Photostimulated Desorption in Laser-Assisted Etching of Silicon

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Photodesorption of SiF_3 groups, which are the principal adsorbates on a silicon surface during etching by XeF_2, is found to be responsible for the etch-rate enhancement observed under illumination by low-power, cw band-gap radiation. It is proposed that desorption is stimulated by a photogenerated-charge-carrier–mediated chemical reaction, and not the simple charge trapping and recombination mechanism usually invoked for desorption from semiconductor surfaces.

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When surface reactions produce volatile products, particularly under bombardment by energetic particles such as photons, it can be difficult to identify the role of radiation in the promotion of both reaction and desorption steps. This is particularly so when pulsed lasers are involved, since steep temporal and spatial gradients in temperatures[1] and collisions above the surface[2] can complicate the identification of intrinsic surface-photochemical and surface-physical processes tremendously. Despite the complexities, it has been learned that substrate excitations, direct and indirect, are central to reaction and desorption whether pulsed or continuous light sources are used. Resonant photodesorption occurs when a specific transition of an adsorbed species is excited with sufficient energy to result in desorption after the energy has been delocalized to vibrations of atoms involved in bonding to the substrate,[3] and to the substrate itself. Photodesorption also occurs as a result of substrate heating,[1,3] as well as much lower levels of phonon excitation.[4] Substrate electronic excitations by x rays or high-energy electrons are known to lead to desorption via electronic transitions of adsorbates to states which are not strongly bonded to the surface.[5] Desorption induced by valence-band electron-hole pair excitations in semiconductors, of specific interest in this work, has not been as well studied. Desorption of NO from Si (Ref. 6) and CO_2 from metal-oxide surfaces[7,8] by low-power, cw band-gap radiation has been ascribed to trapping of photogenerated charge carriers, thus weakening surface bonding. Subband-gap extrinsic excitations may also be quite important, particularly at photon energies near the desorption threshold.[9,10] Desorption is not always the only process stimulated by the laser, and the interplay of carrier-induced chemical reaction and desorption, explored for two systems, NO (Ref. 6) and XeF_2 (Ref. 11) on silicon, is particularly interesting. Dissociation and desorption of molecularly adsorbed NO both occur under illumination, appearing to be independent, competing channels. Photoreaction and desorption are tightly coupled in the XeF_2-Si system, however, and it is the nature of that coupling which is discussed in this Letter.

XeF_2 reacts spontaneously with silicon in the dark, first forming a thick (10–20 Å) layer whose main component is SiF_3,[12] then volatile products, chiefly SiF_4 but also including SiF_3 under certain conditions.[13] Illumination of this surface with low-power, cw 515-nm light enhances the etch rate by promotion of Si-F bond formation, yielding volatile species.[11] Product evolution follows a complex time behavior, comprising an early burst and a lower stable production rate at steady state. The intensity dependence of product formation is first order overall at steady state, but higher order during the initial burst. The change in intensity dependence is not attributable to a change in mechanism, but to a strong depletion of one reactive species whose concentration depends on the light intensity, becoming rate limiting. Only two gas-phase products are found in significant amounts: SiF_4, dominant at low intensities (< 20 W/cm^2), and SiF_3, dominant at high intensities (> 40 W/cm^2). Since SiF_3 generation is correlated with an onset of significant photoenhancement of the etch rate, processes leading to formation of that species are of central interest.

Measurements of SiF_3 and SiF_4 yields and translational temperatures as functions of light intensity have been made with molecular-beam mass spectrometry. The basic experimental apparatus has been described in detail elsewhere.[13] Briefly, a silicon crystal (0.1 Ω cm, n type) is placed in a high vacuum chamber and reacted continuously at room temperature with an effusive beam of XeF_2 (5×10^{16}/cm^2 s). Products desorbing along the surface normal are modulated at a frequency f of 1000 Hz, 50% duty cycle, travel a distance L of 17.3 cm through two aperatures, and are ionized and detected with a quadrupole mass spectrometer. The chopper reference is used to trigger a multichannel scaler which accumulates the modulated ion counts as a waveform with a dwell time of 10 μs. The modulated signal arises only from those species which have never made a collision with the walls. The phase angle $\Delta\Phi$ between a given ion signal and the chopper reference carries information about the mass(es) of the neutral(s), M_n, decom-
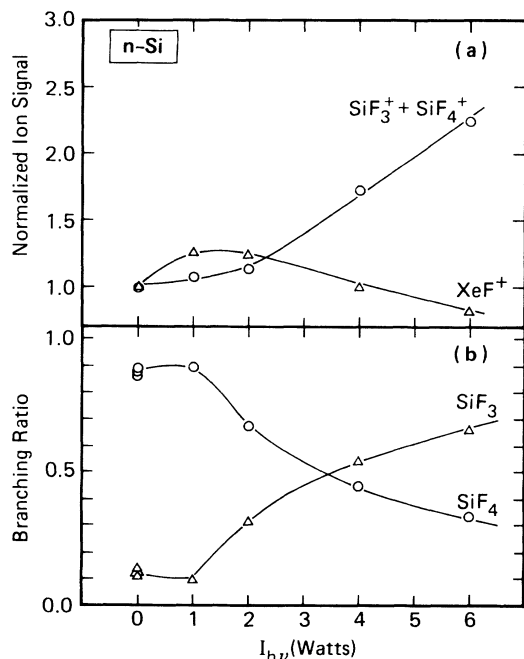
FIG. 1. Product evolution from Si during photoassisted etching by XeF_2 as a function of incident laser power. (a) Total etch rate normalized to the spontaneous rate in the dark and corresponding signal from reflected unreacted XeF_2; (b) apportionment of etch products between SiF_3 and SiF_4.

FIG. 2. Intensity dependence of SiF_3 and SiF_4 formations.

posing to form the ion and its (their) translational energy, T_n, according to the approximate relation

$$\Delta\Phi = \Delta\Phi_{ion} + \Delta\Phi_{inst} + 2\pi fL \left[\frac{2M_n}{\pi k T_n} \right]^{1/2}, \qquad (1)$$

where $\Delta\Phi_{ion}$ is a non-negligible correction for the flight time through the mass spectrometer, and $\Delta\Phi_{inst}$ is a phase offset resulting from instrumental factors. Knowledge of M_n and T_n allows complex mixtures of nascent products desorbing from a surface to be characterized quantitatively.

In the present work, modulated signals are averaged for 6-s periods of illumination of the surface by 515-nm light ranging up to 6 W from a cw Ar-ion laser (near-normal incidence, 3.6-mm $1/e^2$-spot diameter, linear polarization). The data accumulation time spans the initial transient burst of etch products described above, and does not sample the steady-state photoetching regime. 5 min of dark etching are allowed between illuminations to regenerate the fluorosilyl layer which becomes depleted. The results of each illumination cycle are uploaded to an IBM model PC-XT for storage. 80 illumination cycles are averaged for SiF_4^+, the weakest ion signal, and 30 for SiF_3^+, the strongest, for each laser power. Dark, unenhanced etch product spectra are also accumulated each day to normalize for small drifts in XeF_2 flux. Ion intensities are obtained by integration of the modulated signal over one chopper period. Using the electron-
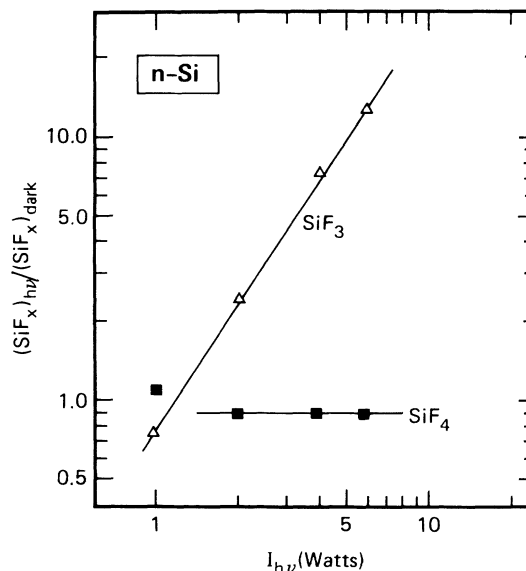
impact fragmentation pattern for SiF_4, relative amounts of SiF_4 and SiF_3 contributing to SiF_3^+ are estimated.[13] Waveform subtraction is used to obtain the net SiF_3 signal. The smaller fluorosilyl ions are ignored for the purposes of this analysis since they have been found to be only a minor constituent of the total product ion current.[11] $\Delta\Phi$ is evaluated at the center of the full width at half maximum of the waveforms, $\Delta\Phi_{ion}$ is subtracted, and the resulting shift related to the most probable translational temperature T_{mp} of the neutral product with use of experimentally calibrated simulations of the waveforms.[14,15] Quantitative reproducibility of the data is good as long as care is taken in preparation of the fluorosilyl layer to illumination.

In agreement with earlier results,[11] it is found that the total etch rate increases with increasing light intensity above a threshold power, 2 W in this work (the value depends on XeF_2 flux). At this power, SiF_3, a minor product in the dark, starts increasing rapidly relative to SiF_4, to which it is a precursor. Data are presented in Fig. 1. At 6 W, SiF_3 accounts for nearly 70% of the total product flux, up from 17% at 0 W. Dependence of product formation on light intensity I is shown in Fig. 2. It can be seen that of the two etch products, only SiF_3 involves photoexcitation in the rate-determining step: The formation of SiF_4 is independent of light intensity when averaged over 6 s. The exponent of I is 1.6 ± 0.05. The most probable translational temperatures are shown in Fig. 3. In the dark, SiF_4 has a T_{mp} of 275 K, and SiF_3 180 K, in agreement with earlier measurements.[13] As I increases, the T_{mp} for SiF_4 increases gradually. SiF_3, on the other hand, exhibits an abrupt step, rising sharply at the laser power at which substantial amounts of SiF_3 are formed (Fig. 1). Substrate heating is unlikely to be responsible for the elevated translational temperatures of the prod-
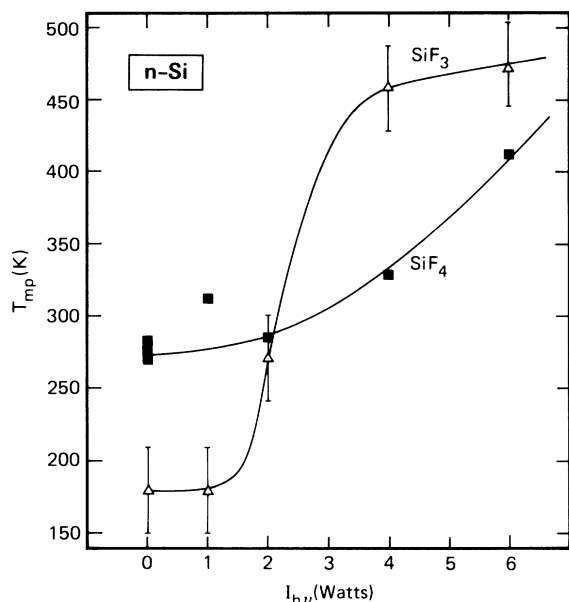
FIG. 3. Most probable translational temperatures for SiF_3 and SiF_4 etch products. Absolute error bars are indicated for SiF_3 and are similar for SiF_4. Relative errors are much less.

ucts formed under illumination. An upper limit to the temperature rise at the surface is calculated to be 43° at 6 W, assuming inefficient heat sinking by the sapphire sample mount.[16] This is supported by measurements with a thermocouple. It is clear that neither product is in thermal equilibrium with the other or with the substrate.

The experimental data in Figs. 1–3 present a consistent picture that SiF_3, the principal adsorbate on the fluorinated silicon surface, desorbs as a result of a photochemical process, and that this is the chief means by which photoassisted etching of silicon takes place. What is the nature of the photochemical process? Silicon is the only absorber in the system at 515 nm,[17] so photodissociation of adsorbates need not be considered. Electrons and holes generated by band-gap excitation of semiconductors are known to induce desorption and/or chemical change as a result of capture by adsorbed species.[18] The classical photodesorption rate, proportional to I,[6,7,18] is governed by trapping of a single charge carrier. The present data exhibit an intensity dependence of $I^{1.6}$. This can only signal classical photodesorption if multiphoton events dominate carrier formation, highly improbable at these low laser powers. Thus, the higher-order dependence suggests that two species, each proportional to I, participate in the rate determining step of the photoetching reaction. These species are proposed to be adsorbates which become charged on illumination, thereby becoming more reactive. The experimental data place certain constraints on their chemical nature. They, or short-lived intermediates derived from them, must be adjacent or mobile in order to be involved

simultaneously in the slow step. Their reaction must result in net SiF bond formation and not simple SiF bond redistribution since an exoergic process is required to break a Si-Si bond and eject SiF_3. Assuming that all components of the fluorosilyl layer [SiF, SiF_2, and SiF_3 (Ref. 12)] have roughly equal probability of trapping charge, the most kinetically important sites will be those whose concentration is highest and which can be converted to gaseous SiF_3 by a single fluorination step. It is known that SiF_3 is by far the most abundant moiety near the surface ($> 40\%$), and that SiF_2, the other possible precursor, the least ($< 10\%$).[19] By this reasoning, -Si-SiF_3 sites are the most likely source of desorbed SiF_3. The other reactant is proposed to be F atoms newly dissociated from Xe and not yet bound to Si.

The charge state of these species under illumination remains to be argued. F atoms are expected to trap electrons rather than holes, becoming F^-. This ion is unlikely to be strongly bound to any specific site, being isoelectronic with neon, and would be relatively mobile. Since photogenerated electrons and holes are equal in number and in excess over the doping level under the present conditions,[11] the concentration of F^- would be proportional to I. F^-, in its noble-gas-like state, would be relatively inert to neutral, closed-shell fluorosilyl moieties. If, however, holes (ionized Si-Si bonds) are trapped by -Si-SiF_3 groups forming -Si^+-SiF_3 ($\propto I$), reactivity toward them would be high. The overall process, seen to be effectively photodesorption, can be written

$$-Si^+-SiF_3 + F^- \rightarrow -SiF + SiF_3, \qquad (2)$$
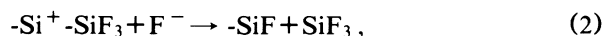
giving a rate law R depending on the numbers n of reactants

$$R_{SiF_3} \propto n_{F^-} - n_{-Si-SiF_3} \propto I^2. \qquad (3)$$

Experimentally, $I^{1.6}$ is measured: This is expected if $n_{F^-} \ll$ or $\gg n_{-Si-SiF_3}$. Observations described in full elsewhere[15] suggest that it is the SiF_3 groups which become more depleted. The subintegral order is not likely to be due to unequal numbers of electrons and holes.[11] The exothermicity of (2) is difficult to estimate since the energy levels are unknown, but is likely to be over 3 eV: Sufficient energy is available for considerable translational excitation of SiF_3. Additional dynamical factors such as passage of newly released SiF_3 through a region of high potential energy may also be important.

Reaction between F^- and -Si^+-SiF_3 could also lead to formation of SiF_4, yet SiF_4 is not found to be a primary photoproduct. The dark reaction, in contrast, shows a competition between SiF_3 and SiF_4 formations dependent on XeF_2 flux and doping.[13] The selectivity toward SiF_3 desorption under illumination may be a consequence of the electronic structure of the charged fluorosilyl group. SiF_3 is highly polar, with a significant posi-

tive charge on the central Si due to the high electronegativity of fluorine. To minimize energy, a hole at a -Si-SiF$_3$ site will most likely lead to increased positive charge on the Si to which SiF$_3$ is bound, and not on the SiF$_3$ group itself. Interaction of F$^-$ with the more positive Si of the -Si$^+$-SiF$_3$ site to form a new SiF bond and displace SiF$_3$ would be strongly favored.

This study provides evidence that low-power, cw laser-assisted etching of silicon by XeF$_2$ is essentially photostimulated desorption of SiF$_3$. Recombination of charge carriers cannot account for the data: A chemical reaction is proposed to be involved. The experiments provide a new view of how photogenerated charge carriers can lead to desorption of an adsorbate from a semiconductor surface. They also extend the scope of surface photochemical systems in which photoreactions and photodesorption are strongly coupled.[3]

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