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Chemical sputtering of fluorinated silicon

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Sputtering can be defined as the process whereby particles leave the surface as a direct consequence of the presence of incident radiation. When particles leave the surface as a result of receiving momentum from the collision cascade induced by the incident radiation, the process is called "physical sputtering." If the incoming radiation (ions, electrons, or photons) induces a chemical reaction which leads to the subsequent desorption of particles, the process could be classified as "chemical sputtering." There are a number of molecules such as CH_4, CF_4, CF_3H, CF_3Cl, etc., whose binding energy to a large variety of surfaces is believed to be only a few kcal/mole. Therefore, these molecules will not remain adsorbed at room temperature. Consequently, if they are generated from surface atoms by radiation-induced processes, they will almost immediately desorb into the gas phase. This process is one type of chemical sputtering. Recent data obtained in plasma environments suggest that this type of reaction is a widely occurring phenomena; however, few systematic quantitative investigations of the subject have been completed. As a prototype system the chemical sputtering of silicon and SiO_2 under argon-ion bombardment in the presence of a molecular beam of XeF_2 has been investigated. Under these conditions, 25 or more silicon atoms can leave the surface per incident argon ion. About 75% of the silicon is emitted as SiF_4 (gas) and the rest leaves as silicon atoms or SiF_x radicals. The total yield (silicon plus fluorine) is greater than 100 atoms/ion. The measured yields are a strong function of XeF_2 flux and a much weaker function of ion energy in the range 500–5000 eV. The chemical-sputtering yield for SiO_2 is smaller than that of silicon by about an order of magnitude, but it is still larger than the physical-sputtering yield. Moreover, SiO_2 is also sputtered by electrons. These results indicate that the incident radiation induces a chemical reaction between silicon and adsorbed fluorine which produces SiF_4, and the SiF_4 is subsequently desorbed into the gas phase. We define this process as chemical sputtering. The large yields are probably a consequence of weak binding between the surface and the SiF_4 molecule.

I. INTRODUCTION

There is a significant number of inert molecules which interact weakly with even the most chemically active surfaces; i.e., the interaction energy between the molecule and the surface is so small that the molecule will not remain on the surface at room temperature. Moreover, the probability that the molecule will dissociate (dissociative chemisorption) is also small. Therefore exposure of a surface to an atmosphere of these gases produces a steady-state situation where a molecule approaches the surface and becomes adsorbed into a weakly bound state which has a very short lifetime (e.g., 10^{-6} sec). They are subsequently desorbed back into the gas phase. The steady-state concentration of adsorbed molecules on the surface is usually small under these conditions.

One example of this type of molecule is CH_4. The authors know of no surface where either the sticking probability or the binding energy of this molecule is large. For example, its sticking probability on atomically clean tungsten is $< 10^{-3}$ (Ref. 1) and the binding energy is ~ 7 kcal/mole.[2] Moreover, other experiments show that methane does not react with freshly evaporated titanium films[1] and moreover the sticking probability for CH_4 on clean nickel[3] $\lesssim 10^{-8}$. Our experience also suggests that gases such as CF_4, CF_3H, C_2F_6, C_3F_8, and CF_3Cl are similarly inert.[4] SiF_4 is not quite so inert[5] but appears to behave in a similar manner under a variety of conditions.

Moreover, a very chemically active surface often becomes inert when there is an adsorbed layer of gas on it. For example, exposure of an oxide surface to oxygen molecules (O_2) may not produce a chemical reaction. An oxygen molecule which approaches the surface may by physically adsorbed for a brief period of time and then desorbed back into the gas phase. A surface which would react with O_2 when clean is inert when covered with oxide. Furthermore, if an O_2 molecule were generated by some process on such a surface, it is expected that there would be a high probability that it would be desorbed into the gas phase as O_2 after a brief period of time.

One can envision a wide variety of situations where "inert" gases are generated at the surface from solid materials. The interaction of solid carbon with adsorbed fluorine or hydrogen to produce CF_4 (gas) or CH_4 (gas) is an example. Another example is the interaction of fluorine with silicon, to produce SiF_4 (gas). With the exception of the interaction of fluorine with a variety of materials,[6] this type of reaction does not usually occur spontaneously at room temperature. On the other hand, various techniques such as *ion* and *electron* bombardment can be used to induce a chemical reaction.[7] When this occurs, the resulting molecules, which are weakly bound to the surface, are almost immediately desorbed into the gas phase. Solid material is converted to gas-phase products. Etching has occurred. Various names have been applied to this type of chemical reaction. These include etching, plasma etching, reactive ion etching, reactive sputter etching, an ion-induced chemical reaction, or chemical sputtering. In this paper we will generally use the term "chemical sputtering." The purpose of this paper is to describe and interpret quantitative experiments related to the chemical sputtering of Si and SiO_2 in the presence of fluorine and under bombardment by Ar^+ and $CF_3{}^+$.

It is instructive at this time to compare physical sputtering with chemical sputtering. Physical sputtering is produced as a consequence of momentum transfer from the incoming ion to lattice atoms.[8] The resulting collision cascade produces surface atoms which have sufficient energy and momentum to escape the surface. The energy required to escape the surface is often several eV. Sputtering yields are usually limited to values $\lesssim 5$ atoms/ion ($E \lesssim 1000$ eV) because of this strong attractive interaction between sputtered particles and the surface. Moreover, the energy distribution of sputtered particles is non-Maxwellian and is often found to vary approximately as $1/E^2$ in the high-energy tail. In contrast, chemical sputtering can produce inert molecules which are able to leave the surface even though they only have a very small amount of energy. Therefore, there exists the possibility for large yields and also the possibility that the translational-energy distributions will be Maxwellian with a temperature equal to that of the surface. Since momentum transfer between the incoming particle and the target atom is not essential, chemical sputtering can be produced by low-energy electrons and photons as well as ions.

Radicals (e.g., F, CF_3, Cl, etc.), which are generated in a glow discharge, interact with silicon and its compounds to produce SiF_4 (gas) and other volatile products. This type of chemical reaction is the basis for the process called "plasma etching" which is widely used in the semiconductor industry. (For a review of this subject see Ref. 9). In previous papers it has been shown that this type of chemical reaction is greatly enhanced by electron and ion bombardment.[7,9] This enhancement is one type of chemical sputtering. In this paper the term "chemical sputtering" will be applied to those inert molecules which leave the surface as a consequence of ion bombardment, for example, a portion of the SiF_4 molecules. The SiF_4 molecules, which leave the surface spontaneously (no ion bombardment) are important in plasma etching situations but are not appropriately described by the term "chemical sputtering."

The trend toward the use of plasma etching to replace wet chemical etching in the manufacture of semiconductor devices is, among other things, due to its ability to produce straight side walls. The straight side walls are believed to be a consequence of the fact that, the rate of production of inert molecules (e.g., SiF_4) is much more rapid on surfaces being bombarded by ions than those which are not being bombarded. Since straight side walls occur for a variety of materials and for many types of chemical reactions[10–12] and since they are *not* believed to be caused by physical sputtering, we take the straight side walls as strong evidence for the fact that chemical sputtering is a widely occurring phenomenon. Despite its widespread occurrence, it has only recently been subjected to systematic investigations and at present there is virtually no quantitative data of a fundamental nature. The purpose of this paper is to present quantitative information about chemical sputtering for silicon and SiO_2 under bombardment with $CF_3{}^+$ and Ar^+ in the presence of adsorbed fluorine. The product molecule is primarily, but not exclusively, SiF_4 (gas). The widespread use of plasma etching in manufacturing situations[9–18] makes it desirable to understand chemical sputtering processes which occur in a glow discharge. However, it is difficult, if not impossible, to experimentally separate ion-induced chemical reactions from unassisted reactions in a rf-glow-discharge. This can be attributed to the fact that *all* surfaces exposed to the plasma are bombarded to some extent by positive ions and some surfaces are also bombarded by energetic electrons and/or negative ions. The extent of this bombardment by energetic radiation depends strongly upon the geometry of the fixtures and electrodes exposed to the plasma and also upon many operating parameters. (See Refs. 19 and 20 for an excellent discussion of this subject.) Moreover, the flux and energy of particles bombarding a given surface is usually undefined. Consequently, quantitative data about chemical sputtering probably requires nonplasma experiments. This is another motivation for the types of experiment reported in this paper.

This paper is organized in a manner so that a given section tends to answer one question. Section III A addresses questions about the surface composition during chemical sputtering. Section III B compares chemical sputtering yields obtained with CF_3^+ and Ar^+. Section III C demonstrates that chemical sputtering is intimately connected with the production of SiF_4 (gas) but that SiF_x radicals are also involved to a minor extent. Section III D shows the energy dependence of the chemical sputtering yield. Section III E summarizes and interprets the results. It is believed that the results and interpretations presented in this paper can be used rather directly to interpret experiments conducted in a plasma. Section II (experimental) is presented in more detail than is our usual practice because the experiments reported in this paper are subject to a number of artifacts and are reproducible only if care is taken and if experimenters are aware of the difficulties and their origin.

II. EXPERIMENTAL

2-μm-thick silicon films or 6-μm-thick SiO_2 films were deposited by *e*-beam evaporation onto vendor-supplied quartz-crystal microbalances (QCM, Inficon No. 321-25, 6-MHz resonant frequency). The QCM geometry and operating characteristics have been previously described by Lu and Lewis.[21] However, it should be mentioned that one can easily measure the deposition or removal of a fraction of a monolayer of silicon by measuring the frequency at which these devices oscillate. A QCM was subsequently mounted on a carousel manipulator in a stainless-steel UHV system [see Figs. 1(a) and 1(b)]. The QCM could be positioned so that an ion beam, and electron beam, a beam of molecular XeF_2, and an Auger spectrometer could be simultaneously focused upon the sensitive area of the quartz microbalance [see Fig. 1(b)].

Two types of measurement are fundamental to the data presented in this paper. First, the number of silicon atoms leaving the surface was measured using the QCM. Secondly, the number of SiF_4 molecules entering the gas phase were measured using mass spectrometry. As will be shown in Sec. III C, we have reason to believe that these two completely independent measurements are consistent with each other to ~ 10%. That is, under circumstances where all of the silicon is leaving the surface as SiF_4, the mass spectrometric and the oscillator measurements agree to this uncertainty.

These two types of yield measurements are complex and subject to error unless great care is taken. Several months of effort were expended eliminating artifacts (to be discussed subsequently) and performing calibrations. Therefore, it is believed that the absolute yield measurements presented in this paper are good to ± 15%. Since we are interested primarily in trends and mechanisms, other parts of the experiment were not as well controlled. For example, the ion beam was not mass analyzed and the films on the QCM were rough. [Rough surfaces are known to influence sputtering yields in some situations.[22]

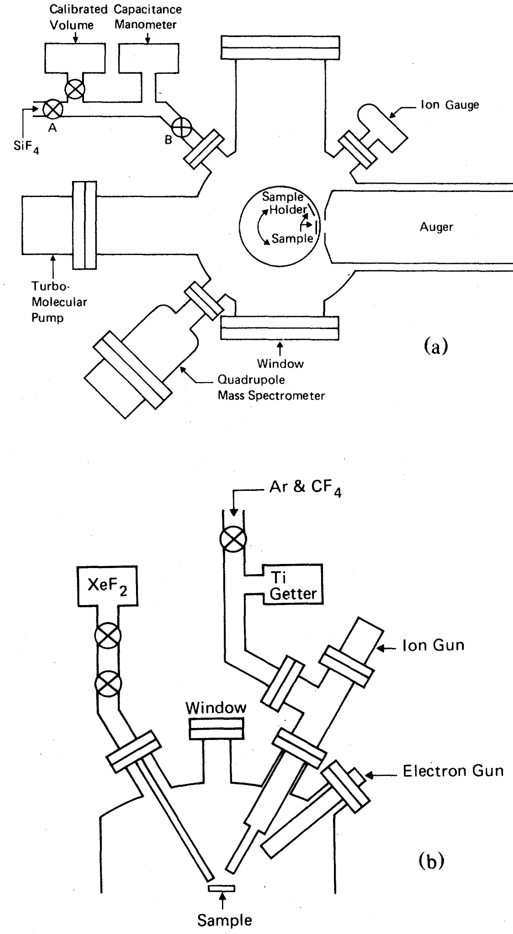

FIG. 1(a). Vacuum system schematic. The volume between valves "*A*" and "*B*" was determined by expanding a known pressure of gas from the "calibrated volume" into this region. A knowledge of this volume allowed one to relate a given SiF_4 flow rate to the pressure measured in the sample chamber (see text). An ion pump, sublimation pump, and poppet valve are not shown. (b) Vacuum system schematic indicating relationship between the ion gun, electron gun, and XeF_2 source with respect to the sample. The flow constriction between the ion gun and the sample chamber created a pressure differential of ~ 100, i.e., *P* (ion gun) ~ 10^{-4} Torr when *P* (chamber) ~ 10^{-6} Torr, the Ti getter in the gun chamber pumped all chemically active gases but did not react with CF_4 or Ar.

Nevertheless, sputtering yields measured by us agree very well with data found in the literature (see Fig. 13).]

A. XeF_2 gas

XeF_2 was used in these experiments to supply fluorine atoms to the surface. The XeF_2 dissociatively chemisorbs on a large variety of surfaces and leaves (presumably) adsorbed fluorine atoms. The Xe is almost immediately desorbed back into the gas phase since it is very inert. No Xe was ever observed upon the surface (see Fig. 2). Other (less convenient) sources of fluorine atoms would be expected to yield experimental results similar to those obtained with XeF_2.

XeF_2 is a white solid with a vapor pressure > 1 Torr at $T = 300$ K. It was stored in a stainless-steel reservoir which was attached to the all-metal vacuum chamber. XeF_2 was introduced into the system through a thin copper tube of length 16 cm and inside diameter of 0.16 cm. During later experiments, the tube dimensions were changed to a length of 15 cm and an inside diameter of 0.64 cm. The end of the copper tube was ~ 2 cm from the specimen surface and at an incidence angle of $\sim 30°$ from the specimen-surface normal. The collimated XeF_2 beam was aimed at the specimen center.

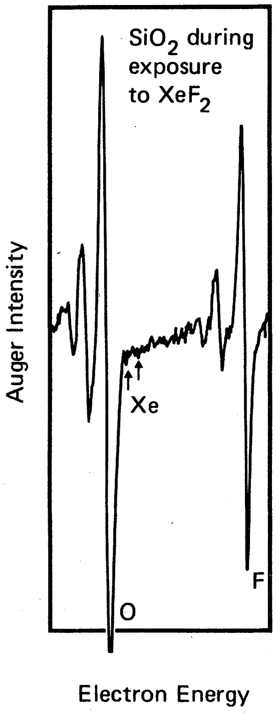

FIG. 2. Auger spectra or SiO_2 during exposure to XeF_2. This figure shows no detectable Xe upon the surface.

B. Ion gun

The ion gun, which was a commerical model obtained from PHI,[23] was separated from the main chamber by a copper tube of length ~ 7.0 cm and inside diameter of 0.80 cm. This configuration generated a pressure differential of ~ 100 between gun and the sample if and when the argon was introduced into the gun chamber and pumped through the tube and out of the main chamber with a turbopump whose nominal speed was ~ 100 l/sec. The pressure differential was needed so that the background pressure in the main chamber was low enough to allow the mass spectrometer to be calibrated for a given SiF_4 partial pressure. This arrangement produces a current of 0.5 μA to 2 μA at the sample. The exact amount depends upon the ion energy. The area of sample exposed to the beam was 0.12 cm^2.

The type of ions extracted from the gun is characteristic of the gas introduced into the gun chamber ($\sim 80\%$ CF_3^+ from CF_4 or $\sim 90\%$ Ar^+ from argon). Under the most extreme conditions $\sim 5\%$ of the ions may be Xe^+ which is a consequence of the background pressure of XeF_2.

C. Quartz-crystal microbalance

The QCM's were mounted in a special holder which ensured their correct positioning. The holder (see Fig. 3) consisted of an element with a 0.39-cm aperture which defined the area of the sample which was exposed to the ions and the XeF_2. The front surface was electrically isolated so that the number of

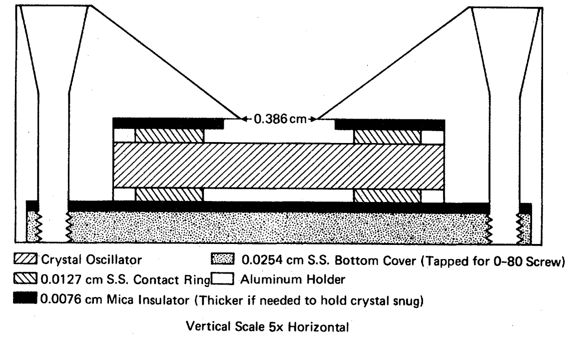

FIG. 3. Custom-made holder for the quartz-crystal oscillator. Electrical contacts to the back side and the front side of the QCM are made through the contact rings which are then connected through small holes (not shown) in the side of the holder to electrical leads.

ions hitting the sample could be determined by a current measurement. The current to SiO_2 samples was determined by measuring the ion current to a silicon sample and then rotating the manipulator to an identical holder which contained a SiO_2 sample. This procedure was demonstrated to produce reliable results through the use of two conducting samples in preliminary experiments. Charging of the SiO_2 surface was prevented by focusing an electron beam onto the metal element which contained the defining aperture. It is easy to demonstrate that the SiO_2 surface is near ground potential by observing the position of a known Auger peak. (Investigators making current measurements in the presence of fluorine should also realize and compensate for the fact that the sputtering of negative ions will influence the current measurement.)

Several oscillators were weighed using a very sensitive mechanical microbalance. They were then installed in our system and bombarded with argon ions. After removal they were again weighed and the sensitivity of the quartz microbalance was determined. A frequency change of 1 Hz corresponded to the removal of 2.97×10^{13} silicon atoms (2.48×10^{14} silicon atoms/Hz cm^2). Our calibration agreed precisely with that supplied by the manufacturer of the QCM. Moreover, the sputtering yields of silicon, which were determined using our calibration, agreed well with data from the literature (see Fig. 13).

D. Mass spectrometry

The number of SiF_4 molecules produced per incident ion was determined mass spectrometrically by observing the SiF_3^+ fragment peak. The SiF_4^+ parent peak exhibited similar behavior but was less intense by ~ two orders of magnitude. Measurements were made in the following manner. The sample was rotated into the XeF_2 beam (no ions) and the increase in the SiF_4 partial pressure over the *ever-present background* was observed. The same procedure was then repeated with the ion beam on. Typical data are shown in Fig. 4. SiF_4 yield measurements were calculated on the basis of the difference in partial-pressure increase between these two types of run. After each measurement and under identical conditions the mass spectrometer was calibrated against a known partial pressure of SiF_4. This procedure was absolutely essential since the sensitivity of the mass spectrometer was a strong function of the XeF_2 partial pressure. Moreover, the sensitivity changed as a function of time. When sufficient care was taken, the experimental data were quite reproducible.

The mass spectrometric technique was calibrated on an absolute scale by establishing the relationship between the pressure of SiF_4 in the main chamber and the number of SiF_4 molecules which were being leaked into the system through valve *A* (see Fig. 1). This was accomplished by generating a constant flow of SiF_4 through valve *A* and then closing valve *B* and measuring the rate of pressure increase in the known volume using a capacitance manometer (an absolute-pressure measuring device). This measurement allowed a determination of the flow rate. Valve *B* was then opened and the partial pressure of SiF_4 was measured with the mass spectrometer and ion gauge. (Under these conditions, the partial pressure of SiF_4 is determined by the flow rate and the pumping speed of the turbomolecular pump.) In this manner a linear relationship between the number of SiF_4 molecules being introduced into the system and the ion-gauge pressure was established. The accuracy of this whole procedure depends upon the accuracy of the capacitance manometer. The instrument used in these experiments was checked against three similar instruments and a McLeod gauge. There was agreement within 10% in all cases.

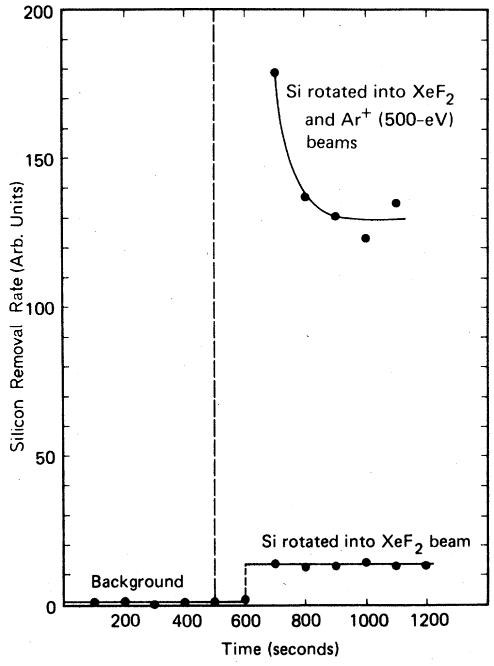

FIG. 4. Typical raw data from the QCM. Silicon rotated into XeF_2 beam with the ion beam off—bottom curve. Silicon rotated into the XeF_2 beam with ion beam on—top curve. The difference between these two curves allows one to deduce an ion-induced chemical-sputtering yield for silicon. The initial decrease (top curve) is believed to be a consequence of a reduction in the fluorine-surface concentration. The runs were always continued until steady state was achieved.

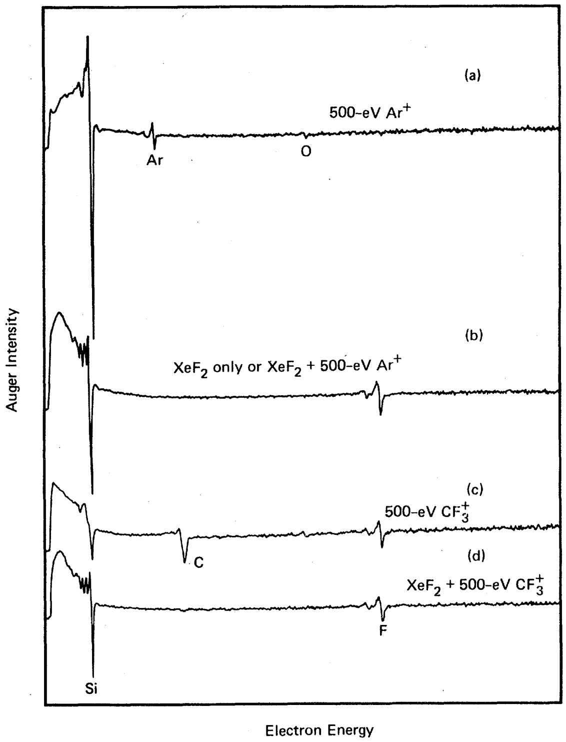

FIG. 5. Auger spectra for silicon. (a) Silicon during bombardment with argon ions. (b) Silicon during exposure to XeF_2 and bombardment with argon ions or during exposure to XeF_2 with no ion bombardment. (c) Silicon during bombardment with CF_3^+. (d) Silicon during bombardment with CF_3^+ and exposure to XeF_2. Note: the intensity of the fluorine peak is probably somewhat attenuated due to electron-stimulated desorption. The peaks are designated by their chemical symbol, e.g., C for carbon.

E. Miscellaneous

When XeF_2 or Cl_2 are introduced into a well-baked stainless-steel vacuum system, large quantities of COF_2, CO_2, and CO are produced through some type of wall reaction. Therefore, significant quantities of gaseous impurities were always present during the experiments which involved XeF_2. Fortunately, these impurity gases reacted so slowly with the silicon and SiO_2 that they did not appear to influence the experiments (see Figs. 5 and 6).

It was determined that at a fixed XeF_2 flow rate, the SiF_4 yield per ion was slightly smaller for a larger current of bombarding ions. This is presumably caused by a decreased fluorine concentration at the surface due to the increased flux of ions. In any case, data which are compared or contrasted in this paper are always taken under conditions where the incident ion fluxes were identical.

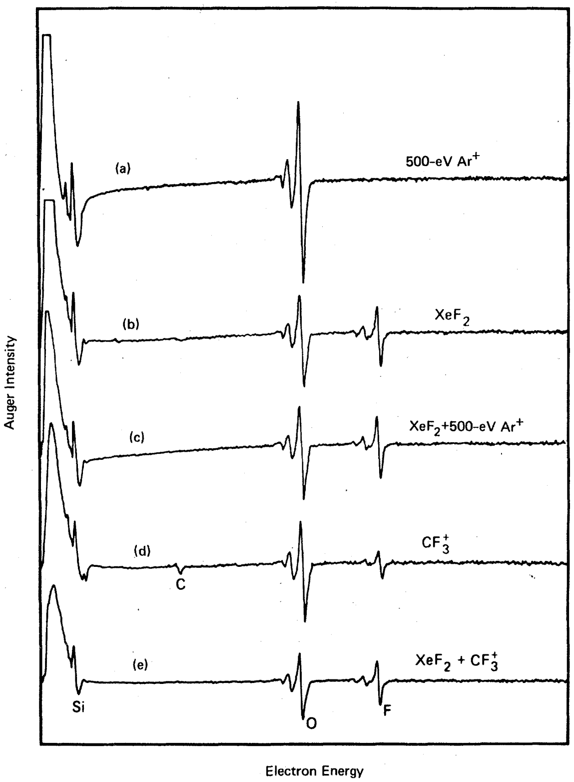

FIG. 6. Auger spectra for SiO_2. (a) SiO_2 during bombardment with argon ions. (b) SiO_2 during exposure to XeF_2. (c) SiO_2 during exposure to XeF_2 and bombardment with argon ions. (d) SiO_2 during bombardment with CF_3^+ ions. (e) SiO_2 during bombardment with CF_3^+ and exposure to XeF_2. The intensity of the fluorine peak is probably somewhat attenuated by electron-stimulated desorption.

III. RESULTS AND DISCUSSION

A. Surface composition

Very useful information would be available if one could quantitatively relate the chemical-sputtering yield to surface composition. Obtaining this type of information would require calibration of the Auger spectrometer for the elements of interest and would require that the spectrometer did not change sensitivity with experimental condition or long-term use. Unfortunately, under the severe conditions imposed by these experiments, the spectrometer sensitivity varied substantially under a variety of conditions and therefore the Auger data presented in this section are qualitative. They can be summarized as follows.

1. Silicon

(i) Bombardment of a Si(111) sample with argon ions produces Auger spectra which exhibit a large silicon peak and a smaller argon peak (see Fig. 5 spectrum "*a*"). The *evaporated* silicon samples would exhibit slightly larger carbon and oxygen peaks (see Ref. 24). The impurities presumably originate from the bulk material.

(ii) Exposure of this clean surface to XeF_2 (or XeF_2 and Ar^+ bombardment) produces etching and Auger spectra which exhibit only silicon and fluorine peaks (see Fig. 5—spectrum "*b*"). This spectrum indicates that trace amounts of bulk impurity are removed from the surface by the XeF_2 and that background gases are not rapidly adsorbed.

(iii) Bombardment of the clean silicon sample (characterized by spectrum "*a*") with primarily CF_3^+ produces significant carbon and fluorine peaks and greatly reduces the size of the silicon peak (see Fig. 5—spectrum "*c*"). Under similar conditions, the silicon peak would have completely disappeared if the ion beam would have approached the surface at normal incidence (see Ref. 24).

(iv) When the surface, which is characterized by spectrum "*c*," is exposed to XeF_2, the carbon peak disappears (see Fig. 5—spectrum "*d*"). This result is a direct experimental verification of our previous suggestion that carbon is effectively removed from a silicon surface by CF_3^+ bombardment in the presence of excess fluorine. Note also that the chemical sputtering of silicon, which will be described later in this paper, takes place at a surface which contains only silicon and fluorine. This is independent of whether the ion is Ar^+ or CF_3^+.

2. *SiO_2*

(i) Bombardment of the SiO_2 samples with argon ions produces an Auger spectrum which exhibits only silicon and oxygen peaks (see Fig. 6—spectrum "*a*"). In contrast to silicon, no argon is observed in SiO_2. SiO_2 is always easy to clean and to maintain in a clean condition.

(ii) Exposure of a surface, which is characterized by spectrum "*a*," to XeF_2 causes a reduction in the silicon and oxygen peaks and produces a large fluorine peak (see Fig. 6—spectrum "*b*"). The fluorine peak is of the same magnitude as the oxygen peak and yet no etching is observed.[25] Simultaneous bombardment with Ar^+ produces little change (see Fig. 6—spectrum "*c*") but does produce significant chemical sputtering.

(iii) Bombardment of a surface characterized by spectrum "*a*" with CF_3^+ produces spectrum "*d*" which exhibits some fluorine and a small carbon peak. Exposure of this surface to XeF_2 (spectrum "*e*") causes the carbon to disappear from the surface. It is clear that the chemical-sputtering experiments are conducted upon an SiO_2 surface which only contains a surface layer of fluorine

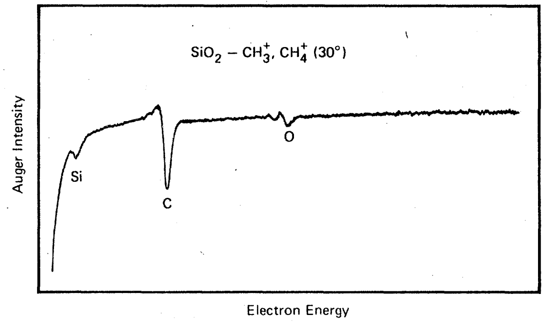

FIG. 7. Auger spectra for SiO_2 during bombardment with ions characteristic of methane, primarily CH_4^+ and CH_3^+. Ion energy $= 500$ eV.

(iv) Bombardment of SiO_2 surfaces with ions obtained from methane (primarily CH_4^+ and CH_3^+) produces completely different results from CF_3^+ bombardment. Methane produces a surface with much carbon as is indicated in Fig. 7. This is to be contrasted with Fig. 6—spectrum "*d*" for CF_3^+ where there is very little carbon. This again suggests that the presence of both oxygen and fluorine on an SiO_2 surface very effectively removes carbon, possibly as COF_2. COF_2 is always observed in plasma systems which contain fluorine and also in our experiments.

B. Does chemical sputtering depend upon the type of ion? A comparison of CF_3^+ with Ar^+

Figure 8 compares the SiF_4 yield as a function of XeF_2 impingement rate for bombardment of silicon and SiO_2 surfaces with 2000-eV CF_3^+ and Ar^+. Similar data for silicon surfaces with 500-eV ions are shown in Fig. 9. These data demonstrate five things.

(i) Silicon has a larger SiF_4 (gas) yield for both CF_3^+ and Ar^+ bombardment than does SiO_2 under all conditions. The same type of behavior is observed for the total yield. In contrast, SiO_2 is sometimes found to be etched faster than silicon in a fluorocarbon plasma. This is probably because the silicon surface in the plasma contains a thin protecting layer (possibly less than a monolayer) of carbonaceous material. This layer is probably a consequence of the adsorption of CF_x radicals from the plasma. The protecting layer is of course absent in our experiments (see Fig. 5).

(ii) The SiF_4 (gas) yields induced by CF_3^+ and Ar^+ bombardment are almost identical for silicon surfaces but are significantly different for SiO_2 surfaces. These results suggest that chemical sputtering for *silicon* is a physical process which is not strongly influenced by the chemical nature of the bombarding ion. It should be noted, however, that the yield appears to be too large to be accounted for by physical sputter-

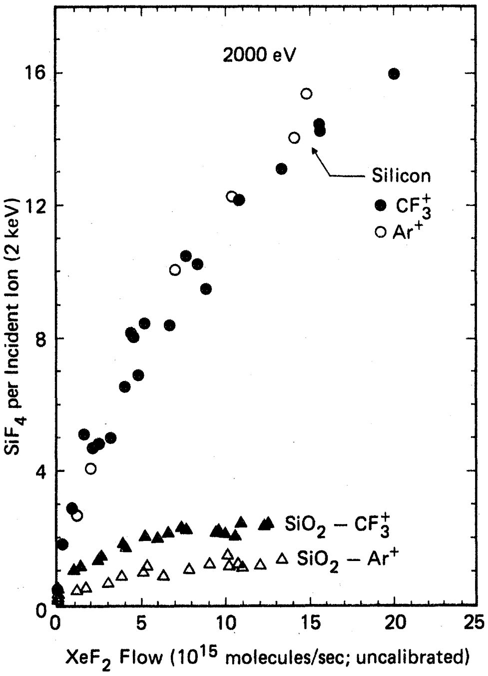

FIG. 8. SiF_4 (gas) yield vs XeF_2 flow rate. The flow varies from zero to $\sim 2\times10^{16}$ molecules/sec. Ion energy $=2000$ eV.

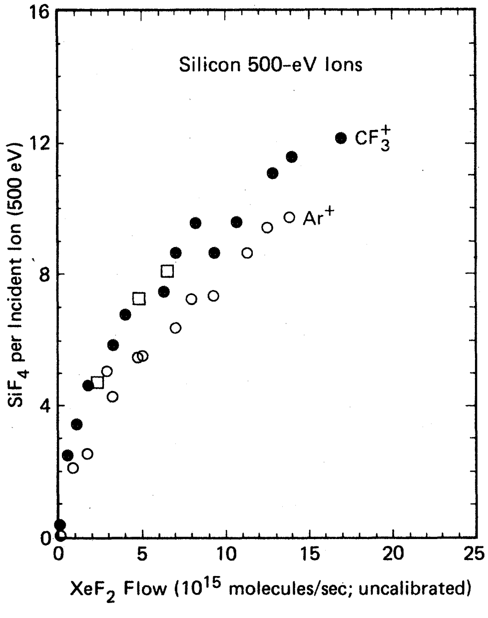

FIG. 9. SiF_4 (gas) yield vs XeF_2 flow rate. Ion energy $=500$ eV.

ing. Moreover, since SiF_4 is not the material contained in the surface region (see Sec. III E), the collision cascade would not be expected to produce large quantities of SiF_4 by a mechanism related solely to physical sputtering.

In contrast to silicon, the SiF_4 (gas) yield for CF_3^+ bombardment of SiO_2 is about two times the equivalent yield for Ar^+. It is quite possible that the chemical nature of the CF_3^+ is important in this instance. It is suspected that the carbon from the CF_3^+ is used to form compounds such as COF_2, CO_2, and CO, which in turn allows production of SiF_4 from the free silicon left upon the surface. The fact that the Auger data indicate that it takes both fluorine and oxygen to maintain a carbon-free surface (see Sec. III A) may indicate that the production of COF_2 is particularly important.

(iii) The fact that the SiF_4 yield is significant when SiO_2 is bombarded with Ar^+ in the presence of XeF_2 and negligibly small in the absence of Ar^+ bombardment illustrates one of the roles which ions play, i.e., to induce a reaction between adsorbed fluorine and SiO_2. This mechanism has of course been discussed previously[7,9] but is conclusively demonstrated in this instance. This is to be constrasted with silicon, where there is a rather slow spontaneous reaction ($T=300$ K) which is greatly enhanced by ion bombardment.

(iv) In a few instances (squares, Fig. 9) SiF_4 yields were obtained on a silicon single-crystal (111) surface (N type, 10-Ω cm resistivity). There was no significant difference between the single crystal and the polycrystalline material. This is to be expected when it is realized that both single-crystal and polycrystalline surfaces become amorphous when bombarded with ions.[26]

(v) The SiF_4 yield for silicon continues to increase with the flux of XeF_2 (within our experimental range) while the SiF_4 yield for SiO_2 saturates. This indicates that the removal rate of SiO_2 is limited by the number of ions while the removal of silicon from the surface is limited by the flux of fluorine (XeF_2). This behavior is independent of whether the bombarding ion is CF_3^+ or Ar^+. [Experimental note: At zero-XeF_2-flow rate, no SiF_4 should be produced when SiO_2 is bombarded with Ar^+. The small but real SiF_4 yield (~ 0.2) observed at the origin of Fig. 8 is an artifact which is believed to be caused by a small flux of fluorine from the walls of the system.]

C. What types of particle enter the gas phase?

One could reasonably expect that the total number of silicon atoms which enter the gas phase would be equal to the number of physically sputtered atoms plus the number of silicon atoms entering the gas phase as SiF_4. The purpose of the experiments reported in this section is to determine whether or not

TABLE I. Comparison of the number of silicon atoms leaving a quartz-crystal microbalance with the number of SiF_4 molecules appearing in gas phase. No ion bombardment.

XeF_2 flow rate in molecules per second (uncalibrated)	Number of silicon atoms per second leaving quartz microbalance	Number of SiF_4 molecules per second appearing in gas phase
1.09×10^{16}	4.05×10^{12}	4.10×10^{12}
1.09×10^{16}	4.38×10^{12}	4.54×10^{12}
1.69×10^{16}	6.77×10^{12}	7.14×10^{12}
1.69×10^{16}	6.59×10^{12}	6.45×10^{12}
7.23×10^{15}	2.91×10^{12}	3.12×10^{12}
4.11×10^{15}	1.60×10^{12}	1.63×10^{12}

this expectation is correct. The QCM was used to measure the total yield in the presence of XeF_2 and the sputtering yield while the mass spectrometer was used to measure the SiF_4 yield.

When the sample is rotated into the beam, both the mass-spectrometer signal and the rate of QCM-frequency change increase (see Fig. 4). Table I compares the number of SiF_4 molecules entering the gas phase and the number of silicon atoms leaving the surface as a function of XeF_2 flow rate. These data were taken in the absence of ion bombardment. All of the silicon leaves the surface as SiF_4 under these circumstances. This demonstrates that the only chemical reaction of importance in the absence of ion bombardment is that which produces SiF_4. SiF_2, for example, is not spontaneously desorbed into the gas phase. The fact that these two quantities agree also gives us confidence in our calibration. Data obtained during bombardment with argon ions are shown in Fig. 10 for 2000-eV ions and in Fig. 11 for 500-eV ions. For reasonable fluxes of XeF_2 about 75% of the silicon leaves the surface as SiF_4. This is the ion-enhanced chemical reaction which we have discussed in previous papers. About 10% of the silicon is expected to enter the gas phase as a consequence of physical sputtering. This leaves about 15% of the silicon unaccounted for.

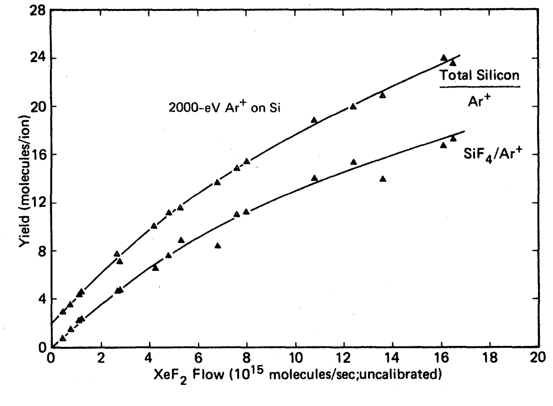

FIG. 10. Yield vs XeF_2 flow rate. Ar^+ bombardment of silicon. Top curve: Total number of silicon atoms leaving the surface per incident 2000-eV argon ion. Bottom curve: Total number of SiF_4 molecules leaving the surface per incident 2000-eV argon ion. The data for the SiF_4 yield and the total yield were taken simultaneously. These curves indicate that most silicon atoms leave the surface as part of an SiF_4 molecule.

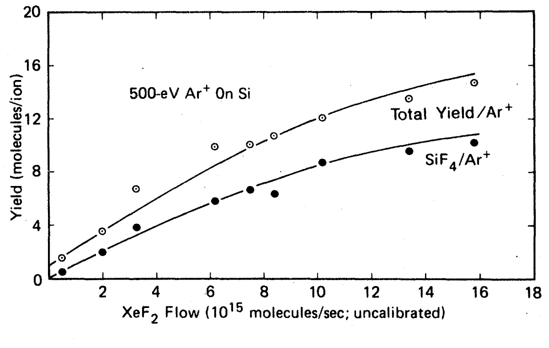

FIG. 11. Yield vs XeF_2 flow rate. Ar^+ bombardment of silicon. Top curve: Total number of silicon atoms leaving the surface per incident 500-eV argon ion. Bottom curve: Total number of SiF_4 leaving the surface per incident 500-eV argon ion. The data for the SiF_4 yield and the total yield were taken simultaneously. These curves indicate that most of the silicon atoms leave the surface in the form of SiF_4 molecules.

Mauer *et al.*[27] have developed a model which suggests that ion bombardment in the presence of fluorine produces large quantities of SiF, SiF_2 and SiF_3 which leave the surface as a consequence of physical sputtering. (In this model the large yields are presumably a consequence of the weak interaction of these radicals with the surfaces). We originally doubted the validity of this model but our data force us to the conclusion that 15–20% of the silicon may leave the surface as a consequence of enhanced sputtering. The desorbed radicals immediately react with the vacuum system walls and hence are not detected by our mass spectrometer. (We have had much experience with various types of radicals and have never found one which remains in the gas phase in a stainless-steel vacuum system of the type used in these experiments.[28] Therefore, we conclude that the influence of ions in a fluorocarbon plasma is dominated by the ion-enhanced chemical reaction (ion + adsorbed fluorine + Si $\rightarrow SiF_4$) but, as was suggested by Mauer *et al.* a chemically assisted physical-sputtering mechanism may also be operative at about the 15% level.

The data for SiO_2 shown in Fig. 12 are not as convincing. But even in this case, there may be a small amount of chemically enhanced physical sputtering; perhaps 0.3 silicon atom per incident ion. However, in the case of SiO_2, the normal amount of physical sputtering is always a significant fraction of the total yield (compare Fig. 14). For example, 2000-eV argon has a sputtering yield of *0.85*, an SiF_4 yield of *1.3*, and a total yield of 2.5. For 2000-eV CF_3^+, the ion yield by itself is 2.15, the SiF_4 yield 2.4, and the total yield 5.5. The SiF_4 yield was not measured as a function of energy for SiO_2 because the yield was too small to be quantitatively detected at low ion energies. However, the 2000-eV data are qualitatively similar to those obtained at both lower and higher energies.

D. Energy dependence

Figure 13 and Table II show the energy dependence of the yields for silicon and Fig. 14 shows similar data for SiO_2. The XeF_2 flux was held constant at a value of ~ 1.5×10^{16} molecules/sec (see Fig. 8) during this set of experiments. Most of the data presented in this paper were obtained with the ion beam approaching the surface at an angle $\alpha \simeq 30°$ with respect to the surface normal. However, the

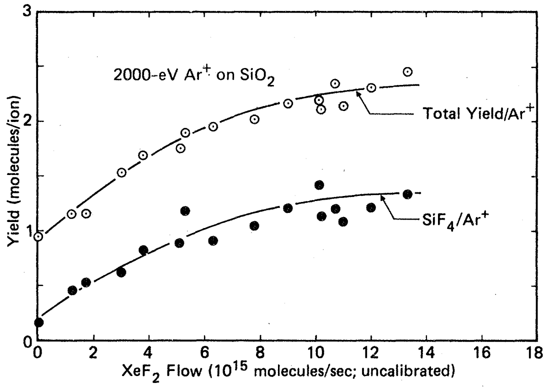

FIG. 12. Yield vs XeF_2 flow rate. Ar^+ bombardment of SiO_2. Top curve: Total number of SiO_2 molecules leaving the surface per incident 2000-eV argon ion. Bottom curve: Total number of SiF_4 leaving the surface per incident 2000-eV argon ion. The data for the SiF_4 yield and the total yield were taken simultaneously. These curves indicate that about one-half of the silicon leaves the surface in the form of SiF_4.

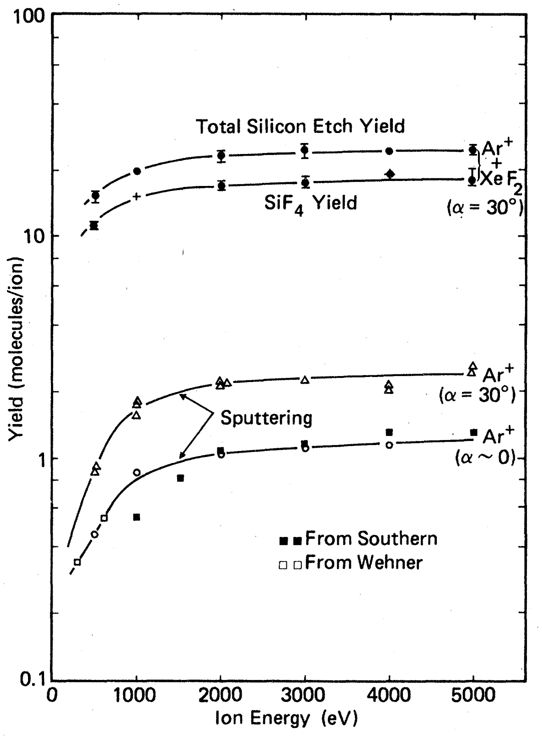

FIG. 13. Silicon yields vs ion energy. The bottom two curves are physical-sputtering yields. Literature data from Southern (Ref. 30) and Wehner (Ref. 29) are included for comparison. $\alpha =$ angle of incidence with respect to surface normal. The top two curves were obtained during simultaneous exposure to XeF_2 and argon-ion bombardment. The top curve is the total number of silicon atoms which leave the surface per incident argon ion. The next curve down is the total number of SiF_4 molecules which leave the surface per incident argon ion. XeF_2 flow is ~ 1.5×10^{16} molecules/sec.

TABLE II. Silicon yields.

Ion energy (eV)	Total sputtering yield ($Ar^+;\alpha=0$)	Total sputtering yield ($Ar^+;\alpha=30°$)	Total yield[a] ($Ar^+ + XeF_2$);$\alpha=30°$	SiF_4 yield[a] ($Ar^+ + XeF_2$)
500	0.45	0.90	15.5	11.2
1000	0.87	1.65	19.8	15.2
2000	1.03	2.15	23.0	16.8
3000	1.12	2.25	24.3	17.5
4000	1.15	2.10	24	19
5000		2.52	25	18.2

[a] XeF_2 flow $\sim 1.85 \times 10^{16}$ molecules/sec.

bottom curve in Fig. 13 was obtained with ions of nearly normal incidence in order to allow comparison of the physical-sputtering yields measured in these experiments with those reported in the literature. The motivation was to check again our calibration procedures and to verify in another manner that our yield measurements were accurate. A by-product was absolute sputtering-yield measurements for SiO_2 with argon, which (to our knowledge) are not available elsewhere (see the bottom curve in Fig. 14). The agreement between our data and those of Wehner[29] is excellent. The 500-eV points are identical. The agreement between our data and those of Southern[30] is also excellent between 2000 and 5000 eV. However, their 1000-eV point is somewhat lower than ours. The agreement between the sputtering yields measured in this work and those found in the literature further substantiate the accuracy of our measurements.

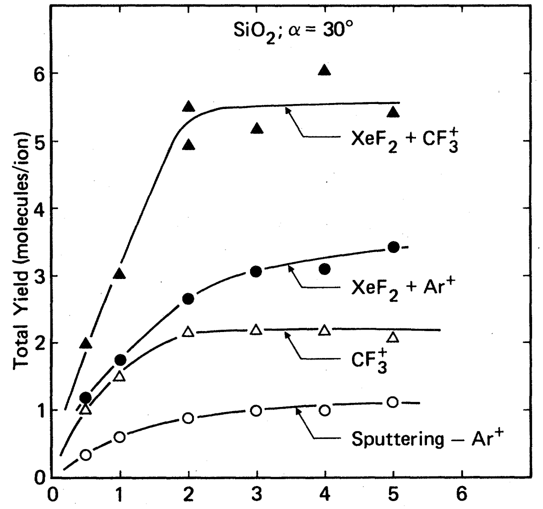

FIG. 14. SiO_2 yields vs ion energy. The bottom two curves were obtained with no flow of XeF_2. Therefore, the bottom curve (argon-ion bombardment) is caused by physical sputtering. The top two curves were obtained with a flow of XeF_2 of $\sim 1.5 \times 10^{16}$ molecules/sec.

Figure 13 also shows that the silicon sputtering yield increases by about a factor of 2 when the angle of incidence is changed from 0 to 30°. This increase is somewhat larger than one might have expected on the basis of trends observed for other materials.[31] It is possible that the angular dependence of the physical-sputtering yields is enhanced by the roughness of our surface. In contrast to physical-sputtering yields, the total yield in the presence of XeF_2 appears from preliminary data to have little angular dependence. The yields obtained in this set of experiments ($\alpha = 30°$) agree roughly with data obtained by Coburn[32] at normal incidence.

The silicon yield in the presence of a flux of XeF_2 is a factor of 10—15 greater than the physical-sputtering yield. About 75% of the total yield is due to the production of SiF_4. The remainder is believed to be due to the sputtering of silicon atoms and probably also SiF_x radicals. This fraction is not a strong function of ion energy or XeF_2 flux. The argon sputtering yield drops off somewhat faster at low energies than does the total yield in the presence of XeF_2. The total silicon yield is also a strong function of XeF_2 flux for the range of flows used in these experiments. It is quite probable that the total yield of silicon would increase to 30 (or more) under saturation fluxes of XeF_2. The sputtering yield of SiO_2 (Fig. 14—bottom) is such that the mass removal rate is about 0.8 times that of silicon (Fig. 13—bottom). However, the *increase in yield* upon exposure to XeF_2 is much less for SiO_2 than for silicon and is never greater than about a factor of 3 for either CF_3^+ or Ar^+.

Based on the data contained in Fig. 14, we would not expect the SiO_2 etch rate in a CF_4 plasma to be more than about 6 times the equivalent rate for pure argon and yet etch ratios of 20:1 have been reported. There are two reasons why this might happen. First, small quantities of oxygen impurities in the argon plasma would tend to depress the sputtering rate as has been demonstrated for oxygen-argon mixtures. In a pure CF_4 plasma, however, oxygen tends to enhance the etch rate. Secondly the average energy of Ar^+ hitting the target in a plasma is greatly reduced because of charge-exchange collisions with neutral atoms in the cathode dark space.[33] This type of charge exchange should be much reduced between CF_3^+ (the primary ion in a CF_4 discharge) and CF_4 and therefore the average energy of CF_3^+ colliding with the target might be significantly greater than the average energy of Ar^+ under roughly equivalent conditions. This effect would also tend to increase the etch-rate ratio for these two ions.

E. How does ion bombardment produce enhanced etching? (Discussion and summary)

The amount of fluorine being deposited upon the surface from the incident XeF_2 flux must be equal to the amount of fluorine leaving the surface (primarily as SiF_4) under steady-state conditions. Therefore, an increased etch rate implies that XeF_2 has an increased sticking probability, i.e., the number of fluorine atoms being adsorbed upon the surface at a given incident flux is increased. Hence, a fundamental question is: *How does ion bombardment cause XeF_2 to have an increased sticking probability?* The thrust of this section will be an attempt to answer this question and also at the same time to put other experiments in perspective and to summarize results.

The experimentally determined characteristics for the interaction of XeF_2 with silicon can be summarized as follows:

(i) It has been shown[5] by using x-ray photoemission spectroscopy (XPS) that exposure of silicon to XeF_2 produces approximately a monolayer of fluorine which does not disappear when the XeF_2 flux is stopped. This experiment is qualitatively substantiated by our Auger data and by experiments involving ion bombardment [see point (ii)] and implies that SiF_4 is not being spontaneously desorbed from this layer.

(ii) Ar^+ bombardment of this stable fluorine layer (no XeF_2 flux) in our experiments produces copious quantities of SiF_4 as indicated by mass spectrometry. The initial yield is higher than ten and it decreases as the amount of fluorine is depleted.

(iii) XPS data[5] show that the fluorine is bonded to the surface in an "SiF_2"-like configuration and that there are no SiF_4 molecules as such on the surface. Exposure of clean silicon to SiF_4 also produces SiF_2 surface complexes. However, SiF_4 would not be expected to dissociate on a surface covered with SiF_2.

(iv) The rate of spontaneous SiF_4 production is a linear function of XeF_2 flux[6] which implies that the sticking coefficient is independent of coverage in situations where this reaction occurs.

(v) Ion bombardment causes the sticking coefficient of XeF_2 to increase as indicated by the argument presented at the beginning of this section.

(vi) Bombardment with either CF_3^+ or Ar^+ in the presence of XeF_2 produces similar quantities of SiF_4 (see Figs. 8 and 9).

(vii) Up to ~20% of the silicon may leave the surface as SiF_x during Ar^+ bombardment $(0 \leq X \leq 3)$. The rest leaves as SiF_4 (see Fig. 10).

(viii) The total number of silicon atoms leaving the surface per incident ion is very large (see Fig. 10). For example, the yield may reach 30–40 for a 2000-eV Ar^+ ion in the presence of large fluxes of XeF_2.

These experimental results can be explained in a plausible manner on the basis of the schematically illustrated sticking probability curve shown in Fig. 15. The model suggests that a clean silicon surface has a large sticking coefficient for XeF_2 where the sticking

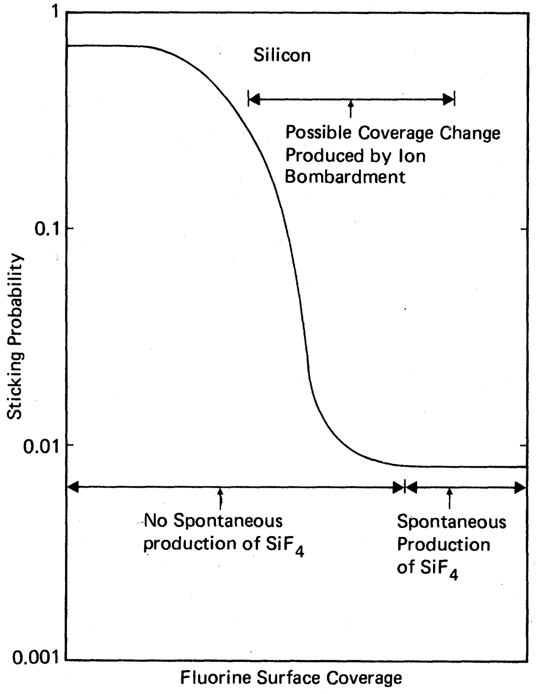

FIG. 15. Schematic of *hypothetical* curve for sticking probability vs fluorine surface coverage for XeF_2. It is known that the sticking probability for XeF_2 is $\sim 10^{-2}$ in the region where SiF_4 is spontaneously produced. A reduced surface coverage is expected to cause an increased sticking probability.

coefficient is defined as the probability that an incident XeF_2 molecule will be dissociated and leave fluorine upon the surface. The sticking coefficient then decreases as the coverage increases. Up to a certain coverage, which may be about a monolayer, there is no spontaneous production of SiF_4 [point (i)]. As the coverage is further increased, the sticking probability again becomes constant at a value of approximately 0.01 [point (iv)]. In this coverage range SiF_4 is generated spontaneously [point (iv)]. When an ion collides with this saturated surface layer a collision cascade of moving target atoms develops which induces the production of large quantities of additional SiF_4 [points (ii) and (viii)], which is subsequently desorbed into the gas phase. The generation of SiF_4 on the surface may, for example, be a consequence of a bombardment-induced reaction between two SiF_2 surface complexes to produce free silicon and SiF_4. As a consequence, a localized region of the surface is depleted of fluorine and the sticking probability of XeF_2 increases [point (v)] in accordance with the sticking probability curve. The ion-enhanced reaction leading to SiF_4 is due to collision processes between the incoming ion and the target atoms; i.e., the reaction occurs because the target atoms have gained some kinetic energy. Therefore, the chemical nature of the incoming ion does not result in greatly different yields [point (vi)]. The fact that the yields are much larger than physical-sputtering yields [point (viii)] suggests that the amount of energy needed is small. However, the fact that the layer is stable at room temperature under some conditions indicates that the activation energy for the reaction is probably greater than 1 eV. The fact that the incoming ion collides with a surface which contains a large number of SiF_2 surface complexes [point (iii)] would also lead one to expect that some of them will leave the surface as a consequence of physical sputtering [point (i)]. (The sputtering of SiF_x radicals was originally suggested by Mauer *et al.*[27]) Hence a simple model based on physically reasonable assumptions accounts for most of the experimental characteristics of the interaction of silicon with XeF_2. However, a quantitative understanding of the dependence of the chemical-sputtering yield on ion mass, incidence angle, and ion energy is completely lacking. This is to be contrasted with physical sputtering where these yield characteristics are quite well understood.

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