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Thermal decomposition of a silicon-fluoride adlayer: Evidence for spatially inhomogeneous removal of a single monolayer of the silicon substrate

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The thermal decomposition of silicon-fluoride adlayers, produced by exposing a clean Si(100) surface to a molecular beam of fluorine, have been investigated under ultrahigh-vacuum conditions with x-ray photoelectron spectroscopy and mass spectrometry. The only gas-phase reaction products detected from temperature-programmed desorption are SiF_2 and SiF_4, the relative yield of each product depending strongly on the coverage of fluorine adatoms. For fluorine coverages below 3–4 monolayers, the major reaction product is SiF_2, whereas above 3–4 monolayers the relative yield of SiF_4 increases continuously, while that of SiF_2 remains constant. Independent of the initial coverage of fluorine, the thermal decomposition is terminated near 800 K by the removal of one monolayer of the Si substrate in the form of SiF_2. Results are presented that suggest the removal of this "final" monolayer proceeds inhomogeneously leaving separate domains in which the *local* coverage of fluorine is either zero or near saturation.

The interaction of fluorine with silicon surfaces has attracted particular interest due to its fundamental role in the processing of microelectronic devices. Considerable effort has centered on model studies employing XeF_2 as a source of atomic fluorine,[1-3] since this radical is conceded generally to be the dominant reactive species in fluorine-containing plasmas.[4] For example, it is known that exposure of silicon to XeF_2 at room temperature results in a "spontaneous etching" of the surface, the dominant gas-phase reaction product being SiF_4.[1] Recent work employing soft x-ray photoelectron spectroscopy (XPS) indicates that this "spontaneous etching" of the silicon surface is dependent upon the buildup of a thick fluorosilyl layer, which involves approximately 6–7 monolayers (ML) of the silicon substrate.[5] The dominant fluorine-containing species in this layer is apparently SiF_3.[5]

Significantly less effort has been directed towards the interaction of fluorine with silicon surfaces in the monolayer regime. Undoubtedly, this has been due to the assumed unimportance of the low coverage regime in regards to the etching of silicon since, for example, early work suggested that submonolayer fluorine adlayers are stable to temperatures near 800 K.[3] Results from both XPS[2] and electron-energy-loss spectroscopy (EELS)[6] indicate that SiF is the dominant species in the monolayer regime on both the (100) and (111) surfaces of silicon. Thermal decomposition of silicon-fluoride adlayers have been found to result in the production of $SiF_4(g)$, $SiF_2(g)$, and possibly SiF(g).[7] Unfortunately, a detailed examination of the kinetics and mechanism of the thermal decomposition was not attempted. Finally, the radicals $SiF_2(g)$ and, to a lesser extent SiF(g), have been observed from the thermal reaction of F_2 and NF_3 with solid silicon at temperatures near 800 K.[8]

We have investigated in detail the interaction of fluorine with the Si(100) surface by employing supersonic molecular-beam techniques, XPS, and mass spectrometry.[9] The experiments were conducted in a turbomolecular-pumped stainless-steel ultrahigh-vacuum chamber, which has been described in detail previously.[10] The apparatus has been designed such that the crystal can be exposed to the molecular beam of the gas-phase reactant while, simultaneously, both the gas-phase reaction products can be detected line of sight by a differentially pumped mass spectrometer (UTI 100C, fitted with a Balzers crossed-beam ion source) and the composition of the adlayer can be monitored in a *time-resolved* fashion by XPS. Accurate temperature control is effected by employing an optimal feedback control scheme, which utilizes a minicomputer as the control element.[11]

The qualitative features of the thermal decomposition of silicon-fluoride adlayers can be assessed from the data shown in Fig. 1. These data were produced by exposing a clean single-crystalline Si(100) surface (*p*-type, 40-50-Ω cm wafer, 1×3 cm^2) at a temperature of 120 K to a molecular beam of fluorine (either 10 mol% F_2–He or 10 mol% F_2–Ar), extinguishing the beam, and heating subsequently the surface at a constant rate of 4 K s^{-1}. The depletion of the fluorine coverage with increasing temperature depicted in Fig. 1(a) was determined via XPS by monitoring the F(1*s*) peak at a single fixed energy (binding energy $\simeq$685 eV). The electron energy analyzer was detuned purposely (200 eV pass energy) in order to minimize effects due to shifts in either the peak position or shape with the coverage and/or configuration of fluorine atoms.[3] Absolute coverages were obtained by comparing the relative integrated intensity of the F(1*s*) peak to that of the O(1*s*) peak [both with respect to the Si(2*p*) peak] for a known coverage of oxygen adatoms.[10] The relative F(1*s*)-to-O(1*s*) sensitivity was accounted for by employing the known photoionization cross sections and the transmission function of the analyzer. Above one monolayer, corrections were made also for the attenuation of the F(1*s*) feature due to the (assumed) penetration of fluorine atoms into the underlying Si substrate layers.[5]

Thermal desorption spectra of the gas-phase reaction

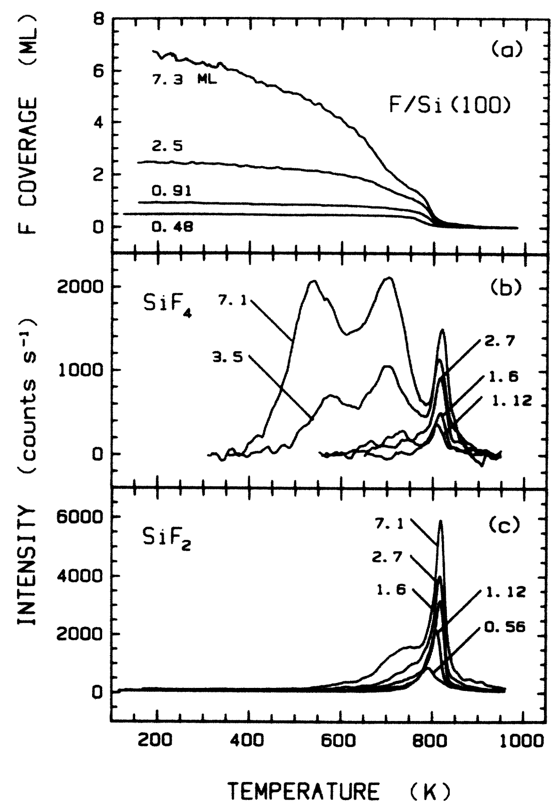

FIG. 1. Temperature-programmed decomposition of silicon-fluoride adlayers. (a) Coverage of fluorine adatoms as determined by XPS (see text). Desorption spectra of the gas-phase reaction products. (b) $SiF_4(g)$ and (c) $SiF_2(g)$, where the mass spectrometric intensity is proportional to the rate of desorption. For all curves, the initial coverage of fluorine adatoms is given in ML where, for Si(100), 1 ML $= 6.8\times10^{14}$ atoms cm^{-2}.

products, $SiF_4(g)$ (monitoring $SiF_3{}^+$, $m/e = 85$) and $SiF_2(g)$ (monitoring $SiF_2{}^+$, $m/e = 66$) detected by the mass spectrometer (electron energy of 110 eV) are shown in Figs. 1(b) and 1(c), respectively. Spot checks indicated that higher molecular weight products [e.g., $Si_2F_6(g)$, monitoring $Si_2F_5{}^+$] were not produced under the reaction conditions considered here. Mass spectra monitoring SiF^+ ($m/e = 47$) were found to be essentially identical to those found for $SiF_2{}^+$, the two sets of spectra differing by a single constant of proportionality in all cases. On the other hand, no such correlation was found between the $SiF_3{}^+$ and $SiF_2{}^+$ spectra, suggesting strongly that these fragments are formed from different parent neutral species. Consequently, the assignment of the mass spectra shown in Figs. 1(b) and 1(c) to their corresponding neutral species (i.e., SiF_4 and SiF_2) is straightforward based on the following observations. $SiF_3{}^+$ is known to be the dominant (~90%) cracking fragment from SiF_4,[12] whereas $SiF_2{}^+$ and SiF^+ are formed in comparable amounts from electron impact ionization of $SiF_2(g)$.[13] *Thus, under the reaction conditions considered here, the only gas phase reaction products produced from the thermal decomposition of the silicon-fluoride adlayers are $SiF_4(g)$ and $SiF_2(g)$.*

A detailed description of the thermal decomposition of the silicon-fluoride adlayers considered in Fig. 1 is possible by collecting the observations concerning the independently measured coverages and desorption rates. Since the heating rates employed here were essentially linear, the x axis in Fig. 1 is representative also of time. Thus, in regions where primarily one product desorbs, differentiation of the data in Fig. 1(a) will give a quantity that is simply proportional to the desorption rates, which are given in Figs. 1(b) and 1(c). We see that this is the case—the rapid decrease in the fluorine coverage at temperature near 675 and 800 K corresponds directly to the desorption of SiF_4 and SiF_2 respectively. In regards to the product distribution, the XPS results permit an absolute calibration of the desorption spectra and, hence, the absolute product yields. An analysis presented elsewhere[9] indicates that the relative yield of SiF_2 increases continuously with the initial fluorine adatom coverage, and saturates at a coverage of approximately 4 ML, which, due to the stoichiometry, represents removal of two monolayers of the Si substrate. However, the fraction of SiF_2 that can be associated with the sharp desorption peak centered near 800 K corresponds to 2 ML, or one monolayer of the Si substrate. On the other hand, the production of SiF_4 remains relatively low for initial coverages below 3–4 ML, and increases continuously with coverage beyond that value. *Thus, for initial fluorine coverages above 3–4 ML, the thermal decomposition of the adlayer is terminated at 800 K by the removal of one monolayer of the Si substrate in the form of $SiF_2(g)$.*

Obviously, above 1–2 ML, the kinetics of the thermal decomposition is quite complicated, resulting in the formation of two gas-phase products, each of which may involve multiple reaction channels. However, as implied by the sharp desorption peak near 800 K, below 1–2 ML the production of SiF_2 is apparently a well-defined process, which suggests that a more detailed examination of the kinetics of its formation is both tractable and desirable. Closer inspection of the thermal desorption spectra of SiF_2 shown in Fig. 1(c), in addition to similar spectra given elsewhere,[9] indicates that there is considerable overlap of the low temperature, leading edge of the spectra, and the spectra are decidedly asymmetric. This behavior is characteristic of *zero-order* desorption kinetics.[14] In order to evaluate explicitly the desorption kinetics of SiF_2, a series of experiments were conducted at a fixed initial coverage, but at different heating rates. This method[14] permits an evaluation of the kinetic parameters at a fixed coverage and, under the appropriate circumstances, a determination of the "order" or molecularity of the surface reaction.

Arrhenius plots of the rate of desorption versus the reciprocal temperature, constructed from desorption spectra of SiF_2, similar to those shown in Fig. 1(c), are shown in Fig. 2(a). Seven different heating rates varying between 0.5 and 10 K s^{-1} were employed, and the initial coverage of fluorine was fixed at 1.26 ML in all cases. Analysis of these data indicates that the activation energy and (zero-order) preexponential factor are essentially independent of fluorine coverage (Θ_F) between 0.2 and 1.0 ML and are given by values of 87 ± 2 kcal mol^{-1} and $2\times10^{22\pm1}$

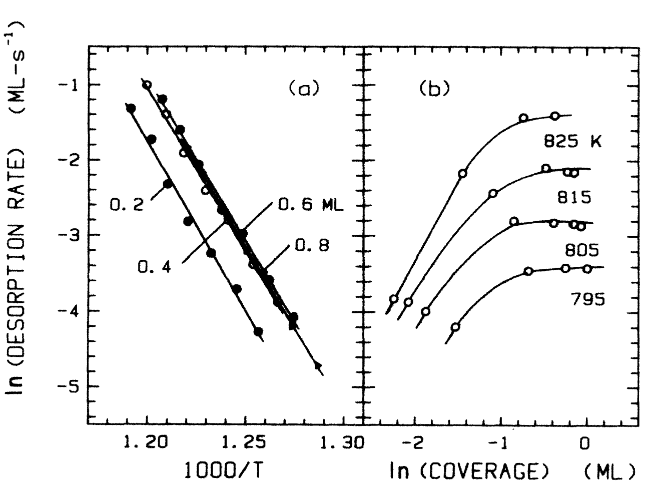

FIG. 2. (a) Arrhenius plots of the rate of SiF_2 desorption vs the reciprocal temperature for four different coverages of fluorine adatoms. (b) "Order plots" of the (ln) rate of SiF_2 desorption vs the (ln) coverage for four different temperatures. In all cases the initial coverage of fluorine adatoms was fixed at 1.26 ML.

ML s^{-1}. Moreover, above $\Theta_F \sim 0.4$, the rate of desorption is essentially independent of coverage, supporting the assignment of zero-order kinetics. However, below $\Theta_F \sim 0.4$, the rate of desorption is clearly positive order in the coverage of fluorine.

The observations concerning the order of the reaction that produces $SiF_2(g)$ may be better quantified by plotting the rate of desorption versus the fluorine coverage at a fixed temperature. Provided the kinetic parameters are only weakly dependent on coverage,[14] which has been demonstrated by the data shown in Fig. 2(a), the slope of these curves (on a log-log plot) will correspond to the order of the surface reaction. These curves, taken from the same set of data utilized in Fig. 2(a), are shown in Fig. 2(b). Again, above $\Theta_F \sim 0.4$ zero-order kinetics is apparent. However, in the limit of low fluorine coverages the apparent molecularity of the reaciton is very nearly second order. In this case, second-order reaction kinetics would be consistent with either addition of F(a) to a SiF(a) species, followed by desorption of $SiF_2(g)$, or possibly displacement of a $SiF_2(a)$ species by F(a), leading also to the desorption of $SiF_2(g)$.

Spectroscopic studies[2,6] indicate that SiF is the dominant species on Si(100) for coverages near one monolayer, these species presumably distributed uniformily over the surface. The small amounts of SiF_2 and SiF_3 that are present are most probably associated with defect sites,[2] such as atomic steps. The kinetics implicated here, i.e., zero order over a large range of coverages, appears to suggest that the decomposition reaction does not involve a simple disproportionation reaction between nearest-neighbor SiF species, since such a reaction would be expected to be second order in F(a). A probable explanation for zero-order kinetics is a mechanism that involves reaction via a minority species and/or site, the concentration of which is weakly dependent on fluorine coverage above $\Theta_F \sim 0.4$ ML. Possible minority species and/or sites could be one or more of the following: (i) "interstitial" fluorine;[15] (ii) defect sites, such as atomic steps; (iii) domain boundaries between high ($\Theta_F \sim \Theta_{F,sat}$) and low ($\Theta_F \sim 0$) fluorine coverage phases;[16] or (iv) SiF_2 species. It is of interest to note that item (iii) [and possibly (ii)] suggests that the decomposition reaction proceeds inhomogeneously, leaving domains where the *local* coverage of fluorine is either zero or near saturation.

Clues to the spatial extent of the decomposition reaction that produces $SiF_2(g)$ can be obtained by examining the *adsorption* kinetics of F_2 on a partially decomposed silicon-fluoride adlayer. This is possible since the kinetics of adsorption on the clean surface are described by a second-order Langmuir model,[9] i.e., the dissociative adsorption is controlled by the availability of two nearest-neighbor vacant adsites. For a homogeneous (uniformly, randomly distributed) adlayer and $\Theta_F/\Theta_{F,sat} = 1 - f$ the probability of dissociative adsorption is proportional to f^2. However, for an adlayer composed of (sufficiently large) separate domains in which $\Theta_F = \Theta_{F,sat}$ and $\Theta_F = 0$ the probability of adsorption at $\Theta_F/\Theta_{F,sat} = 1 - f$ is proportional to f.

Fractional coverage, evaluated via XPS, is displayed as a function of exposure in Fig. 3 for F_2 adsorbed on a partially decomposed silicon-fluoride adlayer. This surface was prepared by adsorbing approximately 1.3 ML of fluorine (i.e., near saturation[9]) on a clean Si(100) surface at 300 K, heating to a temperature near 800 K for approximately 20 s, and cooling to 300 K prior to additional exposure. Similar results were obtained for a surface held at 600 K during the exposure. The two curves represent theoretical *predictions* based on utilizing the kinetic parameters representative of the *clean* surface and assuming the decomposition proceeds (a) homogeneously, and (b)

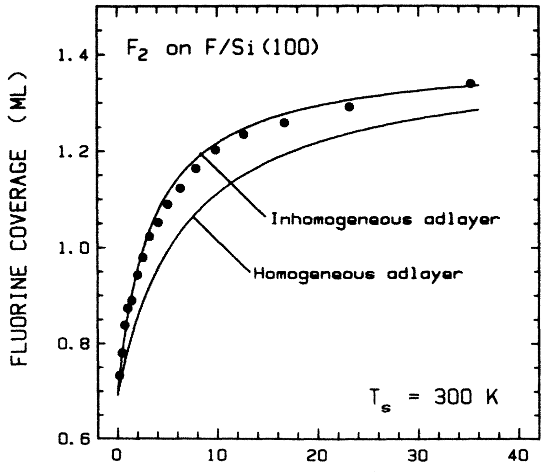

FIG. 3. Coverage vs exposure for the adsorption of F_2 on a partially decomposed silicon-fluoride adlayer (see text). The coverage was determined via XPS. The solid lines represent theoretical predictions based on the kinetic parameters found for the clean surface and employing two different models for the adlayer configuration following partial decomposition (see text).

inhomogeneously. Clearly, the data are represented best by the latter model, suggesting strongly that the thermal decomposition of a silicon-fluoride adlayer proceeds inhomogeneously, leaving separate domains of clean surface and a (locally) saturated adlayer. A separate experiment suggests strongly that the driving force for this domain formation is not solely thermodynamic. In particular, a clean Si(100) surface was exposed to F_2 such that $\Theta_F = 0.6$, and annealed to a temperature near 700 K (i.e., the onset of decomposition). In this case, subsequent adsorption was best described by invoking the homogeneous model, i.e., *annealing,* but not *decomposing,* the adlayer did *not* lead to domain formation.

It is important to note that the reaction we have considered here, the production of $SiF_2(g)$, leads intrinsically to surface defects in the Si substrate. For example, gasification of a single Si atom on a perfect Si(100) surface leads to a point defect— a vacancy in this case. Depending on the active sites for the reaction the number of defects may decrease, increase or remain constant at the decomposition proceeds. Our results, i.e., implicating zero-order kinetics and domain formation, suggest that the reaction may proceed at the SiF_x-Si(substrate) interface, with the interface "area" remaining constant as the reaction proceeds. If this is the proper scenario, we would tend to rule out a model involving (isotropic, two-dimensional) nucleation about a point defect, since such a mechanism would predict that the rate of decomposition should accelerate initially. Separate experiments, employing XPS and examining the rate of isothermal decomposition,[9] do not show any evidence of an acceleratory region. Consequently, the zero-order kinetics suggests that the domain boundaries are either sufficiently rough or follow particular crystallographic directions such that the "area" of the interface remains constant throughout the reaction.

In conclusion, we have examined the thermal decomposition of silicon-fluoride adlayers where, under the reaction conditions considered here, the only gas-phase reaction products observed were SiF_4 and SiF_2, the relative yield of each depending strongly on the initial fluorine adatom coverage. A detailed examination of the kinetics of the desorption of SiF_2 revealed zero-order kinetics spanning a large range of coverages between approximately 1.0 and 0.4 ML. This result could be interpreted as a manifestation of an inhomogeneous decomposition that proceeds preferentially at domain boundaries and/or surface defects such as atomic steps.

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