dissociates into a stable anion fragment and a neutral radical or atom. As in the gas phase,[12] the cross section of DEA for molecules condensed on solid surfaces can display a resonant dependence on the impact electron energy.[11] By tuning the energy of the incoming electrons to a specific DEA resonance of the adsorbates, one can break a specific chemical bond and induce selectively chemical reactions among the adsorbates[3] and, presumably, with the substrate. In this way, we may gain some control over the chemical modification of surfaces. A number of studies in photolysis[8,13–18] and electron-beam experiments[3,14,19,20] have postulated the presence of DEA processes to explain the surface chemistry of some adsorbate-substrate systems involving low-energy electrons. No investigation, however, has shown a resonant behavior in the reaction cross sections which would demonstrate that the products are formed via DEA.

In this paper, we report the observation of a resonance in the electron energy dependence of the reaction cross section for an adsorbate-surface reaction. With x-ray photoelectron spectroscopy (XPS) we observed chemisorption induced by irradiating with 2–13-eV electrons a carbon tetrafluoride overlayer initially physisorbed on a H-passivated and sputtered Si(111) surface held at 35 K. The irreversible conversion from physisorption to dissociative chemisorption of the CF_4 induced by exposure to low-energy electrons results in a partial fluorination of the Si surface. The reaction cross section is found to depend strongly on the energy of incoming electrons with a threshold at 4.0 eV, and a clear resonance peak at 6.0 eV having a maximum value of 4.8×10^{-17} cm^2. By comparing our results with relevant data on DEA cross sections of CF_4 molecules in the gas and condensed phases, we conclude that the fragmentation of the CF_4 molecules through DEA is the major mechanism for inducing the reaction. Our study shows that the energetic selectivity of DEA can provide a valuable mechanism to produce specific modifications on a semiconductor surface.

II. EXPERIMENT

Our experiment was performed with a Physical Electronics 5000 series ESCA (electronic spectroscopy for chemical analysis) spectrometer housed in a conventional UHV chamber operating at a pressure maintained within the $1-2\times10^{-10}$-torr range. XPS analysis was performed with the Mg $K\alpha$ line (1253.6 eV). The sample was cooled to 35 K. The silicon substrate (0.8×1.4 cm^2 in cross section and 0.2 cm thick) was cut from a p-doped Si(111) wafer (ρ=0.05–0.5 Ω cm) and cleaned by argon-ion sputtering (1×10^{-4}-torr Ar, 500-eV beam voltage, 7-μA sample current) for several hours without annealing. The resulting amorphous surface was then quickly exposed to ~100 L of H_2 in the presence of a hot tungsten filament (~2000 K). The H atoms passivated the Si surface by saturating its dangling bonds, and kept it from further residual contaminations in UHV and direct chemisorption with adsorbed CF_4 molecules.[20] It is advantageous to work with an amorphous Si surface in these studies; it minimizes the influence of nonequilibrium carriers generated in the substrate, since these excitations are readily quenched at defect centers.[21] The cleanliness of the hydrogenated surface was checked by XPS. The main impurities were atomic oxygen and carbon with under 1–2 % and implanted Ar with under 3% of atomic concentrations.

CF_4 gas (99.995% purity) was dosed through a small tube facing the 35-K Si surface. CF_4 was physisorbed on the surface as shown by the F(1s) and C(1s) peaks at binding energies (BE's) of 689.3 and 295.9 eV, respectively.[22] As the dosage increased, the intensity of these two peaks increased linearly at first, then each peak developed a shoulder at about 3 eV higher BE (692.0 and 298.4 eV, respectively); afterwards, they grew continually with

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dosage. We considered this behavior as an indication of growth of the second monolayer of CF_4. In the present experiment, the initial coverage of CF_4 was set so as to barely see the second peak (e.g., as in the bottom spectrum in Fig. 1). This corresponded to a coverage of slightly more than one monolayer. The area rate of the F(1*s*) peaks for the as-deposited film was reproducible within $\pm 10\%$. Upon warming the sample to room temperature, the physisorption peaks completely disappeared due to desorption, and the surface was restored to the pristine state, indicating the absence of thermal chemisorption of CF_4 to the surface.

The low-energy electron beam was produced by a modified Kimball Physics electron gun (ELG-2) having an energy resolution of approximately 250 meV. The electron energies were changed by adjusting the bias between the gun filament and the sample. The energy onset of the current flow to the substrate is defined as 0.0 eV, the estimated precision of this measurement was ± 0.25 eV. The electron flux to the sample was measured in each experiment to be in the range 2.0–4.0 μA. The measured beam diameters at 7.2 and 10.1 eV were 2.2 and 3.6 mm^2, respectively; in all cases, the electron spot size was smaller than the sample dimensions, and smaller than the focal area of the photoelectron analyzer. Care was taken during data acquisition to insure that the surface area exposed to the electron beam was positioned at the center of the focal area of the detector. Electron energies ranged from 2.0 to 13.2 eV, with roughly 1-eV intervals. XP spectra of the surface were recorded as a function of electron dose for each of these energies. The effect of x-ray radiation on physisorbed CF_4 adlayer was estimated by exposing the film continuously for 70 min to the x rays at the operational dosage (350 w). The XP spectra taken immediately afterwards and after subsequent desorption showed that $\sim 30\%$ of physisorbed CF_4 was desorbed by the x rays, yet the amount of CF_4 chemisorbed to the surface [indicated by the chemically shifted F(1*s*) peak at a BE of 686.5 eV] was negligible. Previous work by Chuang also showed that the effect of x-ray irradiation on surface chemical composition of the silicon-fluorine system is negligible.[23]

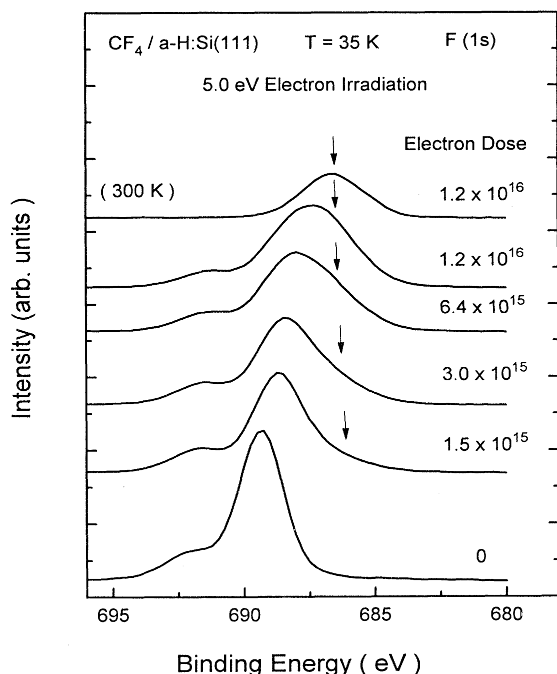


FIG. 1. The evolution of F(1*s*) XPS line of the CF_4/*a*-H:Si(111) system as a function of 5-eV electron dose. The feature indicated by the arrows corresponds to chemisorption of adsorbed CF_4. The bottom and top spectra were measured before electron irradiation and after thermal desorption of the physisorbed CF_4 at the end of electron irradiation, respectively.

III. RESULTS AND DISCUSSION

An example of XP spectra recorded at various doses for 5.0-eV electrons is shown in Fig. 1. The spectrum at the bottom was taken just before the electron irradiation. Only the physisorption features of F(1*s*) are seen with a sharp peak centered at a BE of 689.34 eV and a small shoulder at 692.00 eV, indicating the onset of bilayer formation of CF_4. Upon exposure to electrons, the sharp physisorption peak broadened and shifted to lower BE. Meanwhile, a distinct shoulder appeared on the lower BE side, as indicated by the arrows. With the increase of electron dosage, the integral intensity of the physisorption peaks decreased while that of the shoulder increased up to saturation. Upon warming up the substrate to room temperature (top spectrum), the peaks associated with physisorbed CF_4 were completely eliminated leaving only the signal from the shoulder as a symmetrical peak at 686.50 eV with a 2.8-eV full width at half maximum. This peak is characteristic of direct F-Si bonding.[23–26] In the C(1*s*) BE range, we saw that additional features developed between 288 and 293 eV with electron bombardment, these structures were also observed following thermal desorption of the physisorbed layer. We assign them to CF_x ($x = 1-3$) species permanently bounded to the substrate.[27] The broad F(1*s*) peak at 686.5 eV can be regarded as the combined contribution of the chemical bonds F_x-Si and CF_x-Si. It is therefore clear that a reaction occurred between the CF_4 adlayer and the Si substrate upon the irradiation of 5.0-eV electrons.

Figure 2 shows the integrated F(1*s*) peak areas corresponding, respectively, to the physisorption, chemisorption, and sum of these two as a function of the dose given by 5.0-eV electrons. These results were obtained by fitting the spectra in Fig. 1 into three symmetrical Gaussian-Lorentzian peaks. The parameters of the chemisorption peak were set according to the chemically shifted F(1*s*) peak left after thermal desorption. The total area curve shows that there is about 10% desorption of CF_4, which occurred mostly at the beginning of electron irradiation. This also applies to the other electron energies. Since a steady state of F(1*s*) peaks were already reached through prolonged x-ray exposure before starting the electron irradiation, this part of the desorption was due mainly to the electron impact. The chemisorption

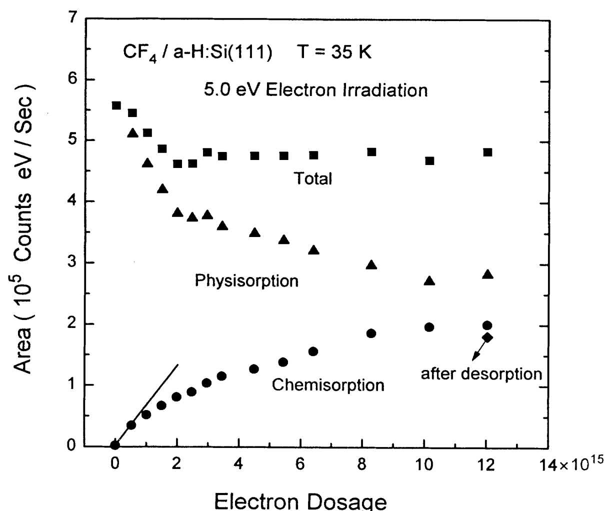


FIG. 2. The deconvoluted intensity of the F(1s) line corresponding, respectively, to physisorption (triangles), chemisorption (circles), and the sum of these two (squares) as a function of 5-eV electron dose. The single data point (♦) shows the intensity of the chemisorption feature following the thermal desorption of the residual physisorbed CF_4 after electron irradiation.

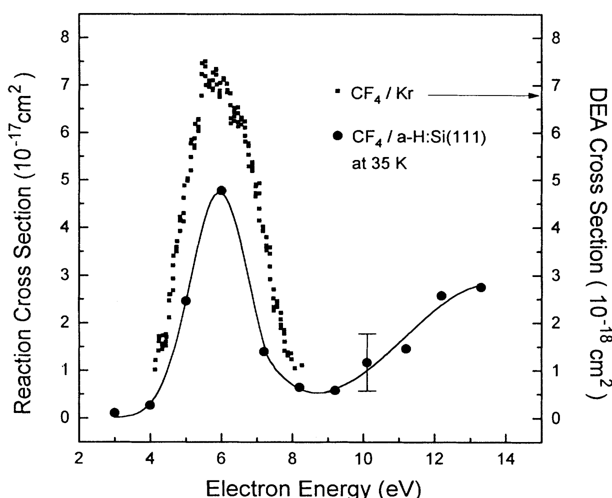


FIG. 3. Experimental cross sections for the electron-induced reaction of the a-H:Si(111) surface with physisorbed CF_4 as a function of the incident electron energy. The solid line is drawn through the data to guide the eye. Also plotted is the result of the total DEA cross section for CF_4 condensed on Kr as measured by Bass *et al.* (Ref. 34).

curve shows that the number of CF_4 molecules converted to chemisorption, which is characterized by the broad F(1s) peak at 686.5 eV, grows exponentially with the electron dosage and eventually saturates upon exposure to about 1.2×10^{16} electrons. It fits well to the following function:

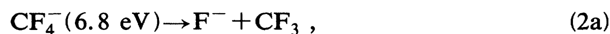
$$I(\phi)=I(\infty)x[1-\exp(-\sigma\phi/A)] , \quad (1)$$

where $I(\phi)$ is the integrated intensity of the chemisorption peak following a dose of ϕ electrons across area A of the sample, $I(\infty)$ is its saturated value, and σ is the reaction cross section. By taking the derivative on both sides we have $\sigma=I(\infty)\rho_i/A$, where ρ_i is the initial slope of the chemisorption curve. The beam area A changes with the electron energy within the focal area of the detector, but $I(\infty)/A$ should be a constant for different electron energies. Its value was deduced from the irradiation of 7.2-eV electrons, for which the beam area was measured to be about 0.1 cm^2. Using this value, we obtained 2.5×10^{-17} cm^2 for the reaction cross section for 5.0-eV electrons. We determined the reaction cross sections at the other electron energies by normalization to this value. The lower curve in Fig. 3 shows the reaction cross section versus electron energy. The error bar on the 10.1-eV data point represents the absolute error; the relative error is much smaller (i.e., of the order of 10%). As can be seen from this curve, there is a pronounced resonance in the reaction cross section between 4.0 and 8.0 eV which peaks at 6.0 eV with a maximum value of 4.8×10^{-17} cm^2. Below 3.0 eV, the surface reaction is below detectable limits. Above 9.0 eV, the reaction cross section increases almost linearly with electron energy. We want to mention that we can also calculate the reaction cross sections by fitting the whole chemisorption curve in Fig. 2 to Eq. (1). The result thus obtained gives a broader resonance which has the same onset, peak energy, and height as that in Fig. 3. Considering that, as we increased the electron dosage, various fragments of the CF_4 molecules might be accumulated on the surface and complicate the surface reactions, we chose to have the data in Fig. 3 on the reactions with the substrate occurring at the beginning of the electron irradiation.

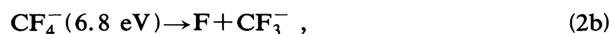
Since low-energy electron irradiation may remove H atoms from the silicon surface,[28] the effect of such depassivation of the substrate on the chemisorption process was verified by adsorbing CF_4 directly on a freshly sputtered Si(111) without hydrogen treatment. Surprisingly, the clean amorphous surface was not more reactive toward CF_4 molecules than the hydrogenated one. At room temperature, CF_4 did not adhere to the clean surface at all, in agreement with the previous observation that fluorocarbon gases have a very low sticking coefficient on silicon surfaces at room temperature.[29] After condensing CF_4 on the clean surface at 35 K, XPS results indicated negligible intensity of the chemically shifted F(1s) peak at 686.5 eV. The subsequent thermal desorption also confirmed the absence of chemically bounded fluorine bearing adsorbates. Thus we conclude that the observed modification of the Si surface is exclusively caused by the interaction of the incoming electrons with physisorbed CF_4 molecules.

The scattering of low-energy electrons by CF_4 molecules has been extensively investigated in the gas phase. Below the threshold for electronic excitation at 12.4 eV, electrons can be captured into two transient negative anion states: one is the ground state CF_4^- at 6.8 eV, and the other an electronic excited state CF_4^{*-} at 7.6 eV.

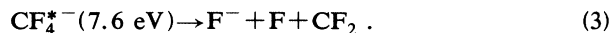
These states dissociate via the following (2) and (3) channels, respectively:[30,31]



$$CF_4^-(6.8\ \text{eV}) \rightarrow F^- + CF_3\ , \tag{2a}$$



$$CF_4^-(6.8\ \text{eV}) \rightarrow F + CF_3^-\ , \tag{2b}$$



$$CF_4^{*-}(7.6\ \text{eV}) \rightarrow F^- + F + CF_2\ . \tag{3}$$

These processes form two overlapping DEA resonances peaking, respectively, at 6.8- and 7.6-eV impact electron energy. The maximum gas phase DEA cross section lies within the range $(1.0-1.6)\times10^{-18}$ cm^2.[32] Recent electron-stimulated desorption and charge-trapping studies have shown that the same DEA processes are also present for the CF_4 molecules condensed on solid surfaces.[33,34] Most of the anion fragments are found to stay at the substrate surface rather than being desorbed upon exposure to the electrons. For CF_4 condensed on a multilayer Kr film, the absolute cross section for stabilized surface anion formation via DEA has been measured by Bass *et al.* using a charge-trapping technique.[34] As also shown in Fig. 3, the electron-energy dependence of this cross section has a broad resonance between 4- and 8-eV electron energy which consists of two structures: a maximum at 5.8 eV and a shoulder at 6.6 eV. They were identified as the same gas phase DEA resonances shifted down about 1 eV in electron energy. The maximum charge trapping cross section is 7.3×10^{-18} $cm^2\pm37\%$, and the maximum total DEA cross section has been estimated[34] to be 9×10^{-18} $cm^2\pm50\%$, which is significantly larger than the corresponding gas phase value. The shift of the DEA resonances to lower energy and the enhancement of the DEA cross section when going from the gas to condensed phase have also been observed for O_2, CO_2, CH_3Cl, and other molecules.[35–37] These modifications are primarily due to the induced polarization or image charge of the substrate which lowers the potential-energy surface of the parent transient anions and, as a consequence, increases the survival probability of the anions against autodetachment.[34]

Our reaction cross-section curve is very similar to that of Bass *et al.* in the range 4–8 eV, even though the data spacing is too large to reproduce the fine structure of their resonance around 6 eV. This similarity demonstrates that dissociation of the condensed CF_4 molecules into reactive fragments via DEA is the mechanism for the surface reaction occurring on the silicon substrate. The large reaction cross section (peak value 4.8×10^{-17} cm^2) cannot be attributed to autodetachment decay of the intermediate anion states as Chen *et al.* did to explain their results of electron-induced oxidation of O_2/InP(110) surfaces,[2] since such decay would lead the CF_4 molecules in their electronic ground state, which have already been shown to be quite inert to the Si substrate. Furthermore, it implies that the DEA cross section of CF_4 is even more enhanced on the hydrogenated Si(111) than on a Kr film. Two reasons for this enhancement may be that (1) the results of Bass *et al.* were measured for isolated CF_4 molecules, while in the present experiment the relevant DEA cross sections could be appreciably modified since the CF_4 molecules are "touching" each other; and (2) the silicon substrate has a stronger polarization interaction than the Kr films.

IV. CONCLUSIONS

We have observed the chemical reaction (partial fluorination) of a hydrogenated amorphous Si(111) surface induced by 2–13-eV electron irradiation of adsorbed CF_4. The reaction cross section shows a pronounced resonance between 4- and 8-eV incident electron energy, which is attributed to DEA to the adsorbate. This observation, combined with the fact that the DEA cross section is greatly enhanced, leading to a large reaction cross section, suggests that, by choosing the adsorbates having appropriate DEA resonances, one could efficiently induce specific surface reactions on semiconductor surfaces via low-energy electron irradiation. Since the mean free path of electrons at low energies (i.e., $\sim$10 eV) is smaller than 10 Å in silicon,[38] reactions induced by DEA should also be fairly well localized in space. We can expect most of the 6-eV electrons incident on the silicon surface to be elastically scattered back to the surface within a sphere of radius of a few times 10 Å. The energy loss and secondary electrons which could reach larger distances would have lower kinetic energies and, consequently, smaller reaction cross sections (Fig. 3). We can therefore speculate that with a highly localized electron beam having a resonant energy such as that flowing through the tip of a scanning tunneling microscope (STM),[39] it may be possible to induce partial fluorination of a Si surface on a nanometer scale via DEA.

ACKNOWLEDGMENTS

This work was supported by the Canadian Centers of Excellence for Molecular and Interfacial Dynamics.

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