

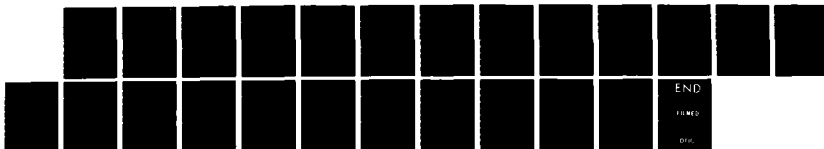
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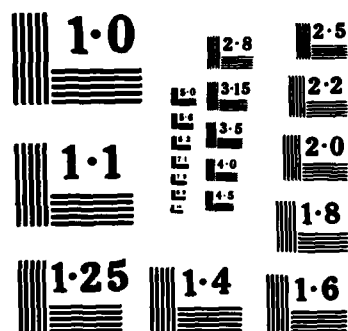
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REACTIVE ION ETCHING OF SiC THIN FILMS
USING FLUORINATED GASES

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ABSTRACT

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 $\text{CF}_4 + \text{O}_2$, $\text{SF}_6 + \text{He}$, 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 $\text{\AA}/\text{min.}$, 600 $\text{\AA}/\text{min.}$, and 375 $\text{\AA}/\text{min.}$ in $\text{CF}_4 + 4\% \text{O}_2$, 8850 $\text{\AA}/\text{min.}$, 500 $\text{\AA}/\text{min.}$, and 560 $\text{\AA}/\text{min.}$ in $\text{SF}_6 + 50\% \text{He}$, and 340 $\text{\AA}/\text{min.}$, 280 $\text{\AA}/\text{min.}$, and 270 $\text{\AA}/\text{min.}$ in Ar, respectively, at $P = 200$ Watts, $p = 20\text{mTorr}$, and 300K. Under these conditions the DC self bias levels are -396 volts for $\text{CF}_4 + 4\% \text{O}_2$, -350 volts for $\text{SF}_6 + 50\% \text{He}$, and -414 volts for Ar. In both $\text{CF}_4 + 4\% \text{O}_2$ and $\text{SF}_6 + 50\% \text{He}$, the etch rates

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of Si, SiO₂, and SiC all increase monotonously with the RF power. However, with increasing pressure the Si etch rate increases while the etch rates of SiO₂ 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 O₂ concentration in CF₄ + O₂ mixture. The DC self bias is not affected by increasing O₂ 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 O₂ plasma. Auger electron spectroscopy data indicates that this layer consists of carbon atoms.

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1. 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. ($500\text{--}1000^\circ\text{C}$)) or in the gas phase (H_2 , Cl_2 ($900\text{--}1750^\circ\text{C}$)) [4], and by sputter etching in Ar gas [5]. At such high temperatures, conventional photo-resist masks are not usable. Only Ar sputter etching makes possible the use of photo-resist 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.

2. 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 ($D = 24.765\text{ cm}$) whose temperature was kept at 300K 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 $2.0 \times 10^{-5}\text{ Torr}$. Emission spectra in the wavelength regime between 200 and 800nm were monitored through a quartz window placed

on the side wall 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, 200W) 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 H₂ ambient for 30 min. To investigate Si etch rates, N-type (0.4-0.6 ohm-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 combined with ion beam etching was used to obtain composition versus depth analyses of both pre- and post-etched SiC samples. In these experiments, the following Auger transitions were monitored while sputter etching with a 1-KV Ar ion beam: Si 92eV and C 272eV.

3. 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 ambient pressure in both $\text{CF}_4 + \text{O}_2$ and $\text{SF}_6 + \text{He}$, and also percentage of oxygen in $\text{CF}_4 + \text{O}_2$ mixture.

In Figure 1, the etch rates versus RF power are shown with the DC self bias, V_{dc} , and the intensity of [F] emission (703.7nm) for $\text{CF}_4 + 4\% \text{O}_2$ (a, b) and $\text{SF}_6 + 50\% \text{He}$ (c, d) at pressure $p = 20\text{mTorr}$, and total flow $f = 20 \text{ sccm}$. 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 of SiO_2 and SiC. The etch rate of Si in $\text{SF}_6 + 50\% \text{He}$, which ranges between $3550 \text{ \AA}/\text{min.}$ at 50W and $8850 \text{ \AA}/\text{min.}$ at 200W, is about ten times higher than that in $\text{CF}_4 + 4\% \text{O}_2$, which ranges between $550 \text{ \AA}/\text{min.}$ at 100W and $1480 \text{ \AA}/\text{min.}$ at 300W. The etch rate of SiC in $\text{SF}_6 + 50\% \text{He}$, which ranges between $90 \text{ \AA}/\text{min.}$ at 50W and $560 \text{ \AA}/\text{min.}$ at 200W is slightly enhanced (about 50%) over than in $\text{CF}_4 + 4\% \text{O}_2$, where it ranges between $130 \text{ \AA}/\text{min.}$ at 100 W and $630 \text{ \AA}/\text{min.}$ at 300W. On the other hand, for SiO_2 both in $\text{SF}_6 + 50\% \text{He}$ and $\text{CF}_4 + 4\% \text{O}_2$ the etch rates show almost the same values for the same power level. Therefore, in $\text{SF}_6 + 50\% \text{He}$, the etch rate of SiO_2 is about the same as that of SiC, while in $\text{CF}_4 + 4\% \text{O}_2$ 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 ambient pressure is illustrated in Figure 2 both for $CF_4 + 4\% O_2$ (a, b), and for $SF_6 + 50\% He$ (c, d) at $P = 200W$ and $f = 20$ sccm. In the pressure ranges presented (20-300mTorr for $CF_4 + 4\% O_2$, 20-200mTorr for $SF_6 + 50\% He$), the etch rate of Si follows the pressure, ranging between $550 \text{ \AA}/\text{min.}$ and $2070 \text{ \AA}/\text{min.}$ in $CF_4 + 4\% O_2$, and between $8850 \text{ \AA}/\text{min.}$ and $11000 \text{ \AA}/\text{min.}$ 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 (110mTorr) for the etch rate than for the fluorine emission (160mTorr). 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 $280 \text{ \AA}/\text{min.}$ at 300mTorr and $600 \text{ \AA}/\text{min.}$ at 20mTorr, and between $120 \text{ \AA}/\text{min.}$ and $375 \text{ \AA}/\text{min.}$ at the corresponding pressures, respectively. In $SF_6 + 50\% He$, the etch rates of SiO_2 and SiC vary between $240 \text{ \AA}/\text{min.}$ at 200mTorr and $500 \text{ \AA}/\text{min.}$ at 20mTorr, and between $210 \text{ \AA}/\text{min.}$ and $560 \text{ \AA}/\text{min.}$, 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 $P = 200\text{W}$, $p = 20\text{mTorr}$ and $f = 20\text{ sccm}$. 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 $1420\text{ \AA}/\text{min.}$, and $600\text{ \AA}/\text{min.}$, respectively, at 10% oxygen. The minimum etch rates for Si and SiO_2 are $530\text{ \AA}/\text{min.}$ at 40% O_2 , and $430\text{ \AA}/\text{min.}$ 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 $330\text{ \AA}/\text{min.}$ at 0% oxygen, increases slightly, but monotonously with $\text{O}_2\%$ increase, up to $470\text{ \AA}/\text{min.}$ at 40% oxygen. On the same range, the measured V_{dc} is not affected by the oxygen concentration.

4. 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 to the SiC etching versus Si etching. In 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).

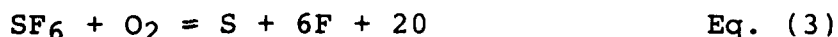
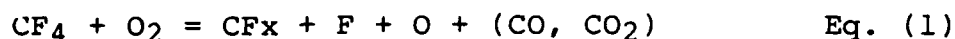
The data shows that there is some relationship between the etch rate of Si and [F] intensity, and also between the etch rate of SiC and DC self bias Vdc. In Figure 4, all of the etch rate data that has been previously presented are replotted as etch rate versus Vdc and as etch rate versus [F] for both CF₄ + O₂ (a, b) and SF₆ + He (c, d). In both gases the etch rate of SiC increases linearly with Vdc, but there is clearly no relationship between Si etch rate and Vdc. On the other hand, the etch rate of Si relates to [F], but SiC etch rate is not. In Figure 4(b), Si etch rate shows two different relationships (solid and broken lines) in lower [F] level. Since the three points on the broken line were obtained in higher O₂% level in CF₄ + O₂, we think that for such conditions etching mechanism of Si is slightly different than in the other conditions. It should also be noted that the etch rate of SiC in SF₆ + He is about 1.5 to 2 times higher than that in CF₄ + O₂ at the same Vdc. From these trends, it is clear that the dominant parameter of SiC etching is Vdc, and that of Si etching is [F]. Since Vdc 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 O₂%

in $\text{CF}_4 + \text{O}_2$ mixtures (Figure 3). The difference in etch rate between $\text{SF}_6 + \text{He}$ and $\text{CF}_4 + \text{O}_2$ may also be due to chemical reactivity differences.

To make clearer these differences, the etch rates of SiC in $\text{SF}_6 + 50\% \text{He}$, $\text{SF}_6 + 4\% \text{O}_2$, $\text{CF}_4 + 4\% \text{O}_2$, CF_4 and Ar under the same conditions ($f = 20 \text{ sccm}$, $p = 20 \text{mTorr}$, $P = 200 \text{W}$) are shown and compared in Table 1. Also indicated are the Si etch rate, V_{dc} and $[F]$. The SiC etch rate difference between $\text{SF}_6 + 50\% \text{He}$ and $\text{SF}_6 + 4\% \text{O}_2$ can be explained by the V_{dc} difference. But there exists significant SiC etch rate differences between Ar, CF_4 , $\text{CF}_4 + 4\% \text{O}_2$, 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 exists 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 $\text{CF}_4 + 4\% \text{O}_2$, we can make two different assumptions as follows: (1) Oxygen in $\text{CF}_4 + \text{O}_2$ plasma reacts with SiC, thereby enhancing the etch rate. (2) The increase of F radicals enhances the etch rate. Since the etch rate of SiC increases slightly with increasing $\text{O}_2\%$ (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 SF₆ is much higher than in CF₄ + 4% O₂. 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 CF₄ + O₂ and SF₆ base gases are well known and occur as follows:



And the reaction process for Si also occurs as follows:



Then we propose the carbon reactions as follows:



In CF₄ + O₂ both the reaction products and decomposed plasma include the same species such as CF_x and (CO, CO₂), but in SF₆ base gases there are no such species. Since these reactions (Eq. (1) to (6)) are reversible in the plasma, Eq. (1), Eq. (5), and Eq. (6) do not go to completion, and thus the reaction

between SiC and $\text{CF}_4 + \text{O}_2$ 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 $\text{CF}_4 + \text{O}_2$. To confirm these reactions, the emission spectra in both $\text{CF}_4 + 4\% \text{O}_2$ and $\text{SF}_6 + 50\% \text{He}$ are shown in Figure 5. The upper three show the spectra in $\text{CF}_4 + 4\% \text{O}_2$, and the lower are for those in $\text{SF}_6 + \text{He}$: without samples (a, d), with Si samples (b, e), and with SiC samples (c, f). In the case of $\text{CF}_4 + 4\% \text{O}_2$ (Fig. 5a), peaks for CF_2 , F and CO, and also the broad CF_x peak around 200nm - 300nm are clearly present. And with Si or SiC samples only the decrease of F peaks is recognizable. On the other hand, in $\text{SF}_6 + 50\% \text{He}$ 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 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, and thus C, a carbon-rich surface layer must be formed during etching. Chemically, carbon is removed by Eq. (5) and Eq. (6). During RIE, the SiC film is also subjected to ion bombardment. Sputtering yield data for 500eV Ar^+ bombardment show that the yield for Si is 0.50 while 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 Figure 6, the Si and C depth profiles for etched and unetched SiC samples are shown. The profiling conditions were identical for both samples. The unetched sample shows no altered surface layer. However, the sample partially etched in $\text{CF}_4 + 4\% \text{O}_2$ clearly shows the carbon-rich layer. 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.

5. SUMMARY AND CONCLUSION

The reactive ion etching of SiC with fluorinated gases such as $\text{CF}_4 + \text{O}_2$, pure CF_4 , $\text{SF}_6 + \text{He}$, and $\text{SF}_6 + \text{O}_2$ 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, ambient 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.

ACKNOWLEDGEMENTS

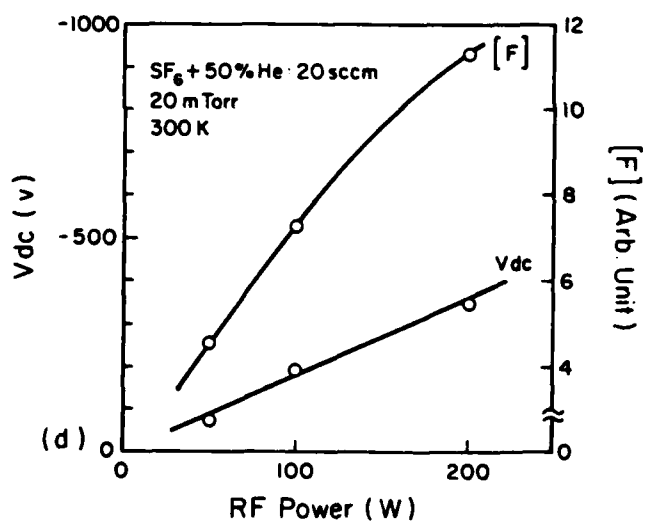
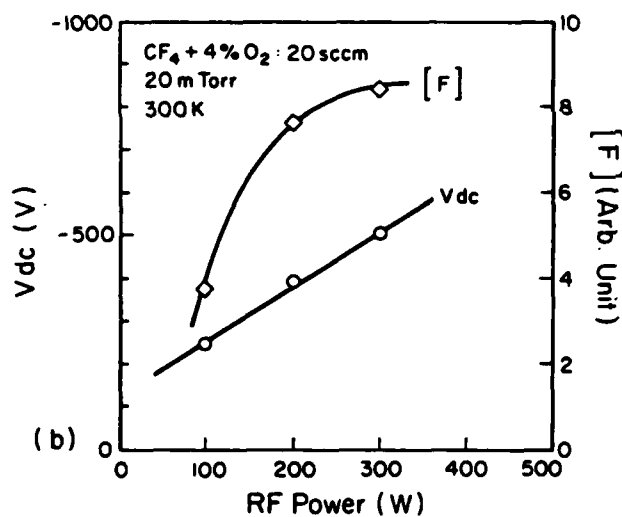
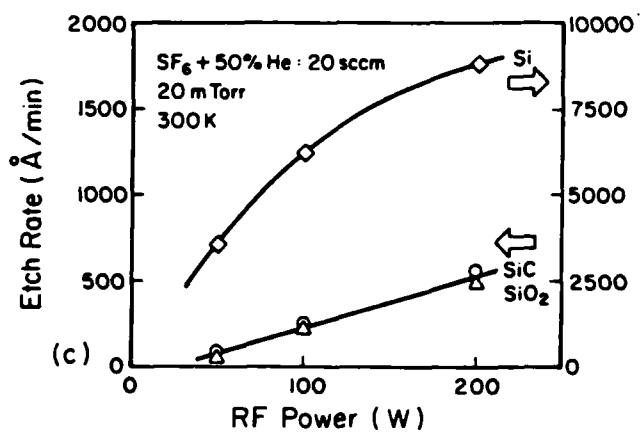
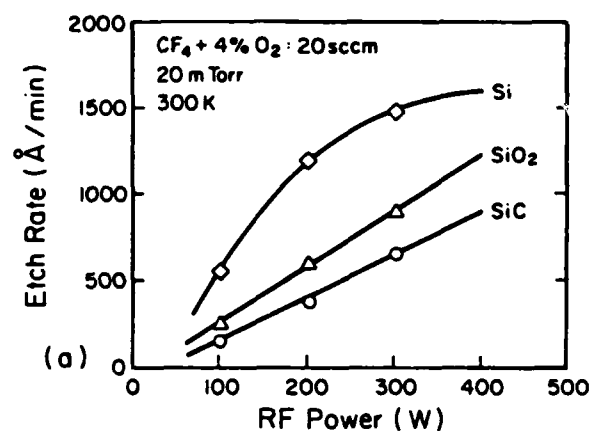
The authors would like to thank Dr. T. Paul Chow for his helpful discussions. J. S. wishes to thank Hitach Ltd. for financial aid. W.-J. L., K. C. C., and A. J. S would also like to acknowledge partial support from the Office of Naval Research under Contract No. N00014-81-K-0605.

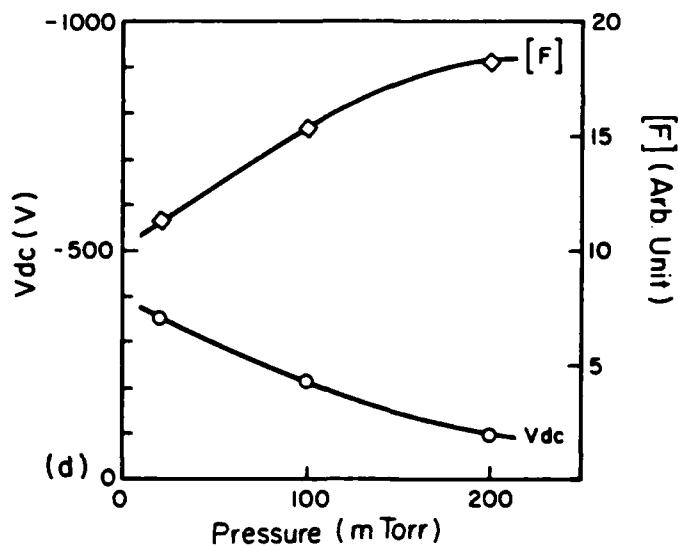
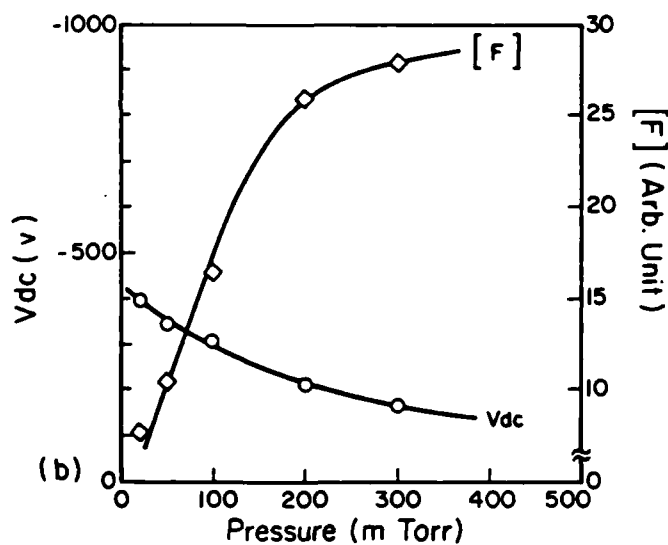
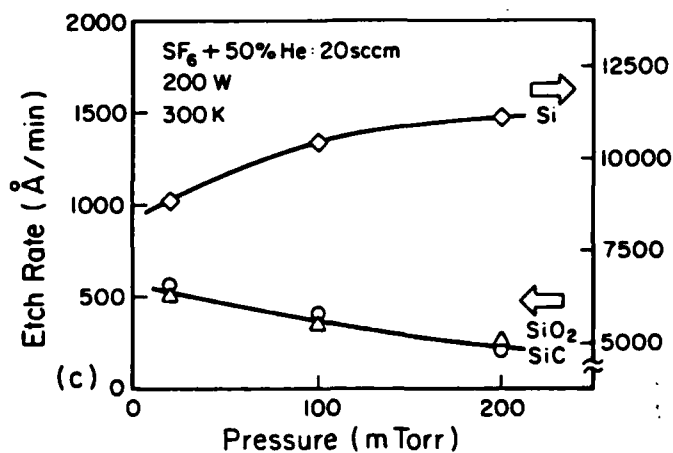
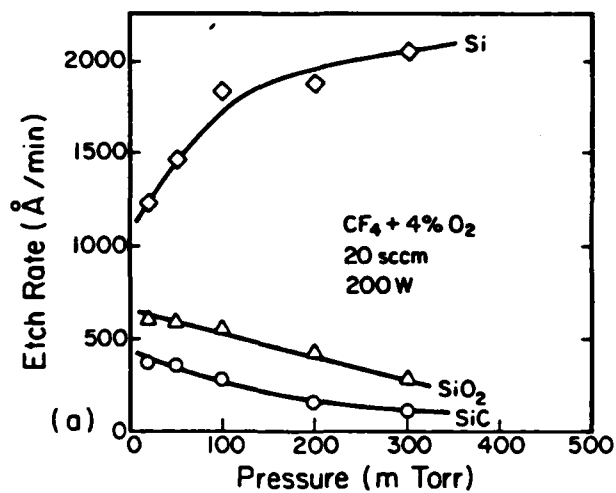
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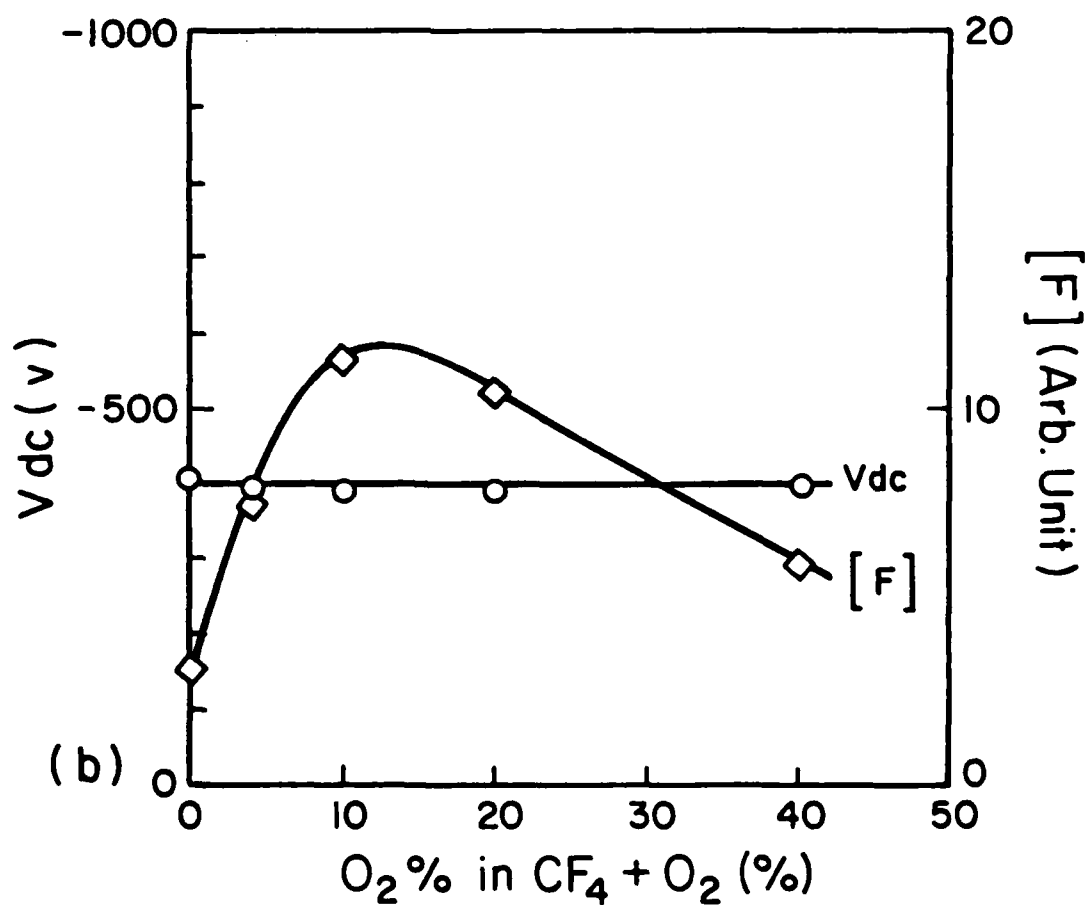
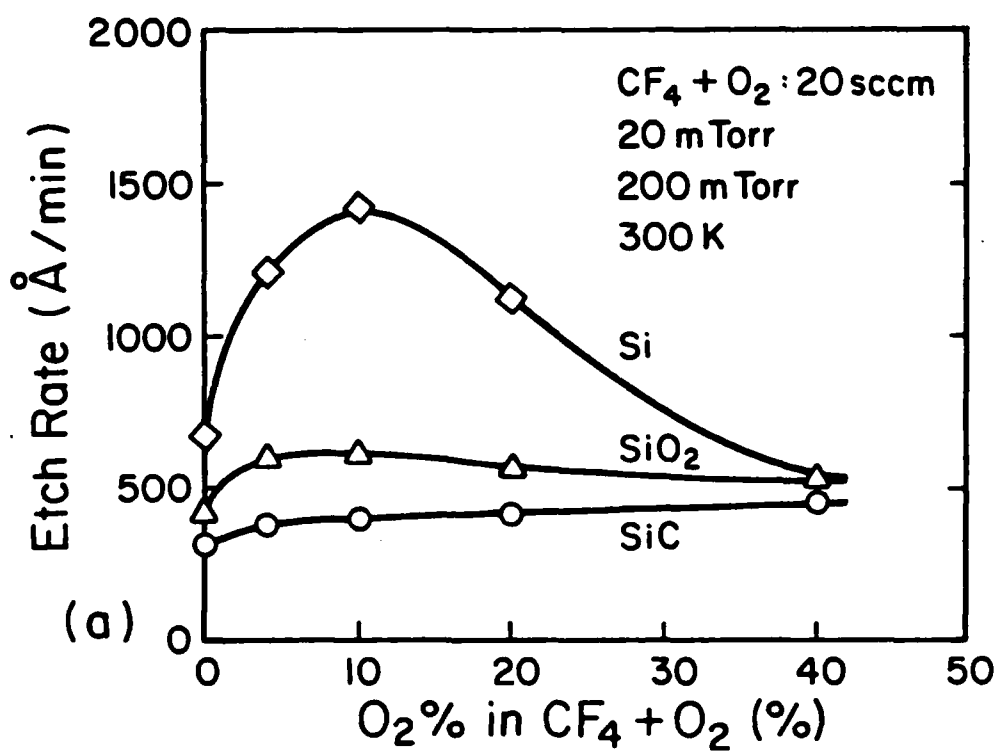
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- Figure 1. Etch rates of Si, SiO₂ and SiC (a, c), DC self bias V_{dc} and fluorine emission intensity [F] (703.7nm) (b, d) as a function of RF power in CF₄ + 4% O₂ (left) and SF₆ + 50% He (right).
- Figure 2. Etch rates of Si, SiO₂ and SiC (upper), DC self bias V_{dc} and fluorine emission intensity [F] (703.7nm) (lower) as a function of ambient pressure in CF₄ + 4% O₂ (left) and SF₆ + 50% He (right).
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- Figure 5. Plasma emission spectra between 200nm and 800nm in wave-length for CF₄ + 4% O₂ (a, b, c) and SF₆ + 50% O₂ (d, e, 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 200nm and 300nm in wave-length.
- Figure 6. Auger electron spectroscopy depth profile of initial SiC (upper) and after partially etched one (lower).







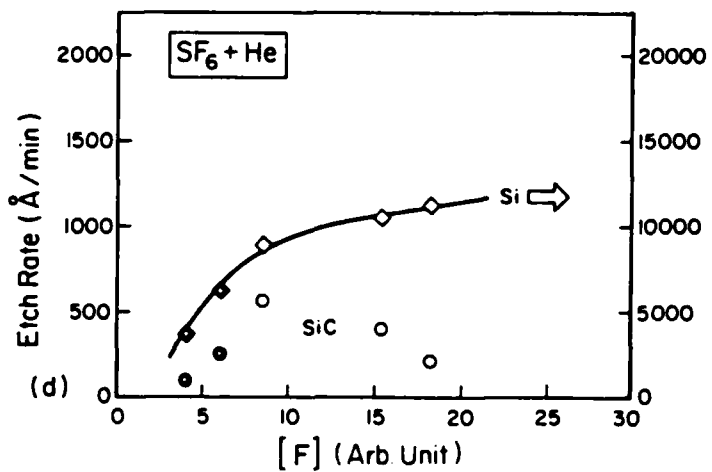
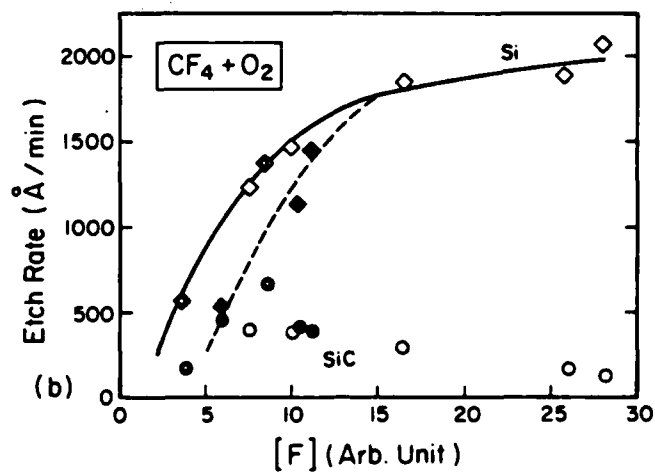
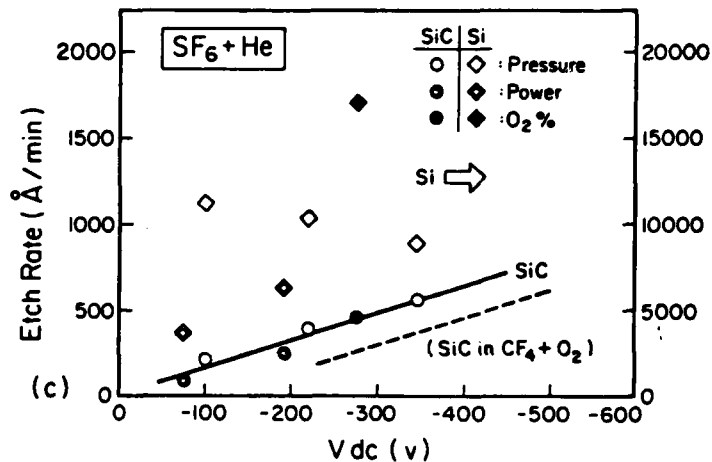
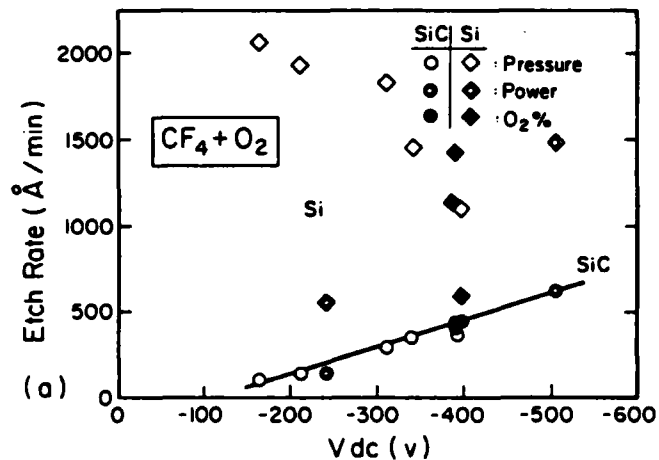
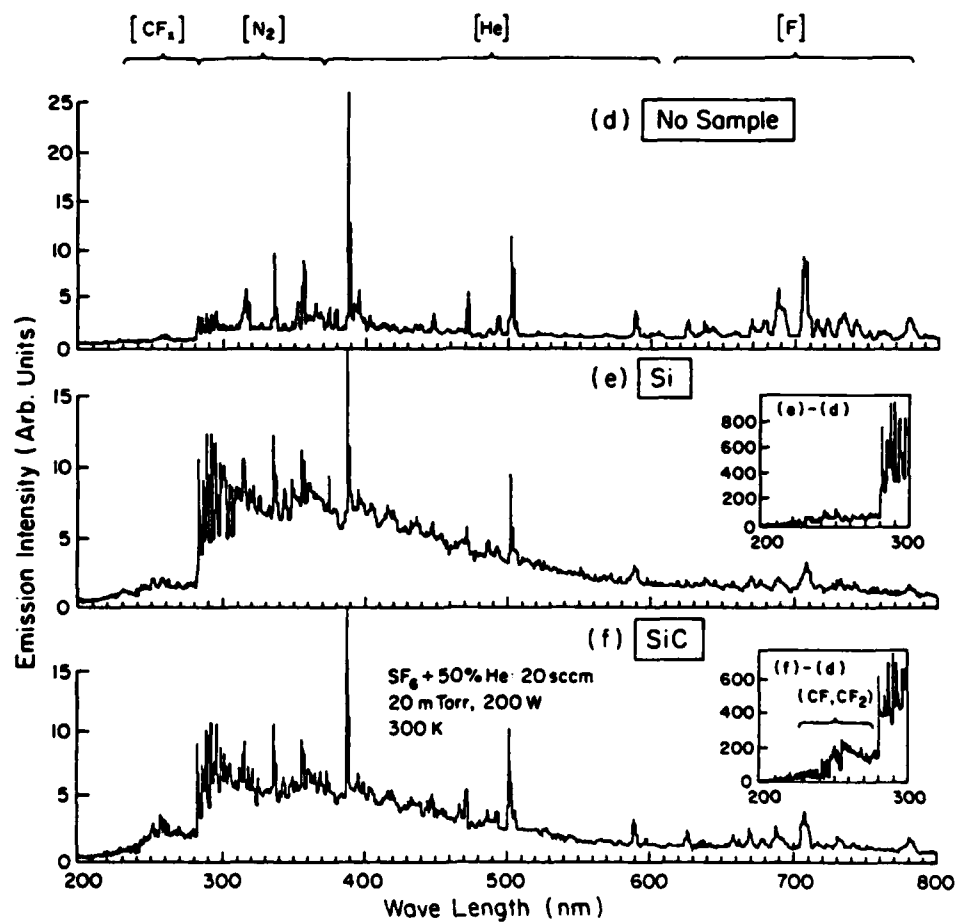
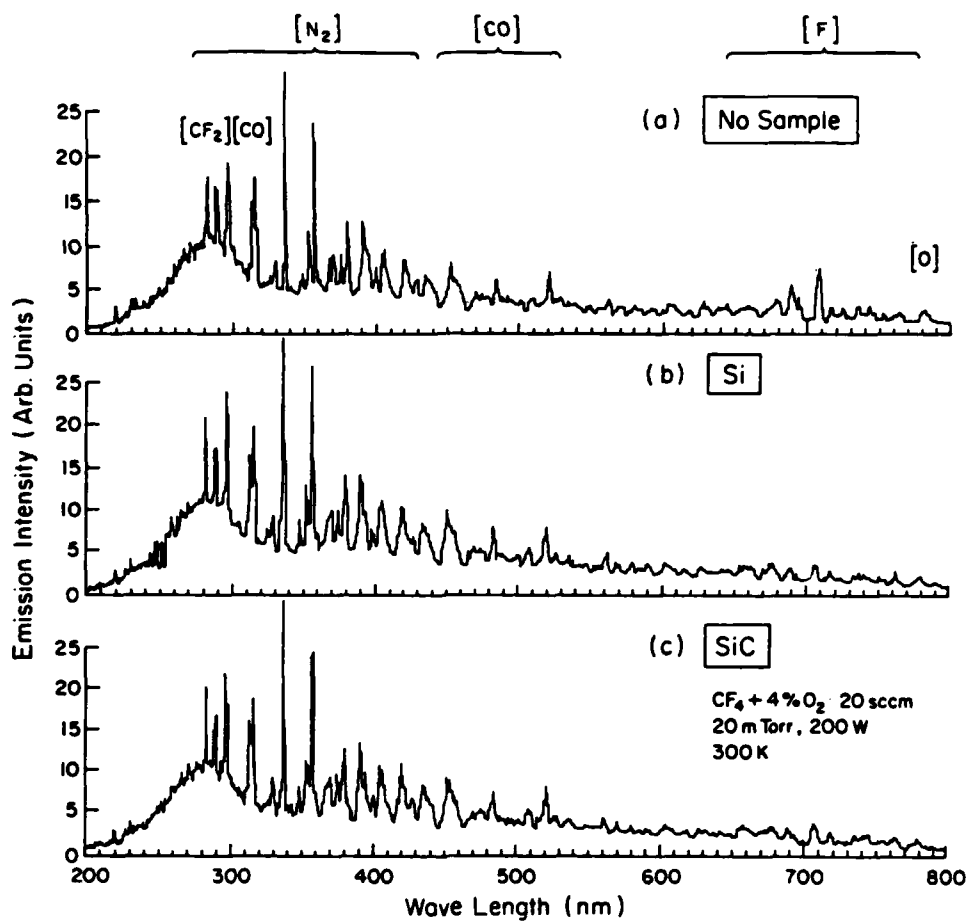
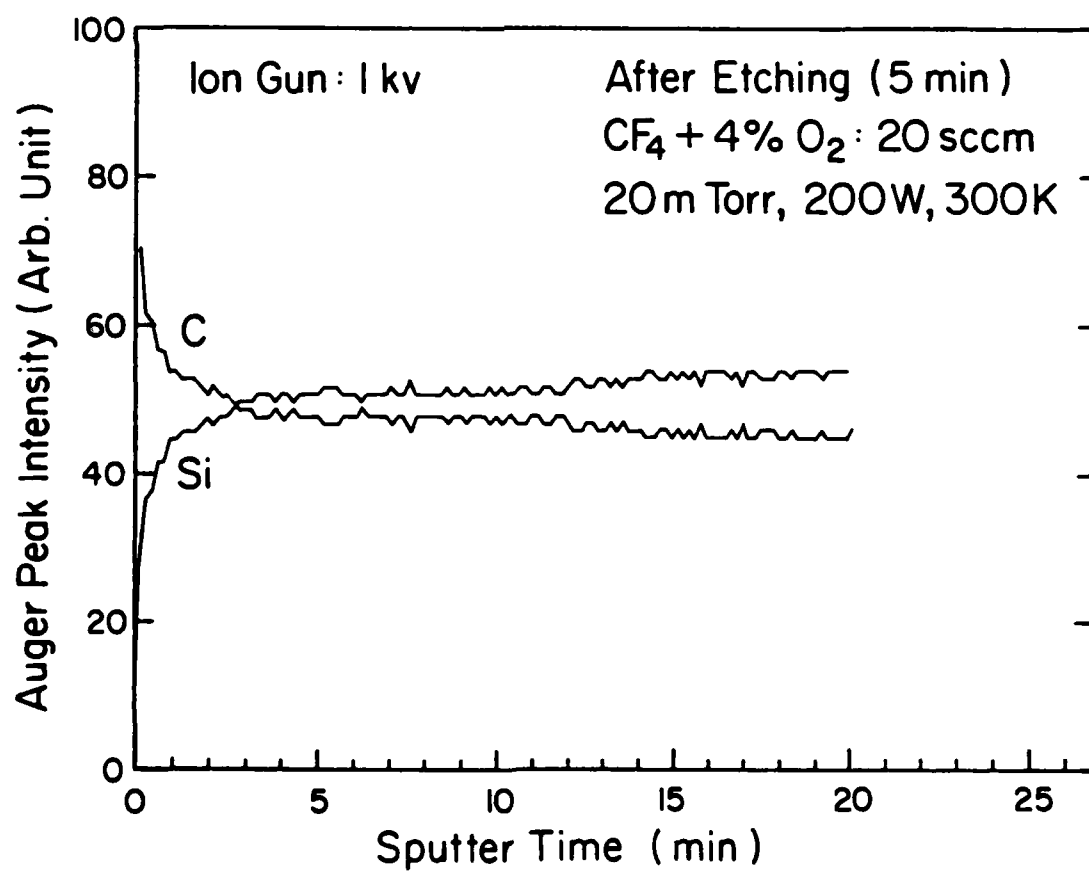
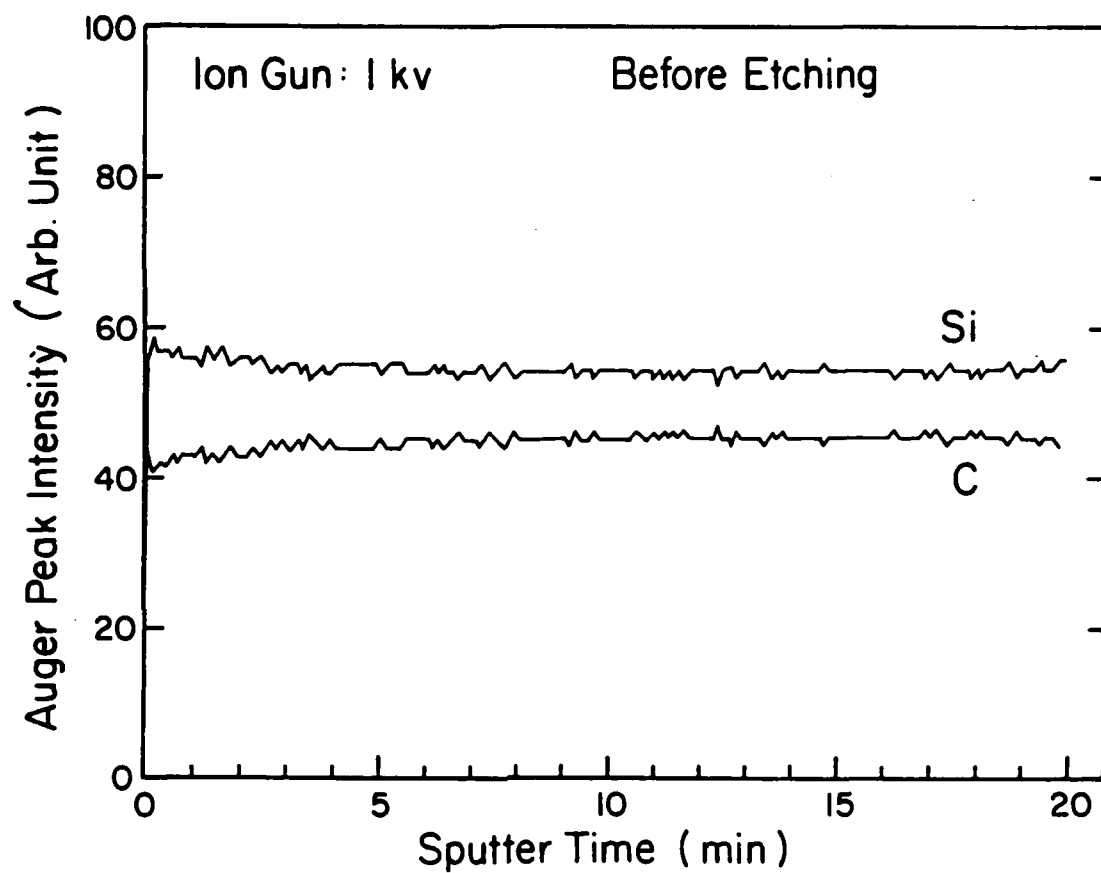


Table 1. Comparison of Etch Rates in Various Gases

		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	17000	1220	660	340
DC Self Bias (V)		-350	-286	-396	-403	-414
[F] Intensity (A.U.)		8.6	19.7	7.6	3.1	0

Etching Conditions: Gas Flow $f = 20$ sccm
 Pressure $p = 20$ m Torr
 Power $P = 200$ W
 Temperature $T = 300$ K





END

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