

Effect of sample doping level during etching of silicon by fluorine atoms

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The rate of silicon etching by XeF_2 is dependent on the type of dopant and the doping level. Soft-x-ray photoemission was used in an effort to elucidate the mechanism responsible for this phenomenon. Si(111) samples were subjected to sufficient XeF_2 to reach the steady-state etching regime, and spectra were collected of the fluorosilyl reaction intermediate species that form on the surface. Samples that were lightly doped (10^{17} cm^{-3}) showed virtually no difference between *p* and *n* doping, while heavily doped samples (10^{20} cm^{-3}) showed a marked difference. The heavily doped *n*-type sample had a slightly thinner reaction layer than did the lightly doped samples, while the heavily doped *p*-type sample had a much thicker layer, in which the composition of the layer was also changed. These results are discussed in terms of possible reaction mechanisms.

I. INTRODUCTION

In order to try to understand some of the basic mechanisms underlying plasma-assisted silicon etching, much attention has been focused on the reaction between clean silicon surfaces and xenon difluoride. This is because this system provides a convenient model for the most fundamental chemical interaction in fluorocarbon-based processes, the reaction between silicon and fluorine atoms. Experiments measuring overall etching rates,^{1,2} the distribution of product species,³⁻⁶ and the nature and distribution of the intermediate surface species^{7,8} have all been performed. From the results of these experiments, a reasonably detailed picture of the nature of this reaction can be synthesized.

The overall reaction between Si and XeF_2 is approximately linear over a wide range in XeF_2 pressure. Mass spectrometry has indicated that the principal reaction product is SiF_4 , with small (15% total) amounts of SiF and SiF_2 .^{3,4} Recently, more sophisticated mass-spectrometric studies have also indicated the existence of SiF_3 and Si_2F_6 as significant reaction products under some conditions.⁵ Photoemission investigations of the reacted surfaces have revealed that the reaction proceeds not by a stripping away of the outermost layer, but rather by the formation of a highly fluorinated disordered reaction intermediate phase.⁷ In this phase, all of the reaction intermediate states of fluorination, SiF , SiF_2 , and SiF_3 , are observed. Trapped SiF_4 reaction products can also be observed under some conditions. The relative concentrations of the subfluorides remains relatively constant over a wide pressure range, with SiF_3 moieties always being the dominant species and SiF_2 groups invariably appearing in the lowest concentration. In addition, the apparent thickness of the reaction intermediate layer, measured by the ratio of fluorinated (exclusive of any SiF_4) to nonfluorinated photoemission intensity, also remains approximately constant over at least four decades of XeF_2 pressure, once steady-state etching has been achieved.

One of the more interesting observations in the fluorocarbon-based plasma etching of silicon is the existence of a kinetic doping effect. It is observed that the reactivity of heavily doped *p*-type silicon is suppressed and the reactivity of heavily *n*-type silicon is enhanced, relative to near-intrinsic substrates.⁹⁻¹¹ Recently, this effect has been observed in the reaction between XeF_2 and silicon, demonstrating that the effect has its origin in the silicon-fluorine interaction.⁶ It has been proposed^{6,12} that field-assisted diffusion is an important effect in the reaction. This would suggest that the differences in reactivity might be due to differences in band bending. In this paper we report the results of synchrotron photoemission measurements that have been used to examine the variations in the amount and distribution of intermediate species as a function of doping. At high doping levels, the results reveal the existence of differences in both the thickness of the reaction intermediate layer and in its composition which are difficult to reconcile with a purely electrostatic model and are highly suggestive of a chemical mechanism.

II. EXPERIMENT

All experiments were performed on polished (111) surfaces, oriented with a precision of $\pm 2^\circ$. The crystals employed for these experiments had two widely varying doping levels. The first set were chosen to represent a fairly low doping level and were boron and arsenic doped, respectively, to a level of approximately 10^{17} cm^{-3} . These crystals are identical to those used by Houle⁵ in a modulated-beam mass-spectrometric study of the reaction products. In Ref. 5 there was little difference found in the overall etching rates for these two lightly doped samples, but there was a considerable difference in the product distributions observed. The *n*-type product distribution consisted of a considerably larger fraction of SiF_4 neutral molecules than did the *p* type. The additional products observed for the *p*-type samples were SiF_3 and Si_2F_6 .

The second set of samples employed were heavily

doped, again with boron and arsenic, to a level of 10^{20} cm^{-3} . These samples were identical to those used in a study of the relative etching rates,⁶ in which it was observed that the *n*-type samples etched at a rate of approximately 2.5 times that of intrinsic silicon, and the *p*-type samples etched at a rate of 0.8–0.85 that of intrinsic silicon. These etching rates were determined via modulated-beam mass spectrometry by monitoring the SiF_3^+ peak as a measure of the amount of SiF_4 produced.

In order to insure that the *p*- and *n*-type surfaces were subjected to identical conditions, a thin wafer of each, measuring 1.9×0.3 cm^2 , was mounted on the same sample holder in a side-by-side configuration, in a manner such that they could be independently heated. The samples were introduced into the vacuum system via a load lock. The crystals were cleaned via standard methods,¹³ with the existence of sharp surface states and characteristic clean Si $2p$ core-level spectra being used to judge cleanliness. The samples were then transferred under vacuum into a separate reaction chamber, which had been previously passivated with flowing XeF_2 at a pressure of 1×10^{-5} Torr for several days. In this chamber the samples were positioned symmetrically with respect to the oxygen-free high-conductivity (OFHC) Cu nozzle which served as the XeF_2 inlet. The samples were reacted with XeF_2 at several pressures, ranging from 4×10^{-8} to 1.25×10^{-4} Torr. For each set of samples, exposures began at the lowest pressures and continued sequentially to the higher pressures without cleaning in between. This was to help in achieving steady-state etching conditions characteristic of the particular flux employed.

The photoemission spectra were collected on beamline UV-8a at the National Synchrotron Light Source using a 3-m toroidal-grating monochromator as the photon source and an angle-resolving hemispherical analyzer at normal emission as the detector.

III. RESULTS

Figures 1 and 2 illustrate the essence of our results. Figure 1 shows spectra of the Si $2p_{3/2}$ core level of lightly doped *p*- and *n*-type silicon following a typical exposure to XeF_2 . The data points from the two spectra are plotted on top of one another to illustrate similarity between the two spectra. The assignments of the various fluorosilyl features have been discussed previously.⁷ The *p*-type sample shown in Fig. 1 has a very slight excess of SiF_3 moieties and a slight decrease in the number of SiF and SiF_2 groups relative to the *n* type, but otherwise the spectra are essentially identical. Figure 2 illustrates the results for the heavily doped crystals. Here the spectra for the *p*- and *n*-type surfaces are dramatically different. While the heavily *n*-type surface strongly resembles the results in Fig. 1, the *p*-type surface shows much more fluorosilyl intensity. In addition, the widths of the individual fluorosilyl peaks and the width of the bulk silicon peak are considerably larger in the heavily doped *p*-type sample than in the lightly doped or *n*-type samples.

A summary of the relative fluorosilyl intensities for a variety of reaction conditions is given in Table I. These values were obtained by numerically fitting each spectra

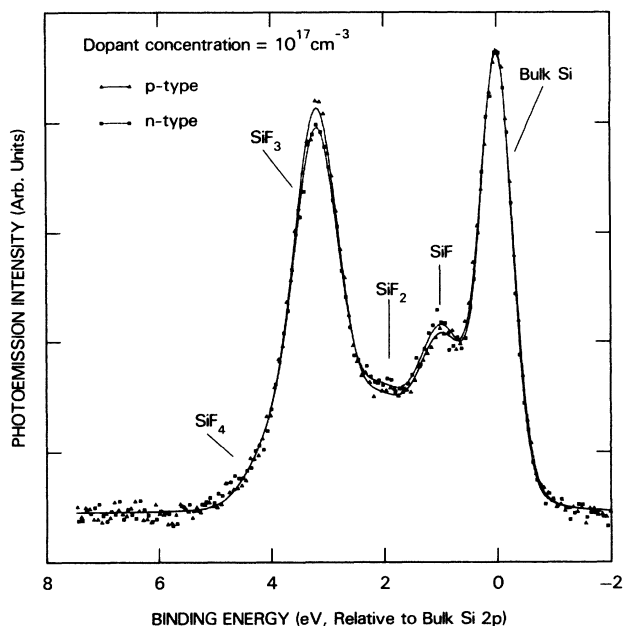


FIG. 1. Photoemission spectra of the Si $2p_{3/2}$ core level for lightly doped (10^{17} cm^{-3}) silicon after reaction with XeF_2 at 1×10^{-6} Torr. The photon energy was 130 eV. The symbols show the experimental data (after removal of the $2p_{1/2}$ component) and the lines show the results of a numerical fit to the data (see text).

to the sum of five Gaussian-broadened Lorentzian line shapes, one for the bulk silicon and four for the various states of fluorination, in a manner employed previously.⁷ The intensity of each fluorosilyl peak normalized by the bulk silicon intensity is listed in Table I in order to eliminate any discrepancies due to changes in the photon flux,

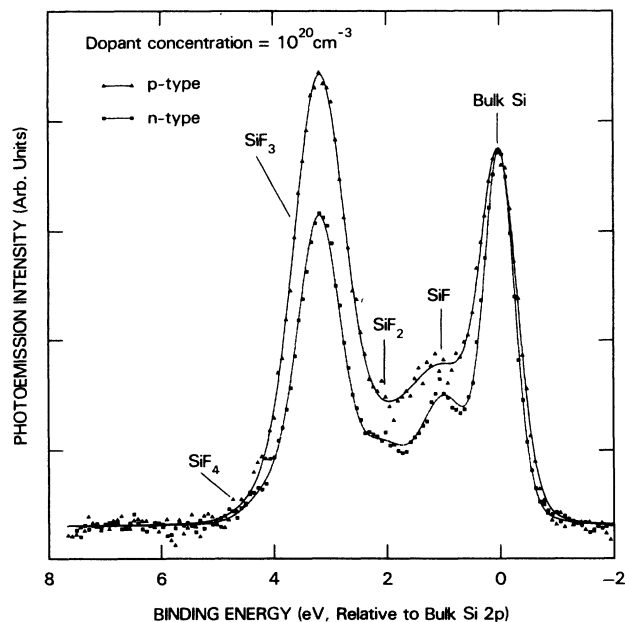


FIG. 2. Photoemission spectra of the Si $2p_{3/2}$ core level for heavily doped (10^{20} cm^{-3}) silicon after reaction with XeF_2 at 1×10^{-6} Torr using the same parameters as in Fig. 1.

TABLE I. The intensity of each fluorosilyl Si 2*p* photoemission peak normalized by the intensity of the bulk silicon peak for various XeF₂ pressures and sample doping levels is shown. Each sample was exposed to XeF₂ at the indicated pressure for a sufficient length of time so as to reach steady-state reaction conditions.

Doping level	Pressure (Torr)	<i>n</i> type			<i>p</i> type		
		SiF	SiF ₂	SiF ₃	SiF	SiF ₂	SiF ₃
10 ¹⁷ cm ⁻³	2 × 10 ⁻⁷	0.549	0.308	1.10	0.519	0.245	1.13
	1 × 10 ⁻⁶	0.597	0.359	1.20	0.545	0.315	1.21
	5 × 10 ⁻⁶	0.612	0.367	1.30	0.535	0.289	1.28
	2.5 × 10 ⁻⁵	0.520	0.347	1.21	0.455	0.281	1.12
10 ²⁰ cm ⁻³	1 × 10 ⁻⁶	0.496	0.290	1.16	0.684	0.370	1.73
	5 × 10 ⁻⁶	0.466	0.244	1.10	0.826	0.459	1.91
	2.5 × 10 ⁻⁵	0.452	0.269	1.07	0.694	0.456	1.92

sample repositioning, etc. The SiF₄ intensity is not shown, as it was too small to contain any useful information. As can be seen, the results for a particular dopant and doping level are quite reproducible from run to run, showing relatively little pressure dependence. The small differences among the lightly doped samples are all within the experimental error, showing virtually no differences in the intermediate fluorosilyl distributions for lightly doped silicon. For the more heavily doped silicon, however, the changes in the layer thickness are readily apparent.

In addition to an increase in the total fluorosilyl signal for a heavily doped *p*-type sample, it is evident that the chemical composition of the fluorosilyl phase has also changed. Table II shows how each of the individual peaks changed in going from intrinsic to heavily doped *p* and *n* types. These values were obtained by averaging the results from all of the reaction conditions listed in Table I assuming that the lightly doped samples can be used to represent intrinsic silicon. On the *p*-type surface, the intensity of all of the intermediate fluorosilyl species increased, but the signal was dominated by an increase in the number of trifluorosilyl groups. On the *n*-type surface, despite the fact that the greater change in etching rate had been observed in going from intrinsic to *n*-type silicon rather than in going to *p*-type,⁶ the reaction layer was only slightly thinner than the layer on intrinsic silicon.

IV. DISCUSSION

We consider now the implications of the above observations for the mechanism of the kinetic doping effect. Since the reaction was interrupted very rapidly and the fluorosilyl distribution was independent of reaction pres-

TABLE II. The ratio of the intensity of a particular Si 2*p* photoemission peak from a heavily doped sample to intrinsic silicon is shown. These values were obtained from the data presented in Table I by averaging over all the pressures shown.

	SiF	SiF ₂	SiF ₃
<i>I</i> (heavy <i>p</i>)/ <i>I</i> (intrinsic)	1.36	1.36	1.55
<i>I</i> (heavy <i>n</i>)/ <i>I</i> (intrinsic)	0.87	0.85	0.93

sure, the spectra should provide a measurement of the distribution of the various fluorosilyl species during steady-state etching. The salient kinetic facts concerning this reaction are (1) at least approximate overall linearity in fluorine flux, and (2) SiF₄ is the dominant reaction product. The simplest reaction mechanism that can be devised that reflects these facts is a sequential fluorine addition model, neglecting all backreactions and disproportionational processes, i.e.,



Certain details of the reaction, such as parallel reaction channels leading to minor reaction products and the superlinear dependence on fluorine flux of SiF₃ products,⁵ cannot be derived from this model, but in conjunction with the assumption of steady state, this model provides a reasonable starting point for the analysis of the major reaction channel.

When the reaction is proceeding in steady state, the rates of each of the elementary reactions (1)–(4) will necessarily be equal. If we treat the reacting substrate as a continuum, the rate of each step may be written in the form

$$R = \int_0^\infty c^{\text{SiF}^x}(z) c_u^{\text{F}}(z) dz . \quad (5)$$

In this equation the reacting surface is denoted by $z=0$ and the positive z axis extends into the bulk solid. The term $c^{\text{SiF}^x}(z)$ represents the concentrations of the silicon reactant species, from bulk Si through SiF₃, and $c_u^{\text{F}}(z)$ represents the concentration of unreacted free fluorine in the substrate at depth z .

From the analysis of photoemission spectra of the reacted surfaces obtained as a function of photoelectron mean free path⁸ and from theoretical modeling of these data,¹⁴ we have some information concerning the forms of the functions $c^{\text{SiF}^x}(z)$ for intrinsic surfaces. Qualita-

tively, the concentration of SiF_3 is at its maximum at the substrate surface, and falls off quite rapidly as z increases. The concentration of SiF , however, is quite small at the surface, initially increases with increasing z , reaches its maximum a few atomic layers from the surface, and tails off more gradually into the bulk. The SiF_2 concentration is approximately intermediate between these two cases, while the concentration of unreacted Si [$c^{\text{SiF}_0}(z)$ in the notation above] is effectively zero at the surface and rises monotonically to the value set by the density of pure bulk silicon.

We can likewise make some general statements concerning the form of $c_u^{\text{F}}(z)$. The magnitude of $c_u^{\text{F}}(z)$ at $z=0$ is, of course, set by the flux of F atoms incident from the gas phase and would be expected to fall monotonically to zero deep in the bulk. The characteristic decay length of this function clearly depends upon several factors. Clearly, it depends on the absolute magnitudes of the rate coefficients of the elementary reactions (1)–(4). If the reaction cross sections all became sufficiently large, no unreacted fluorine could ever pass beyond the first layer of the surface without being captured, and, in steady state, no more than one monolayer of fluorosilyl intermediate species could exist on the surface. Similarly, if the rate coefficients were small, the fluorine could penetrate deep into the material without reacting, and the falloff of $c_u^{\text{F}}(z)$ could be very slow. In addition, it is important to consider the nature of the diffusion of the free fluorine atoms in the substrate and its relation to $c_u^{\text{F}}(z)$. The large electronegativity of fluorine atoms dictates that the unbound fluorine atoms will always have a substantial amount of negative charge. Thus, unless the substrate bands are exactly flat, the diffusion of free fluorine in the system will always be field assisted to some extent. If all other effects were held constant, increasing a field attracting the fluorine atoms into the bulk would serve to increase the decay length of $c_u^{\text{F}}(z)$, since the fluorine atoms would have less chance to interact with silicon atoms near the surface than if they were executing a more directionally random motion.

Winters and Haarer⁶ have proposed a mechanism for the doping effect on the reaction rate which is closely analogous to the Mott-Cabrera mechanism for the oxidation of metals.¹⁵ This model attributes the differences in reaction rates solely to differences in the degree to which the diffusion of fluorine is field assisted. The differences between the reaction rates for heavily p -type, heavily n -type, and lightly doped silicon are thus held to be due to differences in band bending in the three cases. For instance, the increase in etch rate in going from lightly doped to heavily n -doped material is held to result from the expected increase in the degree of band bending and the correspondingly larger electric field pulling the fluorine atoms into the bulk, while the decrease in going to heavily p type is held to be due to a lessening of the band bending and the decrease of this field. We consider now, by means of a *gedanken* experiment, whether this model could account for the photoemission data presented above.

Suppose we had a lightly doped Si(111) surface, and impinged XeF_2 upon it until the reaction reached steady

state. At that point the depth-dependent concentrations of the fluorosilyl species and the unreacted Si [i.e., the $c^{\text{SiF}^x}(z)$ functions] would be such as to give rise to the photoemission spectra in Fig. 1. Suppose we then suddenly decreased the magnitude of the band-bending-induced drift field to the value appropriate for heavily p -type case without changing the rate elementary rate coefficients of reactions (1)–(4) in any way, and waited for the system to settle down to a new steady state. How would the $c^{\text{SiF}^x}(z)$ functions evolve in time and to what new steady-state form should they converge?

It is clear that immediately after the sudden decrease in the drift field, the fluorosilyl concentration distributions no longer constitute a steady-state situation. Lacking a strong drift field to pull F atoms into the bulk, the fluorine atom flux into the silicon-rich region [the region where $c^{\text{SiF}^x}(z)$ is larger] will begin to drop as the F atoms begin to execute a more directionally random motion. The F atoms already present a larger depths will be lost just as efficiently via reaction with bulk silicon, since the rate coefficient k_0 is unchanged; thus $c_u^{\text{F}}(z)$ will begin to decline at large z values. This will cause a slowdown in reaction (1). As each of the reactions are coupled, this decrease in the rate of reaction (1) will tend to decrease the total number of SiF species, slowing reaction (2). The system will, of course, tend to restore itself to a steady state. At the surface, where SiF_3 is the dominant species, the flux of incident fluorine from the gas phase will be unchanged, while the drift field which previously carried it into the bulk is diminished. The transient response will thus consist of the reaction of this now excess concentration of F atoms by reacting the SiF_3 away. Thus, initially, as deep in the sample the free-fluorine concentration is dropping, slowing down the formation of the layer rich in reaction intermediates, the surface is still reacting rapidly away. This latter process will tend to thin the reaction intermediate layer, making it possible for more unreacted F atoms to reach the (continuously decreasing) depth at which significant concentrations of unfluorinated Si exist. Thus the reaction layer should respond to the perturbation of the drift field by thinning until the rates of its formation, initiated by reaction (1), and its removal by reaction (4) have equalized and the system is in its new steady state.

The response of the system can be summarized in the following, perhaps more intuitive, way: If the drift field responsible for pulling the unreacted F atoms into the bulk is decreased, the unreacted fluorine will tend to extend less deeply into the bulk [i.e., $c_u^{\text{F}}(z)$ will become more sharply peaked near $z=0$]. Since reaction occurs, and reaction intermediates are formed, in direct proportion to the local concentration of unreacted fluorine atoms, the reaction intermediate layer reflected in the photoemission spectra will also extend less deeply into the bulk, i.e., it will become thinner. This conclusion is in direct contradiction to the experimental results. The data in Fig. 2 indicate quite dramatically that in going from lightly doped substrates to heavily p -type silicon, the reaction layer gets thicker.

A similar analysis can easily be applied to the effect of increasing the drift field from its value in lightly doped

samples employing the mechanism proposed by Winters and Haarer for the rate increase observed in heavily n -type material. If the drift field were increased suddenly in a sample previously at steady state, the layer of intermediates would be too small to sustain a steady-state reaction. Immediately the larger drift field would begin to pull unreacted F atoms out of the layer rich in intermediates into the silicon-rich bulk. This would start to increase the rate of reaction (1), speeding up the process by which the reaction layer is formed from the bulk side. Similarly, immediately after the field was increased, the reaction of SiF_3 with F, which removes the layer from the top, would not immediately be able to keep pace with the increase in reaction (1) because the unreacted F atom concentration at the surface would not increase. The outrunning of reaction (1) of the other reactions would, as in the case considered above, have a natural damping mechanism. By making reaction intermediate species initially faster than they would be removed from the surface via reaction (4), the effective intermediate layer would grow. This would simultaneously speed up reactions (2)–(4) by increasing the total amount of silicon reactants present, and start to decrease the concentration of free F atoms deep in the bulk Si by serving as a thicker layer of reactive traps for the incoming free fluorine atoms. The process would continue until the rates equalized on a surface characterized by a thicker layer of partially reacted Si. Once again we note that the response of the system predicted by the *gedanken* experiment is not that which is observed in the photoemission data. In proceeding from intrinsic to heavily doped n -type Si the intermediate layer does not become thicker, but rather thins slightly. Thus, once again, a purely field-assisted diffusion model cannot explain our observations.

In support of our analysis of the relationship between the magnitude of drift fields and the thickness of intermediate layers, we refer to the results of a related experiment. In this experiment, Winters¹⁶ studied the transient behavior of a reaction layer too thin for the relevant steady-state conditions. A Si(111) wafer was reacted under a certain XeF_2 flux for a long period. Then part of the reaction layer was removed by sputtering. He observed that with the too-thin layer the overall spontaneous reaction rate was initially increased, then fell back monotonically to its initial value, presumably as the layer grew back to its initial thickness. This demonstrates experimentally the correctness of the argument above, namely, the transient response of the system with too small an intermediate layer is to speed up in overall rate and to return to steady state via a growth of the intermediate layer.

It is clear from the above discussion that more is required than variations in drift fields to describe the data. The most obvious solution is that at least part of the mechanism of the doping effect is a chemical mechanism. By chemical mechanism we mean that the magnitudes of the rate coefficients of the elementary reactions (1)–(4) are themselves altered as a function of doping. Such a mechanism can easily account for the observed relationships between the rates of reaction and the thickness of the intermediate layers. If the reaction-rate constants are

all increased, clearly the overall reaction rate will increase. Additionally, if all the fluorosilyl species are more reactive, they will be more effective in excluding the concentration of unreacted fluorine atoms from the bulk by capturing them. Clearly, in the limit that the reaction cross sections become extremely large, it will become impossible for fluorine to penetrate the bulk at all, but will react entirely on the surface, resulting in no more than a monolayer of reaction intermediate species in total. On the other hand, if all the reaction-rate constants (reaction cross sections) become very small, the fluorosilyl species would become very ineffective in capturing the unreacted fluorine and would not prevent it from diffusing deep into the bulk, resulting in a very thick reaction intermediate layer. A chemical mechanism also has the undeniable merit of being able to explain the changes of composition of the reaction layer in a simple manner. The differences simply reflect different magnitudes of the changes in the rate coefficients k_0 – k_3 as a function of Fermi-level position. Changes in drift-field magnitude provide no simple way to understand the changes in the distribution of reaction intermediates.

That the position of the Fermi level should influence the elementary rate coefficients should in no way be viewed as surprising or unexpected. The formation of a new bond between a fluorine and a silicon atom involves a large degree of charge transfer. Such charge transfer would likely be facilitated by having the highest density of filled electronic states at the Fermi level. Such a higher density of filled states in the n -type sample would provide an electronic mechanism for the doping effect.¹⁷ Thus, in terms of Eqs. (1)–(4), the reaction rate constants for the n -type silicon would be increased over the rate constants for intrinsic p -type silicon owing to the higher density of filled states. This is fully consistent with the observed differences in the compositions of the reaction layers, in which it is the amount of SiF_3 groups which shows the greatest variation. Since the local density of states associated with SiF , SiF_2 , and SiF_3 moieties are undoubtedly different, the individual charge-transfer reactions would be affected to different degrees by the Fermi-level position. The particular charge-transfer reaction which is expected to be the most affected would be the reaction that is associated with the highest activation energy. Intuitively, in agreement with the observed results, one would expect this to be the reaction in which SiF_3 goes to SiF_4 , as SiF_3 is the silicon center that is most depleted of electron density.

Changes in the relative magnitudes of the reaction-rate constants would also most likely affect the distribution of product species. In particular, it would be expected that the amounts of SiF_3 and Si_2F_6 in the product distributions would be increased with the p -type sample, since SiF_3 groups are in larger abundance in the reaction layer, and would be less reactive with fluorine. This has in fact been observed by Houle⁵ for lightly doped p - and n -type samples. Although the overall reaction rates for the lightly doped samples were about equal, the p type had a considerably larger fraction of SiF_3 and Si_2F_6 in the product distributions. Presumably, the same might also be

true for the more heavily doped samples, only more so. Winters⁶ did not find this trend, however.

While our results provide evidence for an electronic mechanism, they should not be interpreted as precluding the action of a transport mechanism as well. A larger etch-rate enhancement was observed for *n* type versus intrinsic than for intrinsic versus *p* type. The thickness of the reaction layer, however, showed a relatively small change in going from intrinsic silicon to *n* type. Since the effect that diffusion would have on the reaction-layer thickness occurs in opposition to that resulting from a reactivity change, this suggests that both an enhanced chemical reactivity and increased diffusivity may contribute to the large etch-rate enhancement observed for heavy *n*-type silicon, while the reduction in rate observed for *p*-type silicon is a result of mostly a decreased chemical reactivity.

V. CONCLUSIONS

The doping effect for the reaction rate of XeF₂ with silicon is small for lightly doped silicon, as observed both in rate measurements³ and in the observation of the intermediate fluorosilyl distributions. For more heavily doped

samples, however, there is a considerable difference between *n*- and *p*-type silicon. The reaction layer on *n*-type silicon is slightly thinner than on intrinsic silicon, and the layer on *p*-type silicon is considerably thicker. The build-up of excess SiF₃ groups dominates that extra thickness. These results show that although the diffusivity of fluorine atoms through the reaction layer may play a role in the reaction-rate determination, it cannot be the only factor. The analysis presented here to show how diffusion and reactivity changes would affect both the intermediate-phase composition and the reaction rate demonstrates the potential importance of chemical mechanisms.

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