PHYSICAL REVIEW B VOLUME 39, NUMBER 14 15 MAY 1989-I

Photochemical etching of silicon: The influence of photogenerated charge carriers

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(Received 30 November 1988)

Low-intensity cw band-gap excitation enhances the etch rate of silicon by XeF_2. It has been proposed that the enhancement mechanism involves participation of photogenerated charge carriers in the fluorination reaction itself. A new study has been made of this system by molecular beam mass spectrometry. The results show that for both *n*- and *p*-type silicon the SiF_3 free radical is the primary etch product at Ar-ion laser powers exceeding 40 W/cm^2. SiF_4 is also observed, but its formation is independent of light intensity. The data, including measurements of most probable translational energies, are consistent with a photochemical process being responsible for SiF_3 formation. Surface heating, which is minimal, cannot account for the experimental results. Since SiF_3 is the principal adsorbate on the surface, it is argued that etching is a result of desorption of SiF_3 stimulated by a chemical reaction involving two charge carriers. This is distinct from the photodesorption mechanism usually invoked for semiconductor surfaces, which involves single charge capture by a surface adsorbate. Evidence pertaining to participation of charge carriers in other stages of the fluorination reaction—adsorption of XeF_2 and diffusion of F^-—has also been obtained. The data indicate that photogenerated charge carriers inhibit chemisorption of XeF_2. Field-assisted diffusion, which has been invoked as a rate-determining process in photoassisted etching of semiconductors, is not found to be so for this system.

I. INTRODUCTION

Charge carriers generated by absorption of band-gap radiation are known to induce reaction and desorption on semiconductor surfaces.[1] Studies of both gas-solid and liquid-solid systems have established that it is capture of electrons or holes, resulting in a change of charge state of an adsorbate, which promotes the various photochemical processes which have been observed. With solar energy conversion as an impetus, efforts have concentrated on photoreduction-oxidation reactions in solution,[2] and a great deal has been learned about reaction mechanisms, rates and energies. Much less is known about photoprocesses in gas-semiconductor systems. Photodissociation of NO,[3] photo-oxidation of Si (Ref. 4) and GaAs,[5,6] and photodesorption of NO (Ref. 3) and CO_2 from metal-oxide surfaces[7–10] have been attributed to electron-hole pair formation in the semiconductor. Involvement of photogenerated charge carriers has also been proposed to be responsible for photoetching of semiconductors by halogens at low light intensities. Etching of silicon by XeF_2,[11–13] Cl_2,[14–16] and a fluorine-containing plasma[17,18] are all thought to be mediated by electrons and holes. Similarly, etching of GaAs (Ref. 19) and $GaAs_{1-x}P_x$ (Ref. 20) by chlorine is suggested to be essentially photochemical in nature. At high light intensities, and hence high surface temperatures, etching of Si by Cl_2 (Refs. 15 and 21) and Ge by Br_2 (Ref. 22) appear to be governed by thermally driven processes, however.

Although there is strong evidence that electrons and holes play an important role in etching, *how* they do so is not clear. The bulk of the experimental data available consists of measurements of macroscopic rate dependences on semiconductor doping, light intensity and wavelength.[11,14–20] These are valuable but can only indicate patterns of behavior, not the character of individual surface reactions. Since photogenerated charge carriers can influence any of the stages of an etching reaction (adsorption, diffusion, reaction between etchant and substrate, and desorption) identification of important microscopic processes is essential if an understanding of this class of surface photochemical reactions is to be developed. In addition, the role of surface heating by the laser, if any, must be identified. An early attempt to address these questions was made in a study of photoassisted etching of silicon by XeF_2 using a cw argon ion laser at 515 nm.[11–13] This system reacts spontaneously, so it was possible to examine the effect of illumination on etching in the absence of heating. The dark reaction produces a thick fluorosilyl layer at the surface (10–20 Å),[23] the principal component of which is SiF_3. Reaction of this layer with incident XeF_2 leads to formation of SiF_4 as the major product,[24] and several minor products whose relative abundance depends on doping and etchant flux.[25] On illumination, a complex time behavior is observed as shown in Fig. 1. Products initially desorb in a strong burst, then evolve toward steady state in a manner which depends on light intensity, doping, and XeF_2 flux.[12,13] The intensity of the initial burst increases with total XeF_2 exposure in the dark. This suggests that photosensitive groups in the fluorosilyl layer are built up during spontaneous (dark) etching. Comparison of photoetching in the presence of XeF_2 and photodecomposition of a previously prepared fluorosilyl layer under vacuum indicates that the burst comprises species formed from reactants already present on the surface. Once this

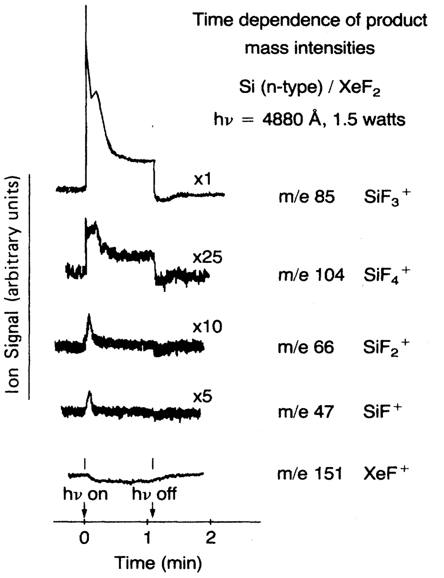

FIG. 1. Typical data illustrating time-dependent mass intensities during photoassisted etching of silicon by XeF_2. Data were obtained in a single chamber instrument (Ref. 12).

population has been depleted etching will only continue if XeF_2 is supplied to the surface. Examination of the steady-state photoetching regime shows that at low laser powers SiF_4 formation is enhanced relative to spontaneous etching, but as power increases SiF_3 appears in ever-increasing amounts with a corresponding decrease in the fraction of SiF_4. The intensity dependences of the initial photoetching rates were obtained for both major products. Formation of SiF_4 was found to be proportional to I^2. Since low laser powers precluded multiphoton processes, this was interpreted to show that two charge carriers, each proportional to the light intensity, are involved in the slow step. Chemically, SiF_3 groups and F atoms dissociated from XeF_2 are the most likely precursors to SiF_4. It was suggested that capture of charge carriers by these species occurs on illumination, forming intensity-dependent populations of SiF_3^+ and F^- in the surface region. The presence of charge at the already chemically active sites would, via electrostatic attraction, result in an enhanced rate of production of SiF_4, and thus a faster etch rate. SiF_3 appeared to exhibit more complex behavior, and no mechanism for its formation was proposed.

The photoenhancement process will not necessarily be the same for all semiconductor-halogen etching systems. For example, it has been suggested that in the Si/Cl_2 system capture of a photogenerated electron by Cl to form Cl^- assists diffusion into undoped and *p*-type silicon, thereby promoting reaction and desorption of polychlorinated products.[14] *n*-type silicon, having a high Fermi level to begin with, is not as strongly influenced by the photogenerated electron-hole pair density. If diffusion is rate limiting an etch rate roughly proportional to the light intensity (i.e., to the concentration of photogenerated electrons) is expected. This is observed experimentally,[14,15] but since photodissociation of chlorine to form Cl atoms is also required for etching, complete interpretation of an intensity dependence is not possible without additional information.[16] The proposal has been made that photoenhancement of the etch rate of Si/XeF_2 is at least in part attributable to enhanced diffusion as well, drawing from calculations of fields and charge distributions.[26] The observed intensity dependence of the reaction product distribution indicates that chemical effects are also important,[13] however. This does not mean that light does not assist diffusion through the fluorosilyl layer, nor that other photoassisted processes such as adsorption or desorption are unimportant. The previous experiments were not sufficiently comprehensive to probe all the means by which light affects the fluorination of silicon. This paper describes new efforts to learn about photoassisted etching in greater detail.[27] Molecular beam mass spectrometry has been used to obtain nascent etch product abundances and translational energies during cw photoassisted etching of *n*- and *p*-type silicon by XeF_2. In agreement with the earlier study,[13] there is strong evidence that two photogenerated charge carriers are involved in laser assisted etching. The primary photoproduct is found to be SiF_3; SiF_4 formation is largely independent of light. This contradicts previous observations, indicating that wall collisions played a role in those measurements.[13] Nonetheless, the data substantiate the idea that photogenerated carriers assist reactions in the fluorosilyl layer. These reactions are proposed to be directly coupled to desorption, leading to efficient volatilization of SiF_3, and thus etching. Photoassisted diffusion through the flourosilyl layer does not appear to be a central mechanism for the etch rate enhancement. Nor does light assist XeF_2 absorption: the data suggest that the opposite is in fact the case.

II. EXPERIMENTAL SECTION

Molecular beam mass spectrometry is a technique which allows sampling of reactive mixtures under collision-free conditions.[28] In this manner, nascent product distributions, even comprising highly reactive species, can be characterized. In addition to measurement of ion intensities, performed in any mass spectrometry experiment, arrival times of the ions can be measured. Since the beam modulation is sinusoidal, it is convenient to express the arrival time as a phase shift in degrees referenced to the chopper. The phase shift $\Delta\Phi$ provides critical information about the mass and velocity of the neutral which has fragmented to form a particular ion. This allows mixtures of neutrals to be characterized, and some information about coupling of energy into product translation to be obtained. An approximate expression relating these quantities is

$$\Delta\Phi=\Delta\Phi_{\mathrm{ion}}+\Delta\Phi_{\mathrm{inst}}+2\pi f L(2M_n/\pi k T_n)^{1/2} , \qquad (1)$$

where $\Delta\Phi_{\mathrm{ion}}$ is the transit time of ions through the mass spectrometer, depending only on the ion mass at constant pass energy, $\Delta\Phi_{\mathrm{inst}}$ is a constant shift arising from instrumental factors which can be calibrated, f is the chopping frequency, L is the flight length traveled by the neutral beam prior to ionization, M_n is the mass of the neutral, and T_n is its translational temperature. If more than one neutral is fragmented to form a specific ion, the last term will be a weighted sum over all the neutrals. As described in full elsewhere, calibrations using gases of known cracking pattern and full simulations of the waveforms allow the phase shifts $\Delta\Phi$ to be converted quantitatively to translational temperatures once the neutral mass has been determined.[25,29]

A. Instrumentation

The spectrometer used in this study has been described in detail,[25] but has been slightly modified for the purposes of this experiment. Briefly, it comprises three differentially pumped chambers separated by plates with 2-mm-diameter apertures. In the first chamber the silicon crystals [0.1Ω cm, n- and p-type, (111) orientation] are placed side by side. They are etched continuously by a 300-K effusive beam of XeF_2 whose flux is estimated to be $5\times10^{16}/\text{cm}^2\,\text{s}$ at the surface. The gas beam is oriented 45° away from the surface normal. A linearly polarized 515 nm beam from a cw argon-ion laser (Coherent Innova I-15) is directed into the vacuum chamber and retroreflected onto the silicon at near-normal incidence by a right-angle prism. The beam is unfocused, with a radius of 1.8 mm at the $1/e^2$ points. Powers range up to 6 W. Products desorbing along the surface normal are modulated at 1000 Hz and 50% duty cycle with a tuning fork chopper (Frequency Control Products), pass through an intermediate chamber, and are detected by a quadrupole mass spectrometer. 70 eV electrons are used for ionization. The full modulated ion signal is measured as follows. The chopper reference signal triggers a Tektronix 2101 pulse generator, whose output in turn synchronizes a Canberra 35 Plus multichannel scalar with 20 MHz pulse counting to the chopper. Acquisition of data from the mass spectrometer is initiated using pulses from an IBM PC-XT microcomputer, which simultaneously signals drive circuitry to open the electromechanical shutter blocking the laser beam. After averaging a preset number of scans, the data are uploaded to the PC for storage and analysis.

B. Procedure

Waveforms for $SiF_4{}^+$ (m/e 104), $SiF_3{}^+$ (m/e 85) and XeF^+ (m/e 150) are obtained for both crystals at each laser power. Data for each mass are acquired separately, averaging for 6-sec illumination periods followed by 5 min of spontaneous etching in the dark to allow the fluorosilyl layer, which becomes severely depleted, to be regenerated. From previous studies[12,13] this illumination period mainly samples the initial burst of products desorbing from the surface, and not the steady-state photoetching regime (see Fig. 1). Using a dwelltime of 10 μs/channel, five complete 1-ms chopper periods are acquired sequentially in one 512-channel scan, and 1000 scans are averaged. After uploading, the first and second 2-ms data segments are averaged together and stored. The fifth period (1-ms segment) is discarded. In this manner acquisition of at least one complete and continuous waveform for each ion is ensured regardless of the magnitude of the phase shift with respect to the chopper reference. This procedure, together with near 100% live time pulse counting, serves to maximize the duty cycle of the experiment. The results presented in this paper are the average of 80 separate waveforms for $SiF_4{}^+$, the weakest ion, 20 for $SiF_3{}^+$, and 8 for XeF^+. Waveforms for all ions were also obtained during spontaneous etching each day to normalize for small drifts in XeF_2 flux and instrument performance. Calibration of the mass spectrometer sensitivity and of phase shifts between the chopper reference and arrival of an ion of a given mass were made using effusive beams of SF_6, SiF_4, and Ar.[25,29] A limited number of experiments in which effusive beams of argon were scattered off the fluorine-covered silicon surface during illumination were also performed.

C. Data Analysis

The XeF_2 flux used in this study was chosen to simplify interpretation of the product distribution as much as possible. As shown in Ref. 25, essentially all the ion intensity at $SiF_3{}^+$ and $SiF_4{}^+$ is attributable to SiF_3 and SiF_4 during spontaneous etching under the present conditions. This also applies to the photoetch products.[12,13] Contributions from other products such as the smaller fluorosilyl radicals are minor, and have been ignored in this analysis.

The phase shift of the ion signal relative to the chopper reference is determined from the center of the full width at half maximum of the waveform. Phase shifts were obtained for SiF_4 etch product from the $SiF_4{}^+$ waveforms. Those for SiF_3 were obtained from $SiF_3{}^+$ waveforms after stripping the SiF_4 contribution from them. They were then converted to most probable translational temperatures using a family of theoretical curves calculated for the various neutral masses using the procedure described in Ref. 29. This method, rather than use of a single universal curve,[28] was found to minimize systematic errors inherent in extrapolations from calibration data. For lack of more accurate information, the energy distributions used in simulations of the photoetch product waveforms were assumed to be Maxwellian. This is no doubt a poor assumption, but it should not invalidate interpretation of qualitative trends in the data. Although full velocity distributions can be extracted from the waveforms,[29] this was not done in the present study because the signal-to-noise ratio was diminished by a smaller chopper aperture and short data accumulation times.

Ion intensities were measured by integrating the modulated portion of the waveform over one chopper period and correcting for the $1/v$ sensitivity dependence and the mass discrimination of the mass spectrometer. The m/e 104 ($SiF_4{}^+$) to m/e 85 ($SiF_3{}^+$) ratio for SiF_4 was measured experimentally and used to separate the SiF_3 and SiF_4 components at m/e 85. The product distributions at each power were calculated from these two masses alone, ignoring any differences in contributions of SiF_4 and SiF_3 to m/e 66 (SiF_2^+) and m/e 47 (SiF^+).[30]

D. Sources of Error

The raw data and relative amounts of SiF_3 and SiF_4 extracted from them are quite reproducible, but only so if XeF_2 dosing and exposure of the crystals to light are controlled carefully. As noted above, and as reported in earlier experiments,[13] illumination, even at low power for a few seconds, causes notable changes in the photochemistry of the fluorosilyl layer. Run-to-run comparisons can only be made if the history of the crystals (dating from the previous day or so) is the same. In previous work this problem was minimized by multiplexing the mass spectrometer and doing entire laser-power dependences in a single day.[12,13] This could not be done in the present experiments, however, so each set of measurements was made using an identical protocol with timing controlled by the computer and constant XeF_2 flux to the surface. The single biggest source of irreproducibility was depletion of the fluorosilyl layer. If insufficient dark etching time was left between illuminations, the photosensitivity of the crystal was markedly reduced. (As noted in the Introduction this was also observed in previous experiments.) The quantitative importance of this type of systematic error is not readily assessed—every effort was made to keep it small. Errors in determination of phase shifts and ion intensities have been estimated, however. For XeF_2, the absolute error in most probable translational temperature increased from ±10 K at 1 W to ±35 K at 6 W. SiF_3 and SiF_4 have similar error bars, ranging from ±30 K at 1 W to ±40 K at 6 W. It should be noted that these are all absolute errors, relative errors are much smaller. Errors in measuring ion intensities are quite small, of the order of a few percent. Corrections for $1/v$ discrimination, which used the phase data, introduce extra uncertainty. Both of these are minimal, however, in comparison to errors introduced by neglect of ionization cross-section differences and assumptions made in converting ion intensities to neutral product distributions. Although independent cracking patterns are available in some cases, their applicability depends on whether or not any internal excitation in the etch products affects their fragmentation on ionization.[30] Differences in extent of fragmentation between the two products will affect the relative amounts formed, most likely leading to an underestimation of the SiF_3 fraction. Any error is constant since all data were treated in the same way. Hence, qualitative trends as a function of light intensity are unlikely to be strongly affected.

III. RESULTS

On exposure to light, the reactivity of the fluorosilyl layer is increased, leading to a net enhancement of the etch rate. Data are presented in Figs. 2 and 3 for *n*- and *p*-type silicon. The upper part of each figure shows the total product ion intensity as a function of laser power normalized to the corresponding intensities during spon-

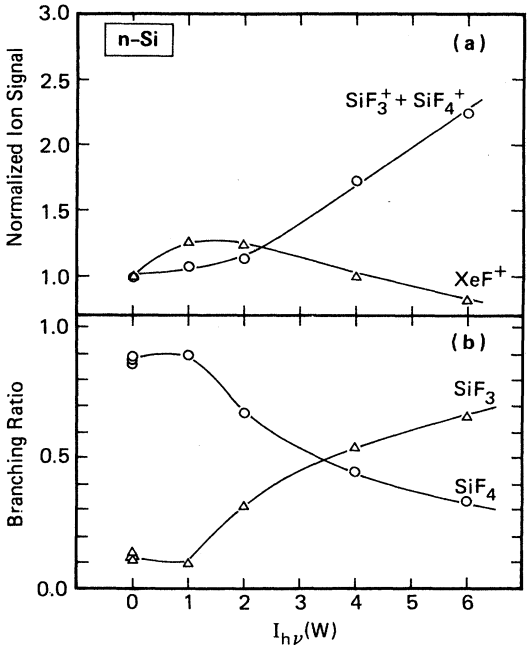

FIG. 2. Laser power dependence of product signals during photochemical etching of *n*-type silicon. (a) Ion signals for fluorosilyl products and reflected, unreacted XeF_2 normalized to values for spontaneous etching (0 W); (b) branching ratios for the two principal products, SiF_4 and SiF_3.

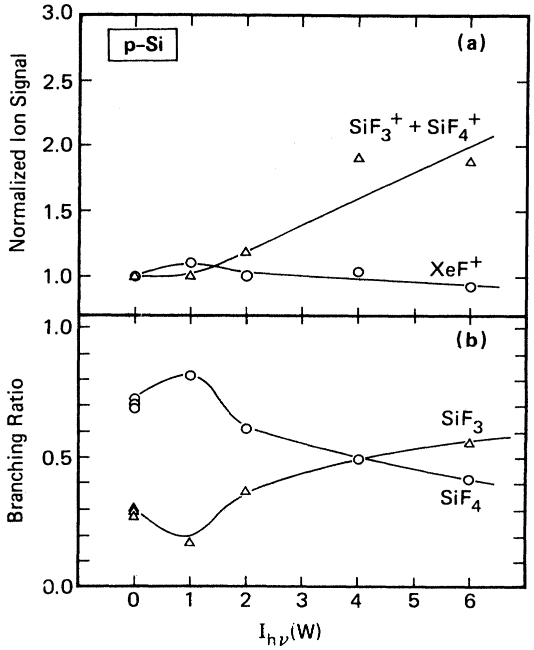

FIG. 3. Laser power dependence of product signals during photochemical etching of *p*-type silicon. (a) Ion signals for fluorosilyl products and reflected, unreacted XeF_2 normalized to values for spontaneous etching (0 W); (b) branching ratios for the two principal products, SiF_4 and SiF_3.

taneous etching. The two types of silicon show very similar etch rate enhancements. The curves themselves show two distinct regimes: below about 2 W the etch rate enhancement is very small and in fact the reflected, unreacted XeF_2 fraction (XeF^+) increases. Above 2 W a net enhancement appears, accompanied by a drop in the reflected XeF_2 intensity. In the lower part of each figure the branching ratio between SiF_4 and SiF_3 is plotted. For *n*-type silicon, the product distribution is essentially unchanged below 2 W, where etching is still unenhanced. A shift toward SiF_4 formation is found for *p*-type silicon. Above 2 W, the change is dramatic for both dopant types. The relative amount of SiF_4 steadily declines, mirrored by an increase in SiF_3 formation. As shown in Fig. 2(b), at 6 W SiF_3 accounts for over 60% of the product flux leaving the surface. Corresponding trends are seen in the phase data for ${SiF_3}^+$, presented in Fig. 4. As laser power increases, any rise in surface temperature should result in a small increase in velocity of inelastically scattered and desorbing neutrals, and a uniform decline in phase shift for all ions. Phase shifts superimposed on this trend will be due to additional factors: a change in neutral product mix and/or changes in velocity of desorbing products.

The difference in net shift between ${SiF_4}^+$ and ${SiF_3}^+$ shows clearly that the two ions do not arise from a single neutral [cf. Eq. (1)]. The abrupt shift in phase of the ${SiF_3}^+$ signal indicates that either the neutral mix at *m/e* 85 is undergoing a strong change above 2 W or the most probable translational energies are changing, or both. That the neutral mix is indeed changing is clear from the data in Figs. 2 and 3. This does not account completely for the change in phase shifts, however. When the phase shifts for the SiF_4 and SiF_3 components of the ${SiF_3}^+$ waveforms are converted into most probable translational energies, as shown in Figs. 5 and 6, it is evident that marked velocity changes also occur. The SiF_4 translational energy increases monotonically with laser power while that of SiF_3 undergoes an abrupt step from a very low value to an elevated one. The increase is not as marked for SiF_3 desorbing from *p*-type silicon as from *n*-type silicon. It should be noted, however, that a much larger fraction of the spontaneous etch products desorbing from *p*-type silicon is SiF_3. The most probable translational energy of this component is low, about 220 K. Since its waveform cannot be reliably separated from that of the photoproduct, the data in Fig. 6 reflect contributions from both.

The intensity dependences of SiF_3 and SiF_4 formation are presented in Figs. 7 and 8, normalized to the spontaneous etch rate. Formation of SiF_3 is proportional to $I^{1.60\pm0.05}$ on *n*-type silicon, and to $I^{1.1\pm0.15}$ on *p*-type silicon. Omission of the 6 W point in Fig. 8 leads to a slope of 1.26±0.05. In both cases SiF_4 production is independent of light. It can be seen that on *n*-type silicon the relative amount of SiF_4 produced is a little lower than in the dark, while on *p*-type silicon it is a little higher. In both cases SiF_3 formation is somewhat suppressed relative to SiF_4 at 1 W, as also evident in Figs. 2 and 3.

It is important to separate the effects of laser heating from those of electronic excitation in order to understand

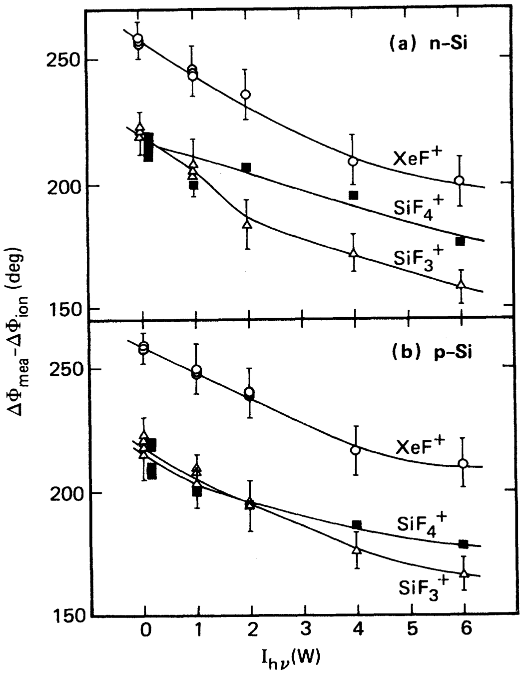

FIG. 4. Phase shifts of ion signals relative to the chopper reference as a function of laser power. The mass-dependent phase shift arising from the transit time of ions through the mass spectrometer has been subtracted. (a) *n*-type silicon; (b) *p*-type silicon.

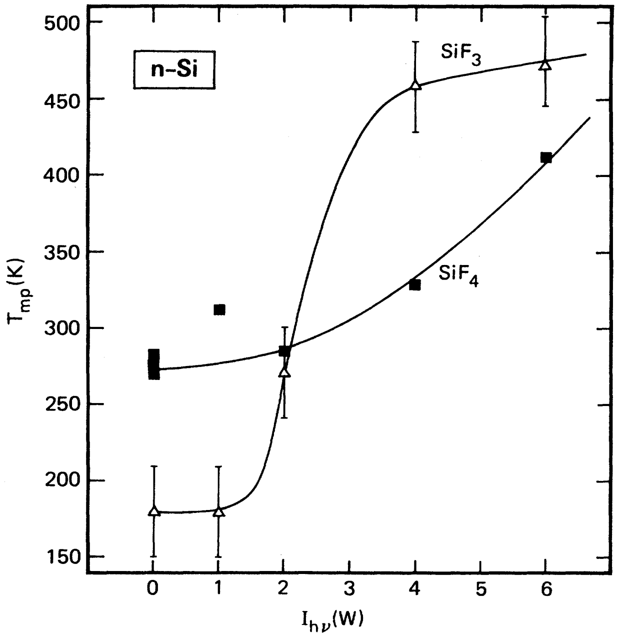

FIG. 5. Laser-power dependence of the most probable translational temperatures for nascent SiF_3 and SiF_4 desorbing from *n*-type silicon.

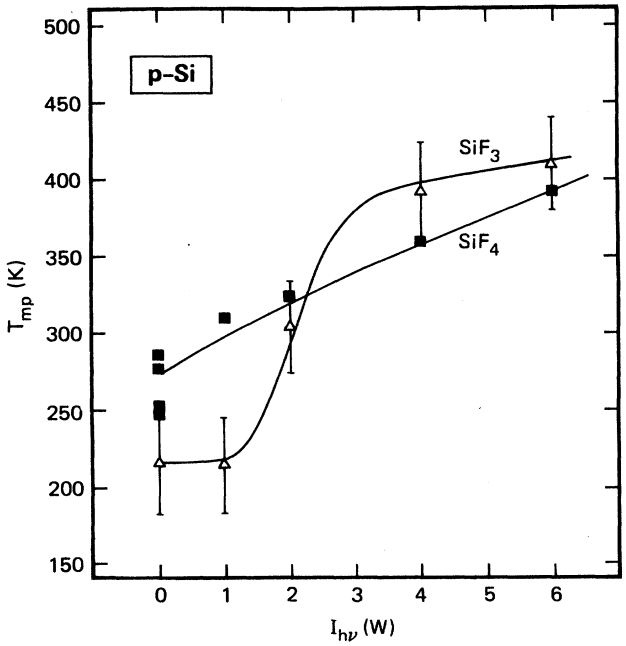

FIG. 6. Laser power dependence of the most probable translational temperatures for nascent SiF_3 and SiF_4 desorbing from *p*-type silicon.

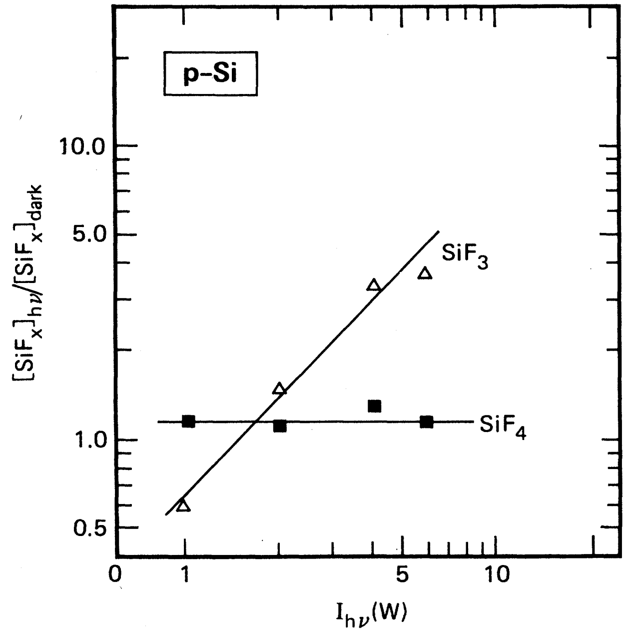

FIG. 8. Intensity dependence of SiF_3 and SiF_4 formation on *p*-type silicon.

the increases in product translational energy with laser power. Although the time-temperature profile in the center of the laser spot was not measured, a thermocouple placed at the edge of the illuminated area indicated that a 23° rise occurred after irradiation for 6 s at 6 W. The temperature rise is calculated to be about 9° at that power, assuming that the thermal properties of the system are those of a semi-infinite slab of silicon and that none of the light is reflected.[31] More realistically, the heat dissipation will be influenced by the thermal properties of the sapphire crystal onto which the silicon is mounted. An increase of 43° is expected in that case. These pessimistic estimates bracket the low temperature increase observed experimentally.

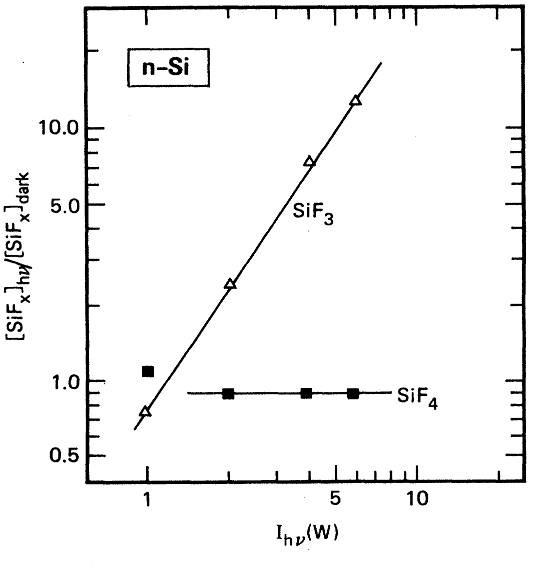

FIG. 7. Intensity dependence of SiF_3 and SiF_4 formation on *n*-type silicon.

In an unsuccessful attempt to find an independent experimental probe of surface temperature, phase shifts of reflected XeF_2 and Ar were also measured. Because the sampling is along the surface normal, 45° away from the effusive beam axis, most of the unreacted molecules are likely to have been trapped for some period of time on the surface. Although they may not be thermally equilibrated with it,[32] at the very least translational temperatures can provide lower limits to the true surface temperature under illumination. Phase shifts for XeF_2 were measured during every experiment. Those for Ar were made using both neat gas and Ar mixed with XeF_2. The resulting translational temperatures are shown in Fig. 9. If translational excitation were a simple result of surface heating, data for *n*- and *p*-type silicon would be superimposable within experimental error since there is essentially no difference in absorbance between the two materials so far above the band gap.[33] Moreover, the two gases might be expected to show roughly the same extent of heating assuming similar interaction strengths with the surface. It is clear that neither gas behaves in a simple manner. Not only are both gases significantly hotter than the estimated surface temperature, but they are also systematically hotter desorbing from *n*-type silicon than from *p*-type silicon. Differences in fragmentation of XeF_2 on ionization were also observed. Relative intensities of

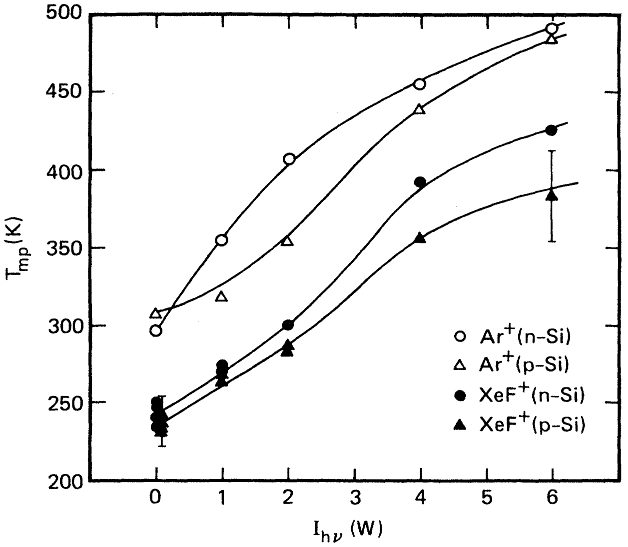

FIG. 9. Laser power dependence of the most probable translational temperatures for Ar reflected from fluorinated silicon, and unreacted XeF_2 reflected from fluorinated silicon during etching.

XeF_2^+ and XeF^+ are shown in Table I. It must be noted that these data were extremely sensitive to the history of the crystal. Although the qualitative trends were always observed, the absolute numbers could vary by as much as 20%. By way of comparison, the quantitive reproducibility of the fluorosilyl ion intensities was typically better than 5%. Despite the uncertainty, it is clear that there is an increasing extent of fragmentation as laser power incident on the sample is increased, and that the trend is somewhat more pronounced for *n*-type silicon than for *p*-type silicon. This result is independent of experimental protocol. The XeF_2 data have been reproduced using a number of crystals on several different sample mounts over the course of this study.[34] It is clear that the physical interaction of otherwise inert species with the rough, fluorinated silicon surface during illumination is complex, and cannot provide a measure of surface temperature. Both calculations and the thermocouple measurement indicate strongly that heating is minimal, however.

TABLE I. Extent of fragmentation on ionization of reflected, unreacted XeF_2.

$I_{h\nu}$ (W)	Si type	$[XeF_2^+]/[XeF^+]$
0	*n*	0.59
	p	0.52
1	*n*	0.49
	p	0.51
4	*n*	0.38
	p	0.43

These data are to be compared to results obtained in two recent studies.[11–13,25] The relative amounts of SiF_4 and SiF_3 and their most probable translational temperatures during spontaneous etching are in quantitative agreement with earlier molecular beam mass spectrometry experiments at 500 Hz.[25] The present data should be considered the more accurate because of the greater precision in measurement of differences in phase shifts afforded by use of 1-KHz modulation. The photoetching data, however, disagree on one major point with the previous work.[13] It appeared that both SiF_4 and SiF_3 were photoproducts, and differences in their intensity dependences indicated that they were formed by distinct mechanisms. As seen in Figs. 7 and 8, however, SiF_3 is unambiguously the only photoproduct. The most likely origin of the discrepancy is the importance of wall collisions in the single chamber instrument used previously. Control experiments with SiF_2 had shown that radicals could survive multiple collisions with fluorinated stainless steel[24] and it was naively assumed that the same applied to SiF_3 since rather large amounts of it were detected.[11,12] It would seem, however, that a portion of the SiF_3 did react at the walls and thus any intensity dependence of SiF_4 is directly attributable to the intensity dependence of the gas phase density of SiF_3. It is difficult to compare directly the magnitudes of the intensity dependences measured in the two studies because of the fundamental differences in the way the data were obtained. Previously, the intensity dependences of the initial rates of change of the rates of reaction were reported, in the present study the intensity dependences of yields of SiF_3 and SiF_4 integrated over 6 s are given. In addition the pressure regime was much lower in the earlier work. This is known to affect the chemistry of both spontaneous and photoassisted etching. Despite the differences in experimental design and the influence of wall reactions on SiF_4, both studies are consistent in showing the involvement of photons in the slow step to be higher than first order for laser powers up to 4 W.

IV. DISCUSSION

The experiments show that under the reaction conditions used photoassisted etching only becomes appreciable above 2 W. Below this power, although the etch rate is unaffected, notable changes are seen in populations desorbing from the surface. The etch product distribution is essentially unchanged for *n*-Si, but undergoes a marked shift toward a higher fraction of SiF_4 on *p*-type Si, leading to very similar product branching ratios for the two doping types. The reflected, unreacted XeF_2 signal is seen to increase. The roughness of the surface ensuring that all inelastic scattering angles are averaged in this measurement, an increase in the XeF_2 signal is not attributable to a change in angular distribution, but to a net decrease in reaction probability of XeF_2 under illumination. The most probable translational energies of the reaction products are notable in that that of SiF_3 is unchanged from spontaneous etching conditions, while those of SiF_4 and XeF_2 have increased somewhat. This increase is not attributable to surface heating, which is very small. At 2 W a new reaction channel opens, leading to removal of material from the surface. SiF_3, the principal component of the fluorosilyl layer, is the primary photoproduct. As desorption of this species becomes more pronounced the relative amount of its surface reaction product, SiF_4 declines. That SiF_3 desorption is indeed a distinct process under illumination is corroborated by the most probable translational energy data: in contrast to SiF_4 which undergoes a smooth and gradual increase in T_{mp} with light intensity, SiF_3 exhibits an abrupt jump. The S shape of the curve is highly suggestive of onset of a photochemical process.[35] The XeF_2 reaction probability increases from its value at 1 W, eventually reaching a value larger than the reaction probability in the dark. Bearing these observations in mind, we can now consider what they tell us about how light can influence the various stages of etching: adsorption of the etchant, diffusion of reactants, reactions between the etchant and the substrate, and desorption of the etch products.

A. Adsorption

The rise in reflected, unreacted XeF_2 signal on illumination at low power indicates that light inhibits one or more of the microscopic steps involved in dissociative chemisorption of XeF_2 to release F atoms on the surface. Very little is known about the adsorption of XeF_2 on silicon. Xenon has never been observed on a fluorinated silicon surface exposed to XeF_2, even at low temperature.[36,37] This has been taken to show that the residence time of undissociated XeF_2 on the surface is extremely short. Kinetic data obtained at relatively high pressures (0.05–0.2 Torr) were presented as evidence for a physisorbed layer of XeF_2, however.[38] Regardless of whether or not physisorbed XeF_2 is present on the surface, it is clear that photogenerated charge carriers reduce the already low reaction probability (0.01–0.025) (Ref. 39) by 10–25%. It might be imagined that this is a simple consequence of reduction of dissociative chemisorption sites resulting from chemical changes to the surface on illumination. While this may be important, and cannot be ruled out, it does not seem to explain the elevated $T_{\rm mp}$ in Fig. 9 or the $[XeF_2^+]/[XeF^+]$ ratios in Table I. The decrease in the latter can result from several processes. XeF could desorb under illumination if complete dissociation of XeF_2 on the surface is inhibited. XeF is so weakly bound (150 meV) (Ref. 40) that this possibility seems remote, however. Further evidence against this possibility is provided by trends in $\Delta\Phi-\Delta\Phi_{\rm ion}$ for XeF_2^+ and XeF^+ with light intensity. If an increasing component of XeF^+ were from XeF a corresponding decrease in phase shift should be observed [see Eq. (1)]. In fact these shifts are the same for both fragments within experimental error. This observation also eliminates the possibility the highly excited XeF_2 dissociates in transit between the chopper and the ionizer. It is more likely that the change in ion intensity ratios is attributable to increasing fragmentation during electron impact ionization because of internal excitation of reflected XeF_2.[41] Although the means by which excess internal and translational excitation is acquired by XeF_2 is not revealed in the present experiments, it is possible to speculate that charge transfer processes involving photogenerated electrons or holes might be responsible. Theoretical studies have indicated that charge transfer can assist dissociative chemisorption by inducing vibrational excitation of the adsorbate as it approaches the surface.[42] If this mechanism is operant, the decrease in extent of dissociation and apparent increase in internal energy of reflected XeF_2 suggests that charge transfer interferes with sticking in this case.

Inelastically scattered Ar, which is chemically inert to fluorinated silicon and hence does not undergo any decrease in intensity on illumination, also appears to be translationally excited. The Ar results are unanticipated by the literature. Studies of scattering of Ne from LiF in the absence of light,[43] the closest model system for fluorinated silicon available, show that energy loss to bulk phonon modes predominates. Similar conclusions were drawn from investigations of Xe scattering at hyperthermal energies from weakly polar GaAs and nonpolar Ag and Ge surfaces.[44] No reports have been made of processes which can preferentially increase velocities of scattered atoms in the absence of significant heating. Charge transfer has not been invoked in scattering studies of rare gases from polar surfaces. The similarity in behavior of Ar and XeF_2 raises the question whether common scattering dynamics are involved for the two systems.

As power increases the XeF_2 signal decreases, eventually reaching a smaller value than in the dark. According to the data in Fig. 9 and Table I, reflected XeF_2 appears to be translationally and internally excited over the whole power range. Hence, there is no reason to believe that photoinhibition of sticking has become unimportant. It is likely that an independent process leading to a net increase in reaction probability is competing. Studies of the correlation of fluorine coverage with reaction probability have shown that as the fluorosilyl layer is depleted, sticking of XeF_2 increases.[45] This phenomenon is suggested to be important here. Given the greatly increased rate of removal of SiF_3 from the surface at higher laser power, it is expected that overall coverage by fluorine drops during illumination. If coverage effects and not a new photoassisted adsorption channel are important then there should be evidence for increased reaction probability after illumination has ceased. Indeed as can be seen in Fig. 1 the reaction probability of XeF_2 remains high for some period of time in the dark, reflecting a marked decrease in surface fluorine concentration.

Although a plausible explanation for an increase in XeF_2 reaction probability can be offered, the reason for inhibition of adsorption and dissociation by photogenerated charge carriers remains to be understood. More precise experiments on model systems may be quite valuable in this regard.

B. Diffusion

It has been proposed[26] that the silicon etching system can be modeled by an insulating fluorosilyl layer over a semiconductor. The features of the model are as follows. F atoms on the surface of the fluorosilyl layer will be negatively charged because of the high electron affinity of that element. A compensating positive charge will accumulate at the silicon-fluorosilyl layer interface. Assuming that the Fermi level is pinned at the surface by F^-, a doping-dependent potential ϕ will be established across the layer (thickness l). The etch rate is proposed to be proportional to the number of F^- at the surface, or field strength ϕ/l. One effect of an electrostatic field in this system would be to govern the transport of F^- across the fluorosilyl layer to the underlying silicon. According to this model, qualitative changes in ϕ/l (or number of negative ions) can be taken to predict trends in etch rates under various conditions. Absorption of light will cause an increase in the Fermi level and establishment of flat band conditions in the silicon,[1] leading to a higher surface potential ϕ_I and an increased field strength. Any thinning of the fluorosilyl layer will independently increase the field. Thus, according to the model, field effects can account at least in part for the observed increase in etch rate of both *n*- and *p*-type silicon under band-gap radiation. If this model is correct, and the rate of formation of volatile fluorosilyl species is dependent on field-assisted processes, then one would expect that all the reaction products under illumination will show some dependence on light intensity, although the product distribution may not necessarily remain the same as in the dark. In this study it has been observed that the rate of formation of only one of the products, SiF_3, is dependent on light intensity. Moreover, the high translational energy of this species indicates that it is formed at the surface and desorbs promptly. Processes such as field-assisted transport through the fluorosilyl layer would not be likely to influence gas-phase SiF_3 production. These data provide strong evidence that fields as described in the model have very little influence on the rate-determining process in photoetching of silicon by XeF_2.

It might be argued that this conclusion applies to the initial burst phase of etching, but not necessarily at steady state. The present experiments do not probe the steady-state regime explicitly; however, they are relevant to it. The product distribution and its dependence on light intensity at steady-state are very similar to those found here, taking into consideration wall reactions in the earlier work,[11,12] and it can be surmised that the chemistry is much the same in both regimes even though the etch rates are different. The burst phase involves species already present in the SiF_x layer, reducing their concentration to the point where photoetching ceases altogether unless new fluorine is supplied from the gas phase. Even when this supply is present the layer remains depleted throughout steady-state etching. According to the field model, the thinning of the fluorosilyl layer should increase the field strength and hence the photoetch rate. The opposite trend is always observed: the fastest photoassisted etching occurs after prolonged exposure to XeF_2 in the dark, and the slowest at steady state. Suppression of etching even occurs under certain conditions.[12]

Although the field model is appealing, it cannot account for the data described here. Processes such as transport of F^- under the influence of a potential drop may be taking place, but if so they are background processes which are not rate limiting, and thus not probed in these experiments.

C. Reaction

In the previous study of photoassociated fluorination of silicon, the conclusion was drawn that the primary means by which light enhances the spontaneous etching of silicon by XeF_2 is promotion of Si—F bond formation.[12] The kinetics of the initial response of the fluorosilyl layer to light provided evidence that more than one photogenerated charge carrier was involved in the fluorination reaction.[13] The reaction sequence proposed was

$$F+e\rightarrow F^- , \tag{2}$$

$$F^- + h \rightarrow F , \tag{3}$$

$$SiF_x + h \rightarrow SiF_x{}^+ , \tag{4}$$

$$SiF_x{}^+ + e \rightarrow SiF_x , \tag{5}$$

$$F^- + SiF_x{}^+ \rightarrow SiF_{x+1} , \tag{6}$$

where e and h denote electron and hole, respectively, SiF_x are the various fluorosilyl groups, and F is free (nonbonded) fluorine. Reaction pairs (2),(3) and (4),(5) lead to net production of charged reactants, the concentration of each being proportional to the photocarrier density and thus the light intensity. Since F^- is isoelectronic with neon, this species is not expected to be reactive toward neutral, closed-shell SiF_x groups. If, however, fluorosilyl species trap a hole (ionized Si—Si bond), reactivity will be very high, resulting in an enhanced rate of Si—F bond formation, (6). Simulations of SiF_4 formation according to this sequence were carried out. Using reasonable assumptions for carrier populations and trapping and recombination cross sections, the observed intensity dependence of product formation ($\propto I^2$) was reproduced. The present study has shown, however, that SiF_3, not SiF_4, is the photoproduct. This reaction sequence must be reconsidered: as written, it cannot account for selective formation of gaseous SiF_3 over other fluorosilyl species.

SiF_3 groups are the primary components of the fluorosilyl layer, and are found in greatest concentration ($\approx 40\%$ of total fluorine) at and near the surface.[23,46] SiF and SiF_2 are less than 20% and 10%, respectively. Two distinct routes to gas phase SiF_3 are possible, (i) stimulated desorption of SiF_3 and (ii) addition of F to SiF_2 followed by rupture of a Si—Si bond and desorption. The product branching ratios allow arguments to be made against the importance of (ii). Assuming that a general reaction sequence such as (2)–(6) applies, that is, that light promotes formation of Si—F bonds, it would be expected that if reaction to form SiF_3 from SiF_2 is important, some intensity dependence for parallel reactions such as SiF_4 formation from SiF_3 should also be observed.

The data in Figs. 7 and 8 show otherwise. Also, if surface SiF_2 reactions are to predominate the etching, their low concentration on the surface forces assumption of a very high reaction rate constant compared to reactions with the other fluorosilyl groups. This does not seem physically reasonable, since attack of F at a Si—Si bond involves highly specific, localized electronic interactions[47] and only relatively minor variations may be expected from site to site. For these reasons photostimulated desorption of SiF_3 is proposed to account for the experimental data. This does not require that the fluorination sequence outlined above to be rejected: as will be argued in Sec. IV D, a specific version of it is likely to be central to the desorption process.

Before discussing this possibility in detail, two other issues deserve examination. The first concerns the observation that at low light intensity a shift toward SiF_4 production at the expense of SiF_3 occurs even though essentially no etch rate enhancement over the spontaneous rate is present (Figs. 2 and 3). The effect is much more pronounced for *p*-type Si than *n*-type Si. It is known from studies of the dependence of the spontaneous (dark) etching chemistry of silicon on doping[25] that when electrons are the majority carrier SiF_4, one of the three volatile reaction products of surface —Si—SiF_3 groups, is more likely to be formed than when holes are in the majority (see Figs. 2 and 3). The doping effect on —Si—SiF_3 group reactions was suggested to arise from the ability of electrons to stabilize additional positive charge as it develops on an already positively charged SiF_3 center during attack by F to form SiF_4.[25] If holes are the majority carrier, the lack of such stabilization would result in a greater probability of forming a new Si—F bond with the other Si of the —Si—SiF_3 moiety, thereby displacing SiF_3 from the surface. Independent evidence for the importance of the majority carrier in the fluorination reaction has also been found in synchrotron photoemission studies.[48] Now, band gap illumination causes electrons and holes to be formed in equal numbers. At 1 W, the steady-state photocarrier density will be in excess of the dopant concentration ($\approx 10^{17}$ cm^{-3}),[13] and electron and hole densities will be roughly equal. Carrier-induced chemical differences among the etch products of *n*- and *p*-type silicon should be minimized. The present data are consistent with this prediction, and reinforce the proposal that chemical effects dominate differences in etching of *n*- and *p*-type silicon.[25,47,48]

The second point concerns the possibility that the fluorosilyl layer is a close analog to amorphous hydrogenated silicon, and that increased reactivity under illumination is related to phenomena leading to the Staebler-Wronski effect.[49] This effect is a significant drop in conductivity due to an increase in defect density under prolonged illumination. Systematic investigations of defect generation lead to a model proposing that the defects were silicon dangling bonds formed by photocarrier recombination-induced rupture of weak Si—Si bonds.[50] The total density of dangling bonds was sublinear in total photon fluence. If such a mechanism were responsible for photo-enhanced etching, providing new sites for Si—F bond formation, all fluorosilyl reaction products should be affected. The present observations of a single photo- product and a superlinear intensity dependence eliminate the possibility that the two materials respond in the same way to illumination.

Although Si—F bond formation is clearly influenced by light, it is not the sole process leading to enhanced etching since it cannot account for the dependences of the etch products on light intensity. A more complex picture is appropriate.

D. Desorption

Photostimulated desorption of adsorbates from semiconductor surfaces is a well documented phenomenon attributable to weakening of the adsorbate-surface bond by carrier capture.[3,7–10] Experimental and theoretical studies have shown that the desorption rate is proportional to I over the intensity range used in this study, and proportional to $I^{1/2}$ at very low powers. Although it is tempting to ascribe formation of gaseous SiF_3 to desorption of surface SiF_3 groups following carrier capture, the observation of an $I^{1.6}$ dependence rules out this possibility. Moreover, the energy available from trapping and recombination is at most 2.4 eV assuming the unlikely involvement of hot carriers. Thermalized carriers would release far less. This is insufficient for rapture of a Si—Si bond (between 2.4 and 3.2 eV) (Ref. 51) in the absence of heating. An alternative pathway to stimulated desorption must be invoked. This process must account for the higher order dependence on I, release sufficient energy to break a Si—Si bond and be highly selective for desorption of SiF_3 from the surface of the fluorosilyl layer. As will be discussed below, the following sequence of steps satisfies these conditions:

$$\mathrm{F}+e \rightarrow \mathrm{F}^- , \tag{7}$$

$$\mathrm{F}^- + h \rightarrow \mathrm{F} , \tag{8}$$

$$\text{—Si—SiF}_3 + h \rightarrow \text{—Si}^+\text{—SiF}_3 , \tag{9}$$

$$\text{—Si}^+\text{—SiF}_3 + e \rightarrow \text{—Si—SiF}_3 , \tag{10}$$

$$\text{—Si}^+\text{—SiF}_3 + \mathrm{F}^- \rightarrow \text{—Si—F} + \mathrm{SiF}_3 . \tag{11}$$

The proposed mechanism is similar to that of (2)–(6) in that the reactive species are suggested to be components of the fluorosilyl layer which have trapped a photogenerated charge carrier. The key difference between the two mechanisms is that *volatile product formation results from reaction at a specific type of site, and not from a generally enhanced fluorosilyl bond formation rate.*

As discussed above, this mechanism predicts an I^2 dependence for etch product formation. Experimentally, values of $I^{1.6}$ and $I^{1.1}$ are observed for *n*- and *p*-type silicon, respectively. Previous studies[11–13] showed initial intensity dependences close to 2 for both *n*- and *p*-type silicon, decreasing to apparent first order as the reaction progressed to steady state. The present data probe the transition between these regimes and thus may well reflect a notable depletion of one reactant of the two reactants during illumination, such that one reactant is more strongly rate controlling than the other and nonintegral order kinetics obtain. If this interpretation is correct, the depletion is more profound for *p*-type silicon than for *n*-type silicon. It is not possible at this time to say whether SiF_3 groups or F is being consumed. If the concentration of SiF_3 groups becomes rate limiting, it appears that only certain types of sites are depleted since SiF_4 formation is unaffected (Figs. 7 and 8). As noted earlier illumination causes a reduction in photosensitivity of the fluorosilyl layer. The photoresponse is restored only slowly in the dark even after complete reestablishment of the spontaneous etch rate following illumination. It is possible that there is a connection between these species and those which become depleted. Detailed spectroscopic data on changes in the fluorosilyl layer during illumination may provide some insight to the nature of the reactive sites and to their time dependence. They may also reveal the source of F in the fluorosilyl layer. Investigations of the photodecomposition of the fluorosilyl layer in the absence of gaseous XeF_2 (Refs. 12 and 13) have shown that the initial burst obeys the same kinetics as when XeF_2 is present. This was interpreted to mean that, at least initially, fluorine is generated within the fluorosilyl layer itself. In discussion of the earlier data photoreactive fluorine was proposed to be free, or unbound,[12,13] based on previous x-ray photoemission studies[52] of the fluorosilyl layer which had indicated that two types of fluorine were present: F covalently bonded to Si and interstitial fluorine which had not yet reacted with Si. Subsequent experiments failed to confirm the presence of significant amounts of nonbonded F, however.[53,54] Thus, it would appear that the fluorine which reacts with the fluorosilyl groups under illumination has spectroscopic characteristics of covalently bonded F, but becomes readily mobile under illumination. It is possible to speculate that capture of photogenerated electrons by certain fluorosilyl groups may lead to formation of free F^- in appreciable quantities. Few data exist on the behavior of fluorosilyl species on trapping negative charge, save to indicate that SiF_3^- and SiF_5^- are stable.[55] If the extra electron were to be trapped into an orbital localized on a covalently bonded F within a fluorosilyl group, the SiF bond energy could become sufficiently low for the F^- to be readily transferred to an adjacent site (particularly if it were positively charged). *In situ,* real-time infrared and x-ray photoemission spectroscopies would allow this hypothesis to be tested with a minimum of unwanted perturbation to the fluorosilyl layer. Such measurements might also provide information on the differences in reactivity between *n*-type and *p*-type silicon. The two types have nominally the same fluorosilyl layer composition and the same dark etch rate at the present doping level[48] although their reaction product distributions are notably different during spontaneous etching.[25] The present data indicate that more subtle differences exist between them, perhaps relating to fluorosilyl layer structure and characteristics of photosensitive sites, which have not yet been detected in spectroscopic studies.

In addition to satisfying the requirement that the intensity dependence be greater than first order, the photodesorption mechanism must provide enough energy to break a Si—Si bond and release SiF_3 with a sizable amount of translational excitation. Using current thermochemical data for gas-phase species, reaction between F^- and —Si^+—SiF_3 to form —Si—F and SiF_3 is expected to be about 9.5 eV exothermic.[51,56] Even if substantial differences exist between thermochemical values for gas-phase and condensed-phase silicon fluorides and their charged states, it appears that the energy required to account for experimental observations will be available if a carrier-mediated chemical reaction is responsible for SiF_3 desorption. It should be noted that if all reactants are neutral only about 2 eV would be released using gas-phase data. Indeed the most probable translational temperature of SiF_3 during spontaneous etching is about 200 K (see Figs. 5 and 6), consistent with a lower energy release in the dark.

The third condition placed on this mechanism is that it must account for the selective nature of the photoetching reaction, that is, that only SiF_3 is produced as a result of a photochemical process. This condition is readily met if F^- preferentially attacks the Si to which the desorbing SiF_3 group is bonded, and not the SiF_3 group itself. Such a degree of selectivity is surprising, but can be rationalized by considering the distribution of charge within a —Si—SiF_3 moiety. The three fluorines bonded to the terminal Si atom will each withdraw electron density from it, inducing a partial positive charge. Capture of a hole will place still more positive charge in the region of the Si—Si bond. Because of the already electron deficient character of the terminal Si, it is more likely that the additional positive charge be localized on the Si to which it is bonded. F^- would be more likely to react with the more positively charged of the two Si centers, leading to SiF formation and displacement (stimulated desorption) of SiF_3. This picture is consistent with the influence of *p*-type doping on the reaction of F with —Si—SiF_3 groups during spontaneous etching,[25] as discussed above. Under illumination the density of holes will be significantly higher in the near surface region than that resulting from doping alone, and it might be expected that trends in the product branching ratio would be magnified. Although a preference for SiF_3 formation seems reasonable within these considerations, they are not sufficient to explain the exclusive nature of the photoetching reaction. A theoretical description of the electronic structure of the reactive sites is essential if the stimulated desorption process is to be understood beyond the qualitative level proposed here.

Two studies exploring photoassisted etching of silicon by fluorine using high power pulsed visible and ultraviolet lasers have been reported, and it useful to examine their conclusions within the context of the present discussion in order to learn about aspects which may be peculiar to use of low power cw light sources. Time-of-flight distributions were obtained for fluorosilyl fragments desorbed by 532-nm laser pulses from a silicon crystal previously exposed to XeF_2.[57,58] The coverage was not quantified. At 9 MW/cm^2 the predominant ion signals from the mass spectrometer were Si^+, SiF^+, and SiF_2^+. In contrast to the present data SiF_3^+ was relatively weak.

The most probable translational temperatures of the fragments exhibited a small spread, ranging from 400–560 K. The peak surface temperature was estimated to exceed 800 K. It is intriguing that despite the profound differences in the two experiments a similar product translational energy has been observed. The similarity may be fortuitous, however, since the role of post-desorption collisions of fragments above the surface[59] was not examined in the pulsed laser studies. It is also interesting that such extensive fragmentation was observed. It was suggested that this signaled a nonthermal reaction mechanism, perhaps involving electronic excitation. If this is correct, the operant photochemical etching mechanism appears to be substantially different from that proposed in (7)–(11). Such differences could be the simple result of a kinetic bias introduced by rapid pulsed laser heating, favoring activated photochemical processes with high Arrhenius preexponential factors, compared to the present results which involve essentially no heating.[60] On the other hand, thermal desorption studies of fluorinated silicon have shown that at 800 K SiF_2 is the primary etch product,[61,62] and pulsed laser etching at such high powers may be entirely thermal in nature as has been suggested for the Si/Cl_2 system.[15,21] It is clear that additional experiments are necessary to understand the differences between pulsed and cw excitation in the Si/XeF_2 system.

Pulsed excimer laser-induced etching of silicon by NF_3 has also been investigated using x-ray photoemission spectroscopy to examine the fluorinated surface.[63] An ArF laser operating over the range of 1–3 MW/cm^2 dissociated NF_3 to form F atoms which subsequently etched the surface. Since the laser beam was incident on the surface some excitation of the silicon was occurring as well. It was found that the surface became progressively more fluorinated under illumination, eventually being covered by SiF_3 and SiF_4 groups. Measurements of etch rate as a function of doping revealed a small influence of dopant type and density. This finding is difficult to compare to the present data because of the no doubt significant fluorine coverage differences, and differences in the mode of optical excitation. It is, however, not surprising in view of the present data, which also shows a relatively weak dopant effect overall. The lack of a strong doping effect was interpreted to mean that photogenerated electrons and holes were unimportant in etching of silicon by fluorine under illumination.[63] The results of the present study would seem to argue against this line of reasoning, however, since evidence for participation of photogenerated charge carriers in several surface processes has been found despite the overall similarity in etch rate between *n*- and *p*-type silicon under the reaction conditions used.

V. CONCLUSIONS

Photoassisted etching of silicon by XeF_2 using low power, cw visible light has been studied by molecular beam mass spectrometry. Data have been obtained for both *n*- and *p*-type silicon over a power range of 0–6 W (unfocused beam). Measurements of etch product abundances and most probable translational energies indicate that SiF_3 and SiF_4 are the primary species desorbing from the surface under illumination, and that only SiF_3 is a photoproduct. Information obtained on the formation mechanism of SiF_3 shows that it has a higher-than-first-order dependence on light intensity, and that it desorbs from the near surface region with an appreciable level of translational energy (particularly in comparison to its very low translational energy during spontaneous etching). Reflected, unreacted XeF_2 and Ar also show considerable translational excitation which cannot be attributed to surface heating. These data provide new, more detailed information on the influence of electron-hole pair formation in the various stages of photochemical etching of silicon. Photogenerated charge carriers appear to inhibit adsorption and reaction of XeF_2, yet lead to an enhanced etch rate overall by inducing a surface process leading to stimulated desorption of surface SiF_3 groups. The nature of this surface process is proposed to be a highly selective charge carrier-mediated chemical reaction. No evidence has been found that the etch rate is governed by field effects such as field-assisted diffusion. The results of this study should not be extrapolated outside of the reaction conditions used without more detailed information on this and other systems. This caveat aside, the data reveal something of the complexity which can arise when photogenerated charge carriers participate in a chemical reaction on a semiconductor surface, and suggest new experiments which should be done to deepen our understanding of important microscopic processes.

ACKNOWLEDGMENTS

Helpful discussions with Charles Rettner, Read McFeely, Jory Yarmoff, and Harold Winters are very much appreciated.

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