Laser Chem. 1984, Vol. 5, pp. 35–52
0278–6273/84/0501–0035$12.00/0
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Printed in Great Britain

Interaction of SF_6 Multiple Photon Dissociation Products with Silicon and SiO_2 Surfaces

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Experiments on etching Si and SiO_2 by the multiple photon dissociation products of SF_6 molecule in IR laser field have been carried out. These experiments showed that the etching of Si and SiO_2 is the result of two qualitatively different processes and high selectivity ($>10^3$) can be achieved. The dependences of the etching process of the initial gas mixture pressure and composition, on the laser intensity and the number of laser pulses and on the direction of laser radiation have been studied. It has been found out that the etching rates of "a monolayer per pulse" for Si and $\sim$100 Å/min for SiO_2 are comparable to the rates achieved in low-temperature plasma technique. Possible mechanisms and chemical reactions which can cause Si and SiO_2 etching are discussed. It has been concluded that under the experimental conditions multiple photon dissociation forms the basis for the etching process.

1. INTRODUCTION

The effect of multiple photon dissociation (MPD) of polyatomic molecules in IR laser field discovered some years ago has become the subject of intense theoretical and experimental investigation in many laboratories in the world (see, for example, the monograph Ref. 1). This interest is aroused not only by the nature of the effect itself but also by the prospects of its practical applications. One of the most obvious applications of this effect is isotope separation which has already been accomplished by present in practice.[2,3] The effect of MPD has been also used in attempts to purify some substances.[4] The possibility of applying this effect to etching various materials is also of interest. Indeed, if a solid, instead of usually used gaseous substance, can be used as a scavenger of active radicals produced by MPD process, the surface of the solid may be found etched. The etching

process of this kind is fairly attractive because, first of all, it can be carried out in "pure" conditions, i.e., active radicals can be produced just in the vicinity of the surface under study. In the second place, the number of reactants is not large in such a process and there is a possibility to follow the sequence of homogeneous and heterogeneous chemical reactions initiated by MPD. This is almost impossible to do in the low-temperature plasma etching technique because there are a lot of simultaneous and, for the most part, independant homogeneous and heterogeneous reactions, in multicomponent mixtures especially. There is also a great number of charged particles in the reaction volume. That is why in the case of plasma etching technique, it is almost impossible to set up conditions when one of the processes would not be superposed by the others, the probabilities of these processes being in the most cases unknown. All these features impede to gain an insight into plasmachemical processes.

The possibility of Si and SiO_2 etching is investigated most intensively at present but it is not clear yet whether fluorine atoms F react directly with Si and SiO_2 surfaces. The authors of Ref. 5 believe that fluorine atoms preferably attack silicon. However as it was shown in Ref. 6 the reaction probability of fluorine atoms with SiO_2 in the absence of plasma is also rather high (though the authors of Ref. 6 do not exclude the possibility of ion or electron bombardment of SiO_2 surface). All these questions remain to be solved.

The possibility of Si and SiO_2 etching with the MPD products of SF_6 molecule was first demonstrated in Ref. 7. A little bit later, some papers[8,9] devoted to the interaction of multiple photon excited SF_6 molecules only with silicon surface alone were published. The experimental conditions in Refs. 8 and 9 however were far from being the real ones usually used in practice because a silicon film under study 2 μm thick was deposited by electron beam evaporation onto a quartz crystal.

The object of the present work is the attempt to gain an understanding of the processes taking place on Si and SiO_2 surfaces of the plates really used in practice, during SF_6 MPD in the TEA/CO_2 laser field.

II. EXPERIMENTAL

The schematic diagram of the experimental apparatus is shown in Figure 1. Si or SiO_2 samples were placed into an aluminium cell with

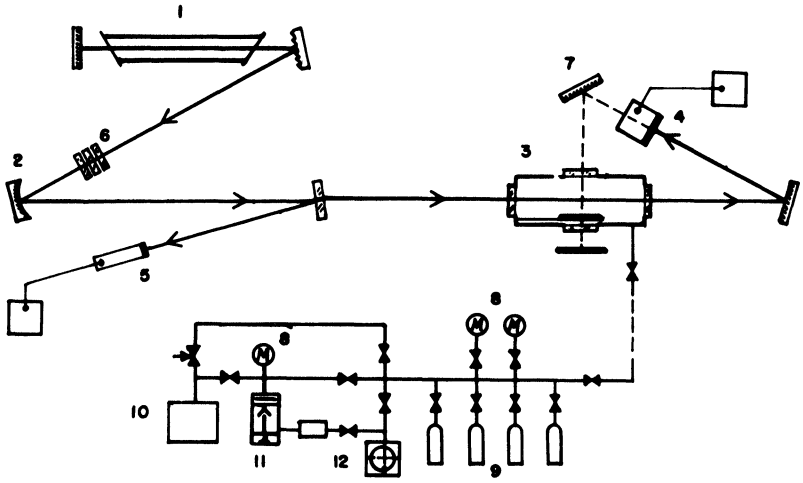

FIGURE 1 Schematic diagram of the experimental apparatus. (1) TEA/CO_2 laser; (2) spherical mirror ($R = 3$ m); (3) cell; (4, 5) laser pulse energy meters; (6) set of attenuators; (7) plane mirrors; (8) pressure gauges; (9) gas containers; (10) mass spectrometer; (11) diffusion pump; (12) preevacuation pump.

four KBr windows. The samples were set so that they could be irradiated either parallel or perpendicular to the sample surfaces as well as in both directions at the same time. The cell could be heated to a temperature of about 100°C. The total volume of the gas cell was 98 cm^3. The irradiated volume depended on the geometry of irradiation and the laser beam diameter. Before the experiment the cell was heated and evacuated to $\sim 10^{-7}$ Torr. A monopole mass spectrometer ROMS-2 was connected to the system for monitoring the purity and the composition of the gases.

Irradiation was performed at the P(24) line of 10 μm TEA/CO_2 laser generation band. The pulse laser intensity within the zone of irradiation was up to 5 J/cm^2, the pulse shape being typical with its half-width of 150 ns in the main pulse and 2 μs in the "tail".

SF_6 gas was purified in several cycles of vacuum distillation at low temperatures. Single-crystal silicon wafers 0.5 mm thick and thermally oxidized single crystal silicon wafers with SiO_2 film 0.5 mm thick on them were used in experiments.

The monitoring of the processes was carried out by means of the determination of the spectral composition of the gases in the cell before and after irradiation. A Specord-75 IR spectrophotometer was

employed recording IR absorption spectra. A special K-201 attachment to the spectrophotometer allowed to increase the recording sensitivity by about an order of magnitude when low gas concentrations were used. Time variation of gas amounts can be recorded as well. For identifying products the spectral results were taken from Refs. 10, 11 and 12. The etching process was characterized by the appearance of absorption bands corresponding to the volatile compound SiF_4.

The quantitative characteristics of the process greatly depended on the cell walls conditions and the cleanness of the sample. It is known[2] that if SF_6 MPD occurs in a clean cell in the absence of any scavenger a complete recombination of the MPD products to the initial quantity of SF_6 is observed. It is also known that the water absorbed on the surface of the cell walls can play a role of a scavenger as it was observed in the very first experiments on SF_6 MPD (see, for example Ref. 13 and 14). Therefore in the present work the cell was heated and evacuated until the decomposition of SF_6 after irradiation in the absence of a scavenger was no longer observed.

III. SILICON ETCHING

In the experiments with silicon samples, a silicon wafer was placed into a cell and SF_6 gas was let in (the notation of this system is Si/SF_6). The silicon wafer was $1.0 \times 1.25\ cm^2$ in size, the cross-section of the laser beam where it cuts the plate (during perpendicular irradiation) being $\sim 1\ cm^2$. Before experimenting with the Si/SF_6 system the plate of silicon was cleaned of the hydroxide film formed as the samples were kept in the air. The procedure of removing the film will be described in the following section.

The experiments with the Si/SF_6 system have shown that SiF_4 is produced only during irradiation, and the amounts of the main products SiF_4 and SF_4 remain constant as the irradiation is over. For illustration, Figure 2a shows a plot of the IR spectrum of the products before and after irradiation of the Si/SF_6 system. Thus, since in the cleaned cell and in the absence of a silicon solid, one could not observe SF_6 decomposition it may be concluded that the production of SiF_4 in the Si/SF_6 system is apparently related to the heterogeneous reactions between the primary products of SF_6 MPD and silicon which can be regarded as a solid scavenger in this case.

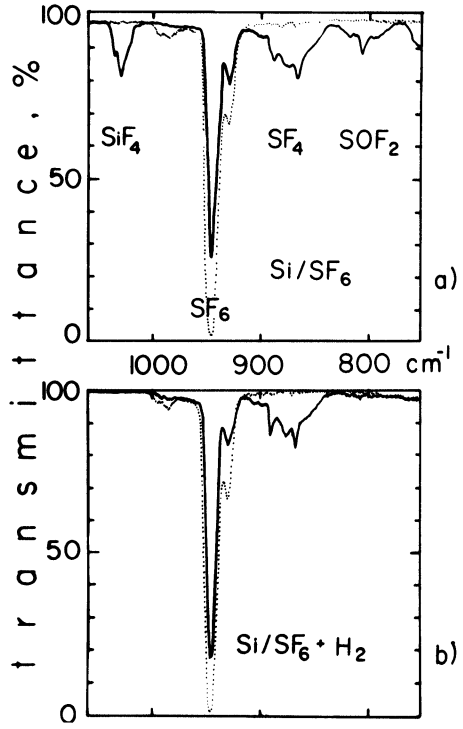

FIGURE 2 Fragments of IR spectra of the gas mixture in the cell before (dashed line) and after (solid line) irradiation of the systems Si/SF_6 (a) and Si/SF_6+H_2 (b). Initial pressure of SF_6 is 1 Torr; pressure of H_2 is 1.5 Torr; irradiation time is 4 min; pulse repetition rate is 3 Hz; pulse energy fluence $E = 3\ J/cm^2$.

With hydrogen added into the cell, that is, in the case of Si/SF_6+H_2 system the process of SiF_4 production is suppressed almost completely (Figure 2b). It was shown[15,16] that in SF_6 MPD with H_2 added the primary product of high-rate chemical reactions taking place within a characteristic time of several microseconds is HF. It may be concluded from here that in case of the Si/SF_6+H_2 system such reactions prevent diffusion flow of MPD primary products to the silicon plate surface, and this suppresses the heterogeneous processes resulting in SiF_4 production.

The typical dependence of the SiF_4 yield on the number of laser pulses is presented in Figure 3. It can be seen that the dependence is

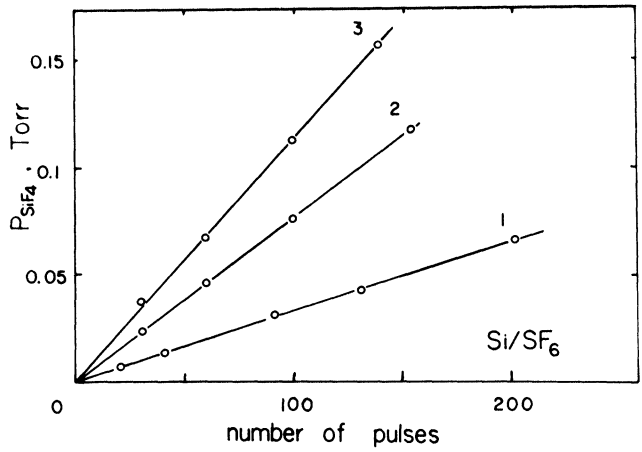

FIGURE 3 Dependence of the SiF_4 yield in the Si/SF_6 system on the number of laser irradiation pulses. Initial pressure of SF_6 is 2 Torr; (1) $E = 1.5$ J/cm^2; (2) $E = 3.1$ J/cm^2; (3) $E = 4$ J/cm^2.

linear by character, i.e., the same quantity of SiF_4 is produced per each pulse. Using this plot one can find the quantity of SiF_4 per pulse and hence the etching depth of silicon h from the relation

$$h = \frac{\mu N}{\rho N_A S} \tag{1}$$

where μ is the gram-atomic weight of silicon, ρ is the density of silicon, N_A is the Avogadro number, S is the silicon plate area, N is the number of silicon atoms (or SiF_4 molecules) produced per pulse of radiation.

The value of N can be easily determined from the relation

$$N = \frac{pVN_A}{RT} \tag{2}$$

Here p is the pressure of SiF_4 produced per pulse in the cell, V is the cell volume, R is the universal gas constant, T is the gas temperature in K.

Figure 4 shows the dependence of SiF_4 production per pulse on the initial SF_6 pressure at different values of laser intensity. It may be seen that the SiF_4 yield increases up to ~1.5–2 Torr and at higher pressures saturation takes place (a similar dependence was observed

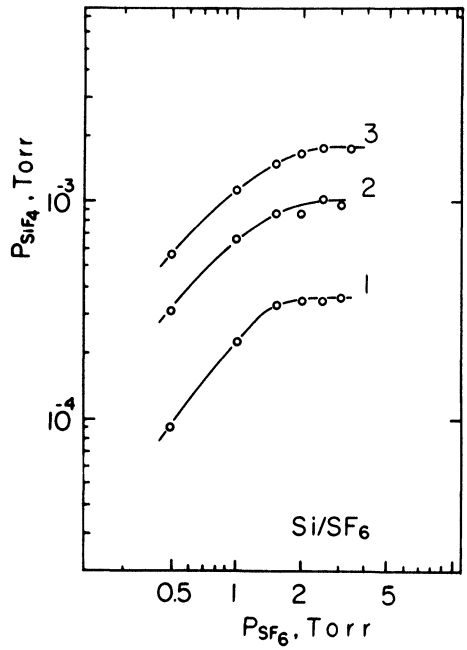

FIGURE 4 Dependence of the SiF_4 yield per pulse in the Si/SF_6 system on initial pressure of SF_6 (1) $E = 2$ J/cm^2; (2) $E = 3.5$ J/cm^2; (3) $E = 4$ J/cm^2.

in Refs. 8 and 9 up to pressures ~14 Torr). As it is known[17] that the primary yield of MPD, at least up to ~1 Torr, is independent on pressure, the SF_6 pressure of about 2 Torr will be obviously optimal for the yield of SiF_4. The question how and in the presence of an appropriate amount of scavenger still remains to be seen.

It is interesting to know how the SiF_4 yield depends on the direction of CO_2 laser radiation. According to the data from Ref. 9, the etching rate at perpendicular incidence of radiation on the plate was about an order higher than that obtained at parallel orientation of the silicon wafer with respect to the laser beam. On this basis it has been concluded in Ref. 9 that for Si etching it is essential to expose the plate surface to CO_2 laser radiation due to the effects of silicon lattice excitation. In our experiments, the SiF_4 yield at parallel irradiation was even somewhat higher than at perpendicular irradiation. This was observed however in cases when the size of the silicon wafer was larger than

the laser beam cross-section, i.e., the SiF_4 yield was contributed to by the parts of the wafer not exposed directly. So all the quantitative measurements, as mentioned above, were taken with the dimensions of the wafer being similar to the laser beam cross-section. Figure 5 (curve 1) shows the dependence of the SiF_4 yield on laser intensity for a sample with an area of 1.25 cm^2 at perpendicular incidence of radiation. For comparison, Figure 5 (curve 2) shows the same dependence when the sample area is equal to 9.2 cm^2. From the dependence (curve 1) it is possible to estimate the etching depth per pulse. This value turned out to be ~3 Å which corresponded to an etching rate of ~"a monolayer per pulse". Figure 6 shows a similar dependence but at parallel orientation of the plate about the laser beam. The comparison of the dependences from Figure 5 (curve 1) and Figure 6 shows that the yields of SiF_4 at parallel and perpendicular orientations almost coincide, the threshold values coincide too. Some differences, such as the yield of SiF_4 at parallel orientation is proportional to $E^{1.5}$ and at perpendicular orientation to $\sim E^{2.7}$ as well as the SiF_4 yield saturation with $E \sim 2.3$ J/cm^2 at perpendicular irradiation, are

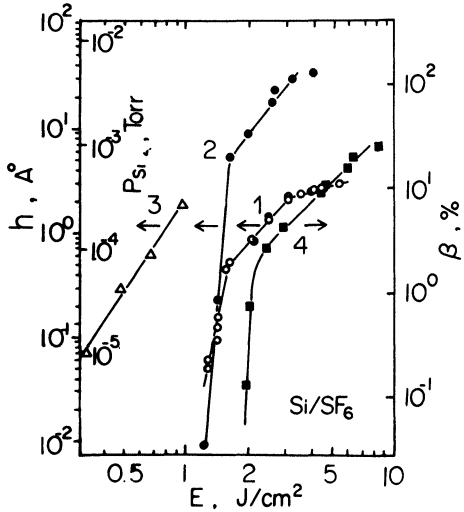

FIGURE 5 Dependence of the SiF_4 yield per pulse in the Si/SF_6 system on laser pulse intensity in case of perpendicular incidence of radiation on the plate. (1) initial pressure of SF_6 is 2 Torr; silicon wafer area is 1.25 cm^2; (2) initial pressure of SF_6 is 2 Torr, silicon wafer area is 9.2 cm^2; (3) results of Ref. 9; (4) dissociation yield from Ref. 18.

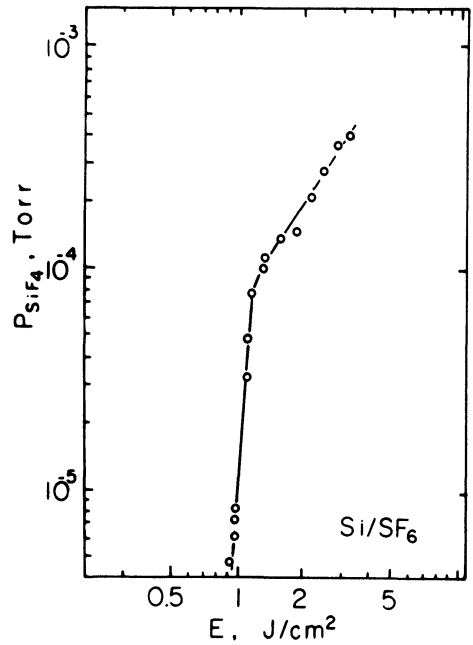

FIGURE 6 Dependence of the SiF_4 yield per pulse in the Si/SF_6 system on laser pulse intensity in case of parallel orientation of the plate about the laser beam. Initial pressure of SF_6 is 2 Torr.

apparently related to the difference in the flows of SF_6 MPD products to the sample surface. This difference may be caused by the irradiation geometry and heating of the sample in case of perpendicular irradiation.

IV. SiO_2 ETCHING

In the experiments with SiO_2 samples it has been found that in the absence of adsorbed water on the surface of the sample and the inner surface of the cell neither SF_6 decomposition nor SiF_4 production can be observed when the SiO_2/SF_6 system is irradiated even by several hundreds of pulses with laser pulse intensity $E \sim 3.5$ J/cm^2. So it may be concluded that SiO_2 is not a solid scavenger for SF_6 MPD process and there is no etching by the primary products of SF_6 MPD.

In the presence of adsorbed water on the sample surface, i.e., in the SiO_2+H_2O (ads)/SF_6 system, we could observe SiF_4 production as a result of the reactions taking place after irradiation, i.e., in the course of secondary chemical reactions. With hydrogen added into the cell, the rate of SiF_4 production increased essentially, and in sufficiently a long time (~5–6 hrs) after irradiation of the SiO_2+H_2O (ads)/SF_6+H_2 system SF_4 decomposed almost completely and, the quantity of resultant SiF_4 tended to be equal to the amount of SF_6 decomposition during irradiation. In these experiments the SF_6 pressure was taken to be ~2 Torr because at higher pressures some difficulties arose which were connected with high radiation absorption in the gas mixture, and the pressure ratio between SF_6 and H_2 was chosen to be 2:3 respectively since at such a ratio a maximum decomposition of SF_6 was observed. These experiments were carried out with a laser pulse intensity of about 3–3.5 J/cm^2 because the SF_6 decomposition in the irradiated volume starting from these values of laser intensity and with the chosen pressure ratio between SF_6 and H_2, was as high as ~100% during the first irradiation pulse (Figure 7).

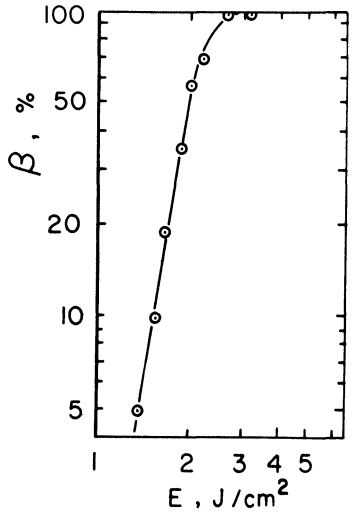

FIGURE 7 Dependence of the SF_6 decomposition in the cell during the first laser radiation pulse on laser pulse intensity. Initial pressure of SF_6 is 2 Torr; initial pressure of H_2 is 3 Torr.

Figure 8 shows the typical time dependence of the SiF_4 yield after the irradiation of the SiO_2+H_2O (ads)/SF_6+H_2 system just by ten laser pulses. The radiation was incident perpendicular to the plate with the area of 9.2 cm^2. It can be seen from Figure 8 that from two minutes after irradiation up to several tens of minutes, this dependence remains linear. The nonlinearity of this dependence during two first minutes is typical to autocatalytic reactions, and the reactions resulting in etching SiO_2 are apparently of this kind.

The etching rate of SiO_2 film can be estimated from the dependence given in Figure 8. For example, after irradiating with 10 pulses, pulse intensity being 3.2 J/cm^2, the area etched was about 1.6 cm^2. The irradiation lasted 7 seconds. In ten minutes after irradiation there was ~0.12 Torr of SiF_4 in the cell. This amount corresponds to SiO_2 etching rate of about 100 Å/min which is comparable to the etching rates in low-temperature plasma technique.

In the foregoing section, it was said that in the experiments with pure silicon samples (i.e., in the Si/SF_6 system), the plate surfaces had been pre-cleaned of hydroxide films. This cleaning was performed through etching this film out (i.e., in the (SiO_2 on Si) + H_2O (ads)/SF_6 + H_2 system) by the procedure described in the present section, and the process went on till the formation of SiF_4 ceased. As shown above, there is no silicon etching under these conditions (in the presence of hydrogen).

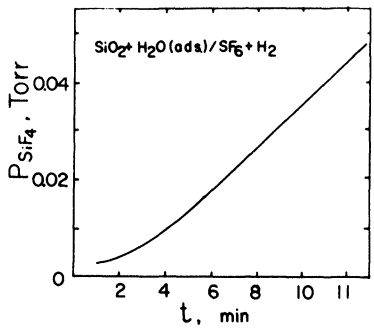

FIGURE 8 Kinetics of SiF_4 production after the irradiation of the SiO_2+H_2O (ads)/SF_6+H_2 system with ten laser pulsed during 7 seconds. Initial pressure of SF_6 is 2 Torr; initial pressure of H_2 is 3 Torr; $E=3.5$ J/cm^2.

V. ETCHING SELECTIVITY

Since the etching processes of Si and SiO_2 are qualitatively different, i.e., the presence of hydrogen in the system suppresses the etching process of Si but SiO_2 can be etched only in the presence of hydrogen and absorbed water, it is possible to achieve selective etching of Si and SiO_2. To estimate the selectivity value two samples of Si and SiO_2, the area of each 9.2 cm^2, were placed in succession into the cell. Irradiation was performed under quite similar conditions both in the presence of only pure SF_6 and in a mixture of SF_6 and H_2 with adsorbed value is determined by the sensitivity of the method for measuring the amount of SiF_4 produced in the case when no etching occurs (a converse system). The Specord-75 IR spectrophotometer allowed recording the pressure of SiF_4 in the cell that was $\sim 10^{-3}$ Torr. It was found that in case of such converse systems as SiO_2/SF_6 and Si/SF_6+H_2 there was not any appreciable production of SiF_4 (to within $\sim 10^{-3}$ Torr) even with the number of laser pulses larger than 10^3. The rough lower estimate for the selectivity value can be obtained from the relation

$$s = \frac{n_{\text{conv}} \cdot p_{\text{etch}}}{n_{\text{etch}} \cdot p_{\text{conv}}} \tag{3}$$

Here p_{etch} is the pressure of SiF_4 produced in the system in which the etching process does take place, p_{conv} is the pressure of SiF_4 produced in the converse system, n_{etch} and n_{conv} are the numbers of pulses for the corresponding systems.

If, for example, in the Si/SF_6 system $\sim 3.3 \cdot 10^{-2}$ Torr of SiF_4 is produced during 10 pulses (this corresponds to an etching depth of ~ 200 Å) and in the converse system less than 10^{-3} Torr of SiF_4 is formed during 300 pulses, it follows from (3) that $s \geqslant 10^3$.

Similar results can be obtained for (SiO_2) etching as well.

VI. DISCUSSION

The threshold nature of MPD is well known.[1] Figure 5 (curves 1 and 4) shows that the threshold of SiF_4 yield and the threshold of SF_6MPD[18] coincide within the experimental error (to within the measuring of pulse energy, laser beam cross-section, etc.). Besides, the dependences of SiF_4 and MPD yields on laser intensity are proportional to $\sim E^{2.7}$. All this enables us to conclude that the process of MPD forms the

basis for the process of etching, that is

$$2SF_6 \xrightarrow{nh\nu} 2SF_4 + 4F$$
$$Si + 4F \longrightarrow SiF_4 \qquad (4)$$

Eqs. (4) explain the blocking of the process of silicon etching when hydrogen is added into the Si/SF_6 system. Hydrogen is known to be a good scavenger of atomic fluorine,[15,16] and HF produced in the system does not react with silicon.

In Ref. 9 another mechanism is offered to explain the silicon etching in the Si/SF_6 system. Figure 5 (curve 3) shows the dependence of the silicon etching rate on laser pulse intensity obtained in Ref. 9. On the basis of this dependence it is concluded that the etching process is not related to MPD since, first, no obvious threshold is observed and, secondly, etching occurs at energies much smaller than the SF_6 MPD threshold. The mechanism of dissociative chemisorption is offered in that work as an alternative mechanism. Such an assumption is made on the basis of work[19] where the reaction of silicon with XeF_2 was studied, and the surface of silicon was probed by the method of X-ray photoemission spectroscopy. Such a mechanism seems not to be impossible but we believe that in our experiments with Si/SF_6 system the process of MPD is the fundamental one because there are significant differences between experimental conditions of the present work and that of Ref. 9: different samples and ways of their production (see "I. Introduction"), different laser pulse durations, dissimilar regard for the laser radiation reflection from the plate during perpendicular exposure, different degree of heating of samples resulting most likely in different secondary reactions occurring on the heated sample after the laser pulse is over. All this may be responsible for the difference between curves 1 and 3 in Figure 5.

Silicon etching process with the SF_6 MPD products resulting in gaseous SiF_4 production is a multistage one. The total process rate is determined by the rate of its slowest stage. Several main stages responsible for the character of the etching process may be distinguished.

1. SF_6 MPD in the IR CO_2 laser field;
2. MPD products diffusion to the silicon surface;
3. Heterogeneous processes on the silicon wafer surface (reactant adsorption, heterogeneous chemical reactions and their products desorption);

4. Diffusion of gaseous SiF_4 from the surface of the silicon wafer. Unfortunately, our technique of studying the interaction of SF_6 MPD products with silicon surface by means of quantitative determination of initial and final products composition did not allow us to study every stage in detail. But it is possible to give the qualitative explanation for the most part of the features of the etching process where either of these stages shows up in the main.

It can be seen from Figure 4 that SiF_4 yield is linear versus the SF_6 pressure up to $\sim$1.5 Torr, and at pressures $>$1.5 Torr saturation takes place. Since the SF_4 yield at saturation varies for different values of laser pulse intensity we can conclude that this saturation is not connected with the saturation of MPD primary products concentration in the layer above the surface but it is due to the rate of active particles transfer to the silicon surface, i.e., on diffusion. Under the conditions of our experiment the diffusion flow was affected, first, by the total number of active particles proportional to the initial SF_6 pressure and, secondly, by the total pressure of the mixture. With an increase of the SF_6 pressure at a fixed value of laser intensity, the general number of dissociated molecules increases and hence the diffusion velocity of active particles flow to the wafer increases as well. On the other hand, however, at pressures over 1.5 Torr the inverse dependence of the diffusion velocity on pressure has to be taken into account. This dependence compensates the increase of active particle concentration in the diffusion flow. At SF_6 pressures lower than 1.5 Torr, the factor of equilibrating influence of the total pressure on the diffusion velocity does not count and, as a result, a linear dependence of SiF_4 yield on the SF_6 pressure is observed (Figure 4), i.e. at such pressures, the SiF_4 yield is determined by active particle concentration. Indeed, if the dependence of the SiF_4 yield on active particle concentration is plotted (Figure 9) in this SF_6 pressure range, it turns out to be linear. The active particle concentration in Figure 9 (in relative units) was determined as a value proportional to the product of SF_6 initial pressure (in a pressure range below 1.5 Torr) and to the 2.7 power of laser pulse intensity because the MPD yield of SF_6 is proportional to $E^{2.7}$. The linearity of this dependence shows again that the etching process is based on the MPD of the SF_6 molecule.

From these considerations, it follows that under the conditions of saturation of the pressure dependence the etching rate is governed by the rate of heterogeneous processes at a constant concentration of

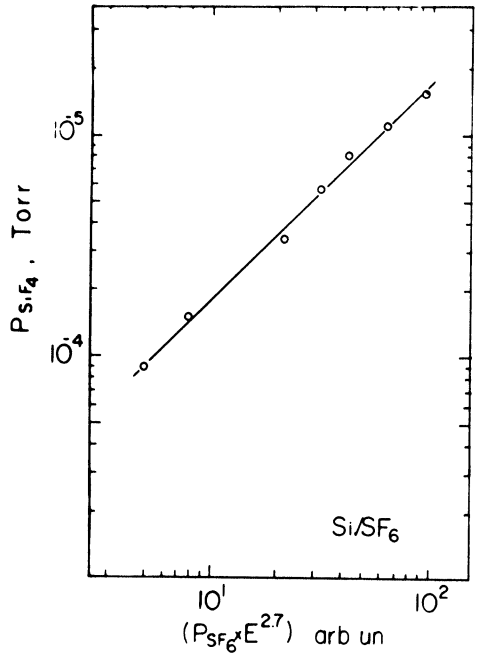

FIGURE 9 Dependence of the SiF_4 yield per pulse in the Si/SF_6 system on the concentration of active particles in the cell bulk with the initial pressure of $SF_6 \leqslant 1$ Torr and perpendicular incidence of radiation on the wafer.

active particles in the layer near the surface. This concentration does not depend on SF_6 pressure but it is a function of laser pulse intensity. At a fixed pressure, the SiF_4 yield grows with an increase of laser intensity since the active particle concentration increases. From Figure 5 (curves 1 and 2) it may be seen that up to 2.3 J/cm^2 the SiF_4 yield is determined by the active particle concentration since it is like the MPD yield, proportional to $E^{2.7}$. With $E \geqslant 2.3$ J/cm^2, a high concentration of MPD primary products can be obtained in the layer near the surface and at such a concentration the etching rate is determined by the kinetics of heterogeneous processes. A further increase in dissociation products concentration does not lead to an increase of SiF_4 yield, that is why the saturation in the dependence of the SiF_4 yield on laser pulse intensity is observed. So the obtained value of etching rate—"a monolayer per pulse"—seems to be quite regular at saturation. From this, it can be assumed that at saturation the limiting

factor is the rate of heterogeneous processes, for example the desorption of SiF_4 from the surface, or the rate of the reaction itself between silicon and atomic fluorine.

In experiments on SiO_2 etching, the SiF_4 production as a result of secondary chemical actions is a complex multistage process. We consider some possible chemical reactions which describe the experimental results obtained for SiO_2+H_2O (ads)/SF_6 and SiO_2+H_2O (ads)/SF_6+H_2 systems.

In the presence of adsorbed water on the cell walls and on the sample surface the SF_6 MPD primary products react with it and hydrogen fluoride is generated.[1] The reactivity of SF_4 is extremely high.[20] It is hydrolized by water almost instantly to yield SO_2 and HF

$$\begin{aligned} SF_4+2H_2O &\longrightarrow SO_2+4HF \\ SF_4+SO_2 &\longrightarrow 2SOF_2 \end{aligned} \tag{5}$$

The intermediate stages omitted, we can write

$$SF_4+H_2O \longrightarrow SOF_2+2HF \tag{6}$$

The subsequent reactions with SiO_2 and HF give birth to SiF_4

$$SiO_2+4HF \longrightarrow SiF_4+2H_2O \tag{7}$$

At the beginning of exposure, these reactions apparently proceed mainly with the participation of the water absorbed on the cell walls and on the surfaces of the samples under study. The subsequent decrease of SF_4 that goes on after irradiation may be due to the water produced in the reaction (7). In the chain of reactions (6)–(7), water is a crucial component, i.e., the final reaction can be written as

$$2SF_4+SiO_2 \xrightarrow{H_2O} SiF_4+2SOF_2 \tag{8}$$

If in the initial gas mixture, there is hydrogen acting as a scavenger, SF_4 and HF produced by high-rate chemical reactions of atomic fluorine with hydrogen will be the basic products after the radiation pulse is over.[15,16] In this case it may be assumed that the etching process proceeds in the following way

$$\begin{aligned} SF_6+H_2 &\xrightarrow{nh\nu} SF_4+2HF \\ SF_4+H_2O &\longrightarrow SOF_2+2HF \\ SiO_2+4HF &\longrightarrow SiF_4+2H_2O \end{aligned} \tag{9}$$

or finally

$$SF_6 + H_2 + SiO_2 \xrightarrow{nh\nu} SOF_2 + SiF_4 + H_2O \qquad (10)$$

The stoechiometry of this reaction fully corresponds to the experiments with the $SiO_2 + H_2O$ (ads)/$SF_6 + H_2$ system where the decomposition of SF_6 was equal to the increase in pressure of SDF_2 and SiF_4, i.e., $\Delta p_{SF_6} = p_{SOF_2} = 0_{SiF_4}$.

VII. CONCLUSION

The experiments performed show that Si and SiO_2 etching occurs as a result of interaction between the MPD products of SF_6 and the surface of the materials. The etching of Si and SiO_2 in this case proceeds in the course of qualitatively different processes.

The etching of silicon is performed by the MPD primary products of SF_6 in the IR field of a pulsed TEA/CO_2 laser only during irradiation, Si acting as a solid scavenger. The etching rate equals ~"a monolayer per pulse" and almost does not depend on the laser radiation direction. The presence of hydrogen in the original gas mixture suppresses the process of etching.

The SiO_2 etching proceeds in the course of secondary chemical reactions taking place after the irradiation is over, and the presence of adsorbed water is necessary here. The presence of H_2 in the mixture activates the etching process, its rate being ~100 Å/min.

The etching of Si and SiO_2 in the considered systems can be accomplished with higher selectivity (no worse than 10^3) which may prove rather useful for various practical applications.

Acknowledgements

The authors are grateful to Prof. P. V. Ambartsumyan for helpful discussions.

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