Reactive ion etching of SiC thin films using fluorinated gases

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Reactive ion etching (RIE) using fluorinated gases, such as admixtures of CF_4 with O_2, has been conducted on sputter deposited films of SiC. For comparison purposes, the same experiments with SiO_2 films and Si wafers have been conducted. The influence of rf power, pressure, and O_2 concentration on etch rate in $CF_4 + O_2$, SF_6 + He, and Ar gases has been investigated. RIE mechanisms were studied using *in situ* monitoring of excited fluorine emission intensity and dc self-bias at the lower electrode. Typical etch rates of Si, SiO_2, and SiC are 1220, 600, and 375 Å/min in CF_4 + 4% O_2; 8850, 500, and 560 Å/min in SF_6 + 50% He; and 340, 280, and 270 Å/min in Ar, respectively, at $P = 200$ W, $p = 20$ mTorr, and 300 K. Under these conditions the dc self-bias levels are − 396 V for CF_4 + 4% O_2, − 350 V for SF_6 + 50% He, and − 414 V for Ar. In both CF_4 + 4% O_2 and SF_6 + 50% He, the etch rates of Si, SiO_2, and SiC all increase monotonically with the rf power. However, with increasing pressure the Si etch rate increases while the etch rates of SiO_2 and SiC decrease. Since the dc self-bias varies proportionally with power and inversely with pressure, it is clear that the etching of Si is chemical reaction rate controlled. On the other hand, the etch rate of SiC depends on the ion bombardment energy and is thus dominantly controlled by a physical reaction. The SiC etch rate exhibits a weak dependence on O_2 concentration in $CF_4 + O_2$ mixtures. The dc self-bias is not affected by increasing O_2 concentration, but the SiC etch rate is slightly enhanced. This suggests that a certain etching inhibitor layer exists on the surface of SiC, which can weakly react with the O_2 plasma. Auger electron spectroscopy data indicates that this layer consists of carbon atoms.

I. INTRODUCTION

Silicon carbide (SiC) is a refractory semiconductor material which has various microelectronic applications, e.g., light emitting diodes,[1] high temperature transistors,[2] and dielectric isolation.[3] Due to its chemical inertness the only successful etching of SiC has been at very high temperatures with molten salts [Na_2O_2, NaOH, Na_2CO_3, etc. (500–1000 °C)] or in the gas phase [H_2, Cl_2 (900–1750 °C)],[4] and by sputter etching in Ar gas.[5] At such high temperatures, conventional photoresist masks are not usable. Only Ar sputter etching makes possible the use of photoresist masks, but at a very low etch rate.

The purpose of this study was to investigate the phenomenology and mechanisms of room temperature SiC etching in fluorinated plasmas.

II. EXPERIMENT

The etching experiments have been carried out in a batch-type commercially available parallel plate reactor (Plasma Therm PK1441). The rf power (13.56 MHz) was applied to the bottom electrode ($D = 24.765$ cm) whose temperature was kept at 300 K during all experiments. The dc self-bias V_{dc} of the electrode was also measured. The vacuum system consisted of a rotary pump and a diffusion pump. The base pressure of the system was less than 2.0×10^{-5} Torr. Emission spectra in the wavelength regime between 200 and 800 nm were monitored through a quartz window placed on the sidewall of the chamber.

SiC films were rf sputtered onto oxidized silicon substrates in a planar system (Veeco). The hot-pressed stoichiometric SiC composite target (99.7% purity) was used as a cathode to which the rf power (13.56 MHz, 200 W) was applied. The system was evacuated to a base pressure of less than 2.0×10^{-6} Torr prior to sputtering, and all deposition was performed at room temperature. After deposition, the films were annealed at 1100 °C in H_2 ambient for 30 min. To investigate Si etch rates, *N*-type (0.4–0.6 Ω cm) CZ (100) substrates were used. Oxidized silicon substrates were made in steam at 1100 °C.

To determine the etch rate in various ambients, samples were patterned with positive photoresist (AZ1350J), which was removed after etching for step height determination by profilometer (Dektak). For the analysis of the etching inhibitor layer, Auger electron spectroscopy was used to obtain composition versus depth analyses of both pre- and postplasma etched SiC samples. In these experiments, the following Auger transitions were monitored while sputter etching with a 1-kV Ar ion beam: Si, 92 eV and C, 272 eV.

III. RESULTS

To characterize in detail the etching process of SiC in fluorinated gases, the etch rates were determined as a function of rf power and pressure in both $CF_4 + O_2$ and SF_6 + He, and also percentage of oxygen in $CF_4 + O_2$ mixture.

In Fig. 1, the etch rates versus rf power are shown with the dc self-bias V_{dc} and the intensity of [F] emission (703.7 nm) for CF_4 + 4% O_2, [Figs. 1(a) and 1(b)] and SF_6 + 50% He [Figs. 1(c) and 1(d)] at pressure $p = 20$ mTorr, and total flow $f = 20$ sccm. For both gases, the etch rates of Si, SiO_2, and SiC increase with rf power. The observed V_{dc}, and [F] also increase with rf power in all cases. Generally, the etch rate of Si is found to be higher than those

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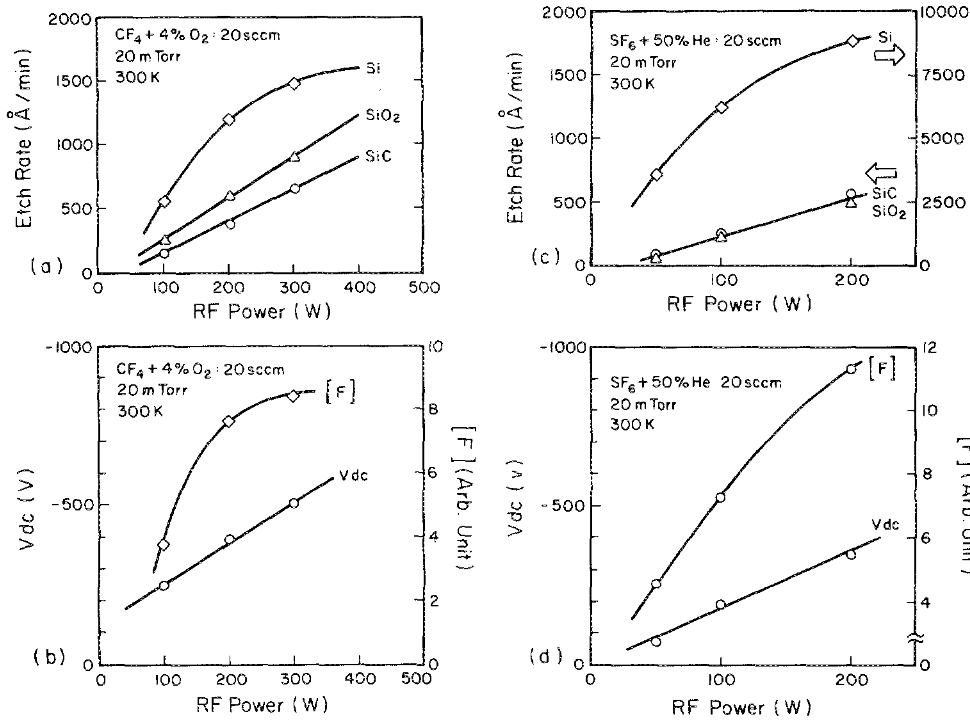


FIG. 1. Etch rates of Si, SiO_2, and SiC (a), (c), dc self-bias V_{dc} and fluorine emission intensity [F] (703.7 nm) (b), (d) as a function of rf power in $CF_4 + 4\%\ O_2$ (left) and $SF_6 + 50\%$ He (right).

of SiO_2 and SiC. The etch rate of Si in $SF_6 + 50\%$ H3, which ranges between 3550 Å/min at 50 W and 8850 Å/min at 200 W, is about six times higher than that in $CF_4 + 4\%\ O_2$, which ranges between 550 Å/min at 100 W and 1480 Å/min at 300 W. The etch rate of SiC in $SF_6 + 50\%$ He, which ranges between 90 Å/min at 50 W and 560 Å/min at 200 W is slightly enhanced (about 50%) over that in $CF_4 + 4\%\ O_2$, where it ranges between 130 Å/min at 100 W and 630 Å/min at 300 W. On the other hand, for SiO_2 both in $SF_6 + 50\%$ He and $CF_4 + 4\%\ O_2$ the etch rates show almost the same values for the same power level. The etch rate of SiO_2 in $SF_6 + 50\%$ He is about the same as that of SiC, while in $CF_4 + 4\%\ O_2$ the former is 40%–90% higher than the latter. In both gases, the etch rate of Si shows some saturation at higher power levels. The same trend is observed in the [F] emission intensity. In contrast, the etch rates of SiO_2 and SiC increase linearly with rf power without any apparent saturation over the range investigated. This linear power dependence is also observed in the dc self-bias.

The dependence of the etch rate [F] and V_{dc} on the pressure is illustrated in Fig. 2 both for $CF_4 + 4\%\ O_2$ [Figs. 2(a) and 2(b)], and for $SF_6 + 50\%$ He [Figs. 2(c) and 2(d)] at

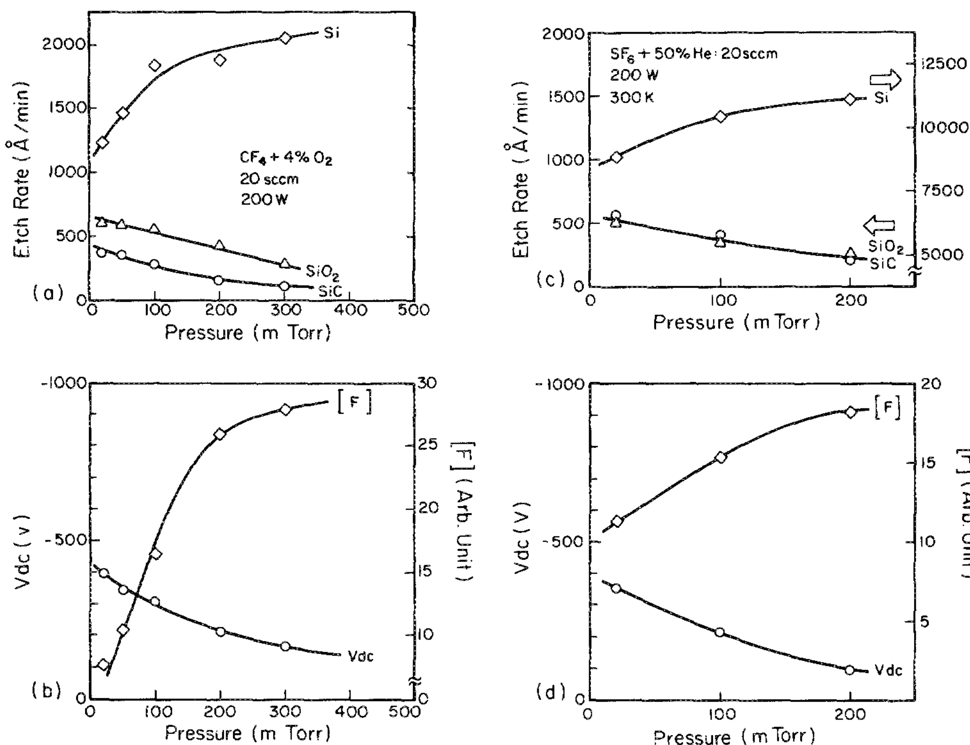


FIG. 2. Etch rates of Si, SiO_2, and SiC (upper), dc self-bias V_{dc} and fluorine emission intensity [F] (703.7 nm) (lower) as a function of ambient pressure in $CF_4 + 4\%\ O_2$ (left) and $SF_6 + 50\%$ He (right).

$P = 200$ W and $f = 20$ sccm. In the pressure ranges presented (20–300 mTorr for $CF_4 + 4\% O_2$, 20–200 mTorr for $SF_6 + 50\%$ He), the etch rate of Si follows the pressure, ranging between 550 and 2070 Å/min in $CF_4 + 4\% O_2$, and between 8850 and 11 000 Å/min in $SF_6 + 50\%$ He. A similar trend is observed in the pressure dependence of [F]. Both [F] and the Si etch rate exhibit saturation behavior at higher pressure. It is interesting to point out that the onset of saturation occurs in $CF_4 + O_2$ at a lower pressure (110 mTorr) for the etch rate than for the fluorine emission (160 mTorr). On the other hand, the etch rates of SiO_2 and SiC, along with V_{dc}, decrease as the pressure increases. The etch rates of SiO_2 and SiC in $CF_4 + 4\% O_2$ range between 280 Å/min at 300 mTorr and 600 Å/min at 20 mTorr, and between 120 and 375 Å/min at the corresponding pressures, respectively. In $SF_6 + 50\%$ He, the etch rates of SiO_2 and SiC vary between 240 Å/min at 200 mTorr and 500 Å/min at 20 mTorr, and between 210 and 560 Å/min, respectively.

Figure 3 depicts the etch rate, V_{dc}, and [F] changes with the percentage of oxygen in $CF_4 + O_2$ gas between 0% and 40% at $P = 200$ W, $p = 20$ mTorr and $f = 20$ sccm. The etch rate of Si shows a strong peak around 10% O_2, while for SiO_2 only a very weak enhancement is observed at about the same O_2 percentage. The maximum etch rates of Si and SiO_2 are 1420 and 600 Å/min, respectively, at 10% oxygen. The minimum etch rates for Si and SiO_2 are 530 Å/min at 40% O_2, and 430 Å/min at 0% O_2, respectively. A similar dependence on O_2 concentration is observed for the fluorine emission [F]. The O_2 concentration for maximum emission coincides with that for Si etch rate. On the other hand, the etch rate of SiC starts from 330 Å/min at 0% oxygen, increases slightly, but monotonically with O_2 percentage increase, up to 470 Å/min at 40% oxygen. Over the same range, the measured V_{dc} is not affected by the oxygen concentration.

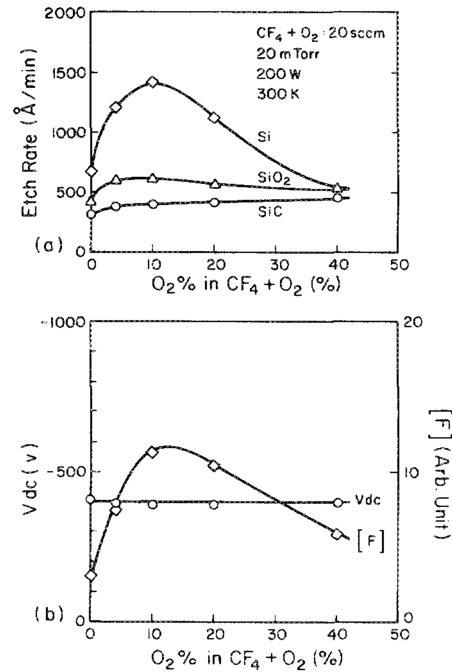


FIG. 3. Etch rates of Si, SiO_2, and SiC (a), dc self-bias V_{dc} and fluorine emission intensity [F] (703.7 nm) (b) as a function of oxygen percentage in $CF_4 + O_2$.

IV. DISCUSSION

While there is a great body of work concerning the etching mechanisms of both Si and SiO_2 in fluorinated plasmas,[6–10] no report has been published to date on the etching mechanism of SiC. In order to develop a SiC etching model in fluorinated plasmas we need to identify the dominant parameters which affect the SiC etching versus Si etching. In

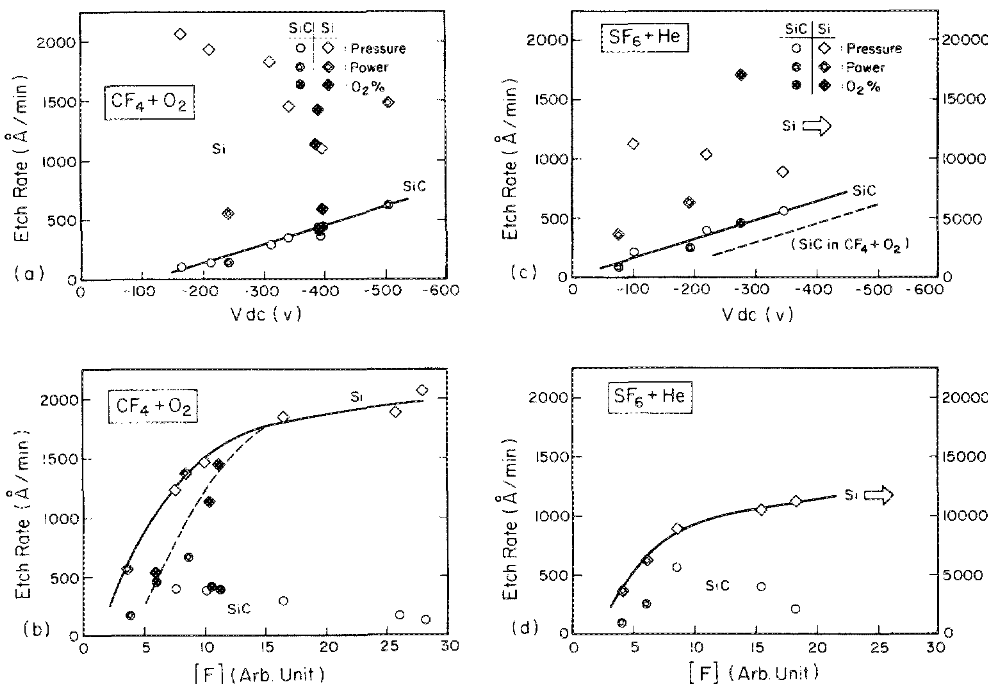


FIG. 4. Etch rates of Si and SiC vs dc self-bias V_{dc} (a), (c) and vs fluorine emission intensity [F] (703.7 nm) (b), (d) in $CF_4 + O_2$ (left) and $SF_6 +$ He (right).

TABLE I. Comparison of etch rates in various gases.

		SF_6 + 50% He	SF_6 + 4% O_2	CF_4 + 4% O_2	CF_4	Ar
Etch rate (Å/min)	SiC	560	470	375	330	270
	Si	8850	17 000	1220	660	340
dc self-bias (V)		−350	−286	−396	−403	−414
[F] intensity (arb. units)		8.6	19.7	7.6	3.1	0

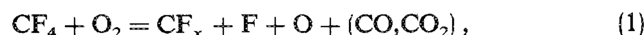
Etching conditions: gas flow $f = 20$ sccm; pressure $p = 20$ mTorr; power $P = 200$ W; temperature $T = 300$ K.

the last part of this section, we will try to verify our model with emission spectroscopy of the plasma and with Auger electron spectroscopy analysis (AES).

The data show that there is some relationship between the etch rate of Si and [F] intensity, and also between the etch rate of SiC and dc self-bias V_{dc}. In Fig. 4, all of the etch rate data that have been previously presented are replotted as etch rate versus V_{dc} and as etch rate versus [F] for both $CF_4 + O_2$ [Figs. 4(a) and 4(b)] and SF_6 + He [Figs. 4(c) and 4(d)]. In both gases the etch rate of SiC increases linearly with V_{dc}, but there is clearly no relationship between Si etch rate and V_{dc}. On the other hand, the etch rate of Si relates to [F], but SiC etch rate does not. In Fig. 4(b), the Si etch rate shows two different relationships (solid and broken lines) at lower [F] levels. Since the three points on the broken line were obtained in higher O_2 percent level in $CF_4 + O_2$, we think that for such conditions the etching mechanism of Si is slightly different than in the other conditions. It should also be noted that the etch rate of SiC in SF_6 + He is about 1.5–2 times higher than that in $CF_4 + O_2$ at the same V_{dc}. From these trends, it is clear that the dominant parameter of SiC etching is V_{dc}, and that of Si etching is [F]. Since V_{dc} represents the ion bombardment energy, and [F] represents the quantity of chemical reactive species in the plasma, we can say that the SiC etching is dominantly controlled by a physical reaction, while the Si etching is controlled by a chemical reaction. It is also evident that the etching of SiC is dependent on a chemical reaction since the SiC etch rate has a weak dependence on O_2 percent in $CF_4 + O_2$ mixtures (Fig. 3). The difference in etch rate between SF_6 + He and $CF_4 + O_2$ may also be due to chemical reactivity differences.

To make clearer these differences, the etch rates of SiC in SF_6 + 50% He, SF_6 + 4% O_2, CF_4 + 4% O_2, CF_4 and Ar under the same conditions ($f = 20$ sccm, $p = 20$ mTorr, $P = 200$ W) are shown and compared in Table I. Also indicated are the Si etch rate, V_{dc} and [F]. The SiC etch rate difference between SF_6 + 50% He and SF_6 + 4% O_2 can be explained by the V_{dc} difference. But there exist significant SiC etch rate differences between Ar, CF_4, CF_4 + 4% O_2, and SF_6 base gases. The difference between Ar and other gases can be easily understood, if we assume the existence of a weak chemical reaction between some active radicals and SiC in the latter gases. Since Ar is inert, the etch rate in Ar is due solely to sputtering. In pure CF_4, the active species should be F radicals because there exist only F and CF_x radicals, and F is known to be more reactive than CF_x.

To understand the etch rate differences between pure CF_4 and CF_4 + 4% O_2, we can make two different assumptions as follows: (1) Oxygen in $CF_4 + O_2$ plasma reacts with SiC, thereby enhancing the etch rate. (2) The increase in F radicals enhances the etch rate. Since the etch rate of SiC increases slightly with increasing O_2 percent (Fig. 3), assumption (1) seems to be true. On the other hand, assumption (2) contradicts the evidence that there is no relation between [F] and the etch rate of SiC. However, the etch rate of SiC in SF_6 is much higher than in CF_4 + 4% O_2. Thus, it is clear that the reaction between F and SiC is slow and is limited by reactions in the gas phase. In order to understand this difference, an understanding of the decomposition and reaction processes occurring in each gas is required. The decomposition processes of $CF_4 + O_2$ and SF_6 base gases are well known and occur as follows:



$$CF_4 + O_2 = CF_x + F + O + (CO, CO_2)\,, \quad (1)$$

$$SF_6 = S + 6F\,, \quad (2)$$

$$SF_6 + O_2 = S + 6F + 2O\,. \quad (3)$$

The reaction process for Si also occurs as follows:

$$Si + 4F = SiF_4\,. \quad (4)$$

Then we propose the carbon reactions as follows:

$$C + xF = CF_x\,, \quad (5)$$

$$C + xO = (CO, CO_2)\,. \quad (6)$$

In $CF_4 + O_2$ both the reaction products and decomposed plasma include the same species such as CF_x and (CO, CO_2), but in SF_6 base gases there are no such species. Since these reactions [Eqs. (1)–(6)] are reversible in the plasma, Eqs. (1), (5), and (6) do not go to completion, and thus the reaction between SiC and $CF_4 + O_2$ should be slow. On the other hand, in SF_6 base gases there exists no such limitation, and the reaction is faster than that in $CF_4 + O_2$. To confirm these reactions, the emission spectra in both CF_4 + 4% O_2 and SF_6 + 50% He are shown in Fig. 5. The upper three plots show the spectra in CF_4 + 4% O_2, and the lower plots are for those in SF_6 + He: without samples [Figs. 5(a) and 5(b)], with Si samples [Figs. 5(b) and 5(c)], and with SiC samples [Figs. 5(c) and 5(f)]. In the case of CF_4 + 4% O_2 [Fig. 5(a)], peaks for CF_2, F, and CO, and also the broad CF_x peak around 200–300 nm are clearly present. With Si or SiC samples only the decrease of F peaks is recognizable. On the other hand, in SF_6 + 50% He CF_x peaks are detected only when SiC samples are present. This evidence shows that carbon in SiC can react with fluorine radicals.

Compounds tend to be etched atomically. For etching to occur, the atomic bond between the elements in the compound must be broken, and then each atom is removed. In

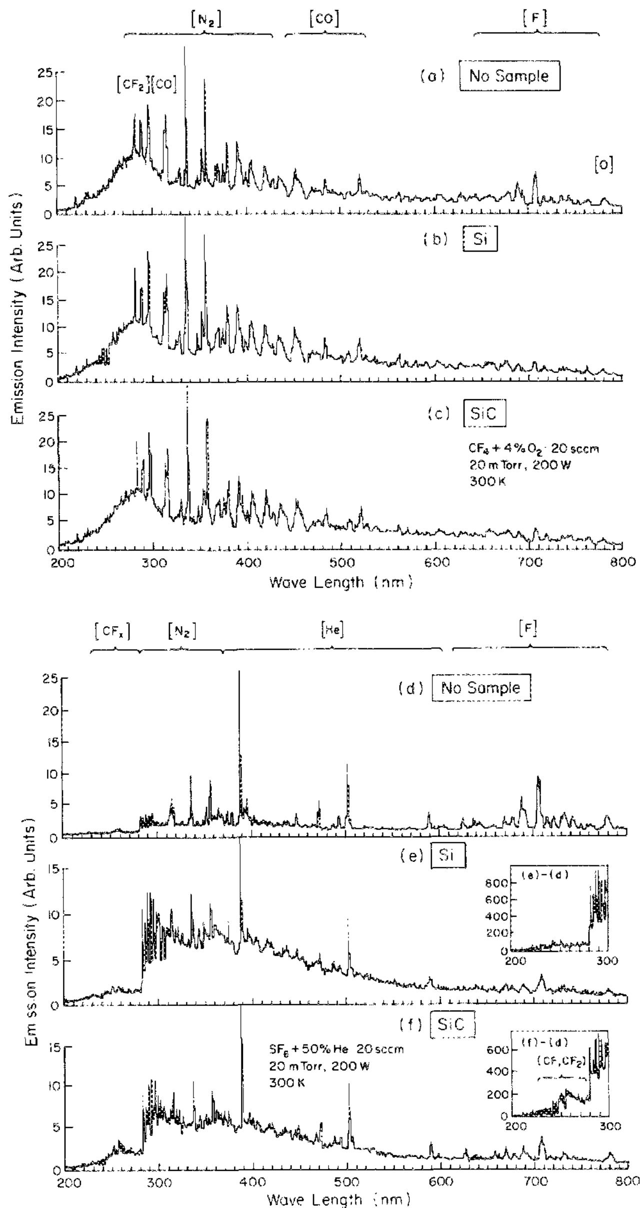


FIG. 5. Plasma emission spectra between 200 and 800 nm in wavelength for $CF_4 + 4\%\ O_2$ (a)–(c) and $SF_6 + 50\%\ O_2$ (d)–(f); without samples (a), (d), with Si samples (b), (e) and with SiC samples (c), (f). The smaller figures in (e) and (f) are the background (d) subtracted spectra between 200 and 300 nm in wavelength.

the case of SiC, this means that we can treat the etching of SiC as the etching of Si and the etching of C. Since the etch rate of Si is much higher than SiC, a carbon-rich surface layer must be formed during etching. Chemically, carbon is removed by Eqs. (5) and (6). During RIE, the SiC film is also subjected to ion bombardment. Sputtering yield data for 500 eV Ar^+ bombardment show that the yield for Si is 0.50 while the yield for C is 0.12.[11] Thus preferential sputtering will also lead to the formation of a carbon-rich surface layer. The existence of this layer has been confirmed by depth profiling using scanning Auger electron spectroscopy (AES). In Fig. 6, the Si and C depth profiles for etched and unetched SiC samples are shown. The profiling conditions were identical

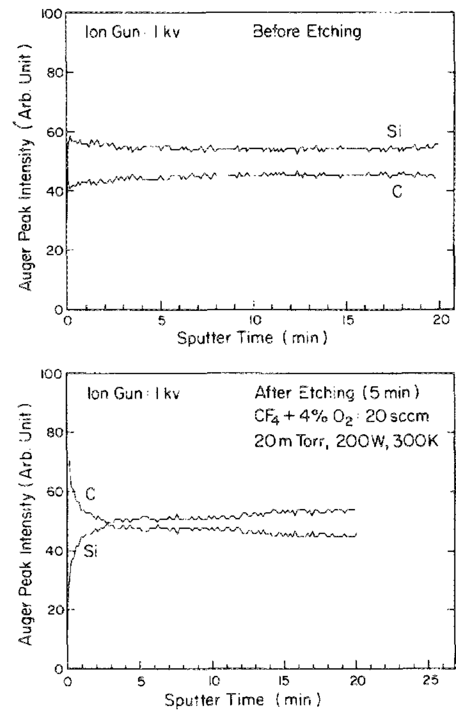


FIG. 6. AES depth profile of SiC before (upper) and after etching (lower).

for both samples. The unetched sample shows no altered surface layer. The increase in the Si/C ratio near the surface is due to the 1100 °C hydrogen anneal. However, the sample partially etched in $CF_4 + 4\%\ O_2$ clearly shows the carbon-rich layer. In this layer, the carbon concentration increases while the silicon concentration decreases as the surface is approached. This indicates that the layer is not due to carbon deposition from the plasma. We believe that this carbon layer, which is due to chemical, as well as physical reactions, is responsible for the low etch rate of SiC with respect to Si.

V. SUMMARY AND CONCLUSION

The reactive ion etching of SiC with fluorinated gases such as $CF_4 + O_2$, pure CF_4, SF_6 + He, and $SF_6 + O_2$ has been investigated. The etching behavior has been compared with Si and thermally grown SiO_2. The dependence of the etch rate on applied power, pressure, and dilution with oxygen has been studied. Measurements of dc self-bias on the rf electrode and the fluorine emission intensity in the plasma showed that the etch rate of SiC is dominantly controlled by the ion bombardment and secondly by a chemical reaction of SiC with fluorine and/or oxygen radicals. AES depth profiles showed that a carbon-rich surface layer is formed during etching. The removal of this layer could be a rate-limiting step for SiC etching.

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