PLASMA ETCHING OF Si BY SF_6, CF_4, AND SF_6/H_2 AND CF_4/H_2 MIXTURES

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ABSTRACT

Silicon chips were etched in D.C. glow discharges in SF_6, CF_4 and in their mixtures. Steady state mass spectrometric signals were measured as a function of the power input. At higher powers, subsequent exposure of the Si to H_2 discharges led to the release of copious amounts of SiF_4 and H_2O. Auger analysis showed S, O and F but no surface Si. CF_4 studied under comparable conditions was found to be far less reactive toward Si.

1. INTRODUCTION

Reactive ion etching of Si in a CF_4 plasma has been studied by many authors (1,2), and recognizing the complexity of this process one should certainly seek to determine the way the overall etch rate and the composition of the plasma depend on several independent parameters, if one wishes to improve our understanding of the individual processes involved.

The present study concentrates on a comparison of the SF_6/Si and CF_4/Si systems, both being studied under similar conditions. Since CF_4 is known to lead to rather tenacious C deposits on Si, it seems very interesting to determine whether any S containing surface layers are formed during SF_6 etching which would perhaps be much more volatile and thus far less detrimental to the etching process. If this is so, one might further expect SF_6 to show little selectivity when comparing the etch rates of SiO_2 and Si. In addition to comparing these chemical systems, the input power constituted another important independent variable in this work, since early exploratory experiments had shown that the relative amounts of long lived species present in such plasmas strongly depend on the input power levels used.

2. EXPERIMENTAL

The discharge vessel consisted of Pyrex tubing, 25mm I.D. and 32cm long, at one end closed by a large tapered joint cap with various electric feedthroughs. The other end of this tube was closed by a flat window with a 0.50mm aperture in its center. This opening led to a differentially pumped region and thence, via a second aperture of 1.59mm I.D., straight to the point of intersection with the electron beam of the ion source of a mass spectrometer.

The medium resolution instrument used was a Hitachi Model RMU-6E with variable entrance and exit slits and electron multiplier detector.

Two parallel stainless steel plate electrodes of $2cm^2$ area were mounted approximately 5mm from the first aperture and 1.0cm apart.

Typical pressures in the plasma cell were 0.110 Torr, in the differentially pumped region $1.6x10^{-5}$ Torr, and in the mass spectrometer $2x10^{-6}$ Torr. The path length from the first aperture to the electron beam was about 7.0cm.

Using several needle valves, the etchant gas was admitted to the plasma vessel at a constant low rate of 0.02sccm, as measured by a Hastings Model ALL-5 flow meter, using the published corrections applicable to each etchant gas, or gas mixture. The discharge cell and electrode surfaces were cleaned before each series of experiments, using dilute HCl and Ar discharges.

Samples to be etched were centered on the lower electrode which was in most cases the cathode. The polycrystalline silicon samples were 99.999% pure, as obtained from the Apache Chemical Company. Etchant gases came from the Linde Division of Union Carbide and were of the following purities: SF_6 - 99.9 mole %; CF_4 - 99.7 mole %; H_2 - 99.95 mole %.

After the SF_6, CF_4, or H_2 mixture plasma treatments, Ar and H_2 discharges were used in order to remove various products which might have been deposited on the sample surface during the etching experiments.

The mass spectrometric signals were corrected for minor instrumental variations, using several internal standards which were known to be unaffected by the plasma chemical changes.

3. RESULTS

Figure 1 shows the results of a series of blank experiments using SF_6, and Figure 2 the corresponding results for the SF_6/Si etching experiments. A slight change of the mass spectrometer sensitivity which occurred between both series of experiments was obvious when comparing the SF_6 cracking patterns at zero power input, that is the points on the ordinates of both figures. All data of Figure 1 were corrected for this shift.

Practically all the ionic species detected mass spectrometrically were created from neutrals effusing from the plasma cell, with only extremely small contributions from ions formed in the plasma.

To demonstrate more clearly the effect of the SF_6 plasma upon the Si sample, the results of Figure 1 were subtracted from those of Figure 2, and the differences plotted in Figure 3.

The SiF_3^+ signals from SiF_4 which resulted from the etching of the internal Pyrex surfaces were at least 20 times smaller than the SiF_3^+ signals coming from the Si sample. For all power inputs, the steady state SiF_4 cracking patterns were constant.

The SOF_2^+ peaks, which contain oxygen originating from the internal walls also are unimportant compared to the SiF_3^+ signals related to the sample. SOF^+ and SO^+ signals were also measured but were not presented in these figures because they are proportional to the SOF_2^+ peaks and can therefore be considered part of the same cracking pattern.

By contrast, the $S_2F_2^+$ peaks (and the related S_2F^+ signals which are not shown) are probably formed from SF_6 fragments, and constitute the only important by-product from that gas.

The electrode on which the sample was placed was negative with respect to the other electrode for all data presented above. For this polarity, etching was always distinctly faster than for the reverse polarity, especially at higher input power levels.

The CF_4/Si etching and CF_4 blank results analogous to the SF_6/Si and SF_6 blank data were obtained under identical conditions but are not presented in detail because they are consistent with results previously published by others. It was observed, however, that the CF_4 etching rates were far lower than those of SF_6, leading to a much more pronounced wall effect in the present apparatus. Also large quantities of oligomers were formed, that is C_2F_6, C_2F_4, and C_3F_6, in that order. Low etching rates of Si under low CF_4 flow rates have been observed in the literature (3).

The plasma cell pressure was observed to drop right after the discharge was established, it went through a minimum and then increased beyond its initial value, both in SF_6 and CF_4 experiments. This led to a few additional, exploratory experiments which will be mentioned below, in the Discussion.

4. DISCUSSION

The mass spectrometric cracking pattern of SF_6 as obtained in this work can be read from the points on the ordinates of Figures 1 and 2. The principal peak of SF_6, that is SF_5^+, drastically decreased with increasing power density, in the blank experiment, showing that SF_6 is readily dissociated (Figure 1). When the sample is present, the SF_6 is consumed at an even faster rate, especially at low input power, resulting in a deep minimum in the difference plot (Figure 3).

It was recognized very early that at least part of the SF_x^+ signals (x=1 to 5) must be due to the fragmentation of SF_6 in the mass spectrometer ion source, while another major contribution originated from the SF_x radicals (x=1 to 5) travelling from the plasma into the ion source. To obtain a closer estimate of this latter contribution to the SF_x^+ signal (x=1 to 4), it was assumed that all the SF_5^+ seen in the mass spectra could be ascribed to SF_6 molecules reaching the ion source, and the SF_x^+ signals (x=1 to 4) were corrected for these contributions.

Next, the cracking pattern corrected peaks (4) were used again to calculate corrected difference curves, shown as dashed curves in Figure 3, except for the SF_4^+ differences, which were extremely low. The SF_3^+, SF_2^+, and SF^+ difference signals, when corrected in this fashion, are seen to peak at successively higher power levels but it must be added that the reaction steps responsible for the increase of several species at even higher input powers can not as yet be characterized, from the present data.

$S_2F_2^+$, the most important by-product in these experiments, peaks at a much higher input power than SF^+, indicating that the supply of SF^+, a possible precursor of S_2F_2 is not the only important factor. Either the consumption of S_2F_2 varies greatly with input power, or other precursors are to be considered.

As mentioned above, it seemed as if some plasma generated species might be depositing on the sample surface. To explore this, it was attempted to clean the etched samples by Ar, O_2, and H_2 discharges. Ar and O_2 plasma treatments produced only small amounts of released gases, but the H_2 plasma produced large amounts of SiF_3^+ and H_2O^+, plus some H_2S. Auger spectra showed large amounts of S, O, and F to be present in the surface, but no Si, before or after the H_2 plasma treatment.

One might ask whether the efficient etching by SF_6 can occur simultaneously with the improved release of SiF_4 as induced by H_2, but the etching rate of SF_6/H_2 mixtures was found to be lower than what corresponded to the SF_6 mole fraction. One can thus conclude that the scavenging effect of H_2 is far more detrimental than its facilitating of the SiF_4 release. The production of HF was correspondingly high in these mixture experiments.

Returning briefly to the CF_4/Si results, it was found that the C_2 and C_3 fluorinated species formed, very much obliterated the CF_3^+, CF_2^+, and CF^+ peaks present, preventing the analysis of possible trends analogous to those found for the SF_x^+ species (x=1 to 3).

REFERENCES

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(3) B. N. Chapman, V. J. Minkiewicz, J. Vac. Sci. Technol., 15, 329 (1978).

(4) The cracking pattern corrected curves are not shown in Figures 1 and 2, for the sake of clarity, but copies of these drawings can be obtained by writing to the author.

Discharge Cell Pressure - 91 mtorr SF_6

SF_6 Flow Rate - 0.02 sccm

Figure 1

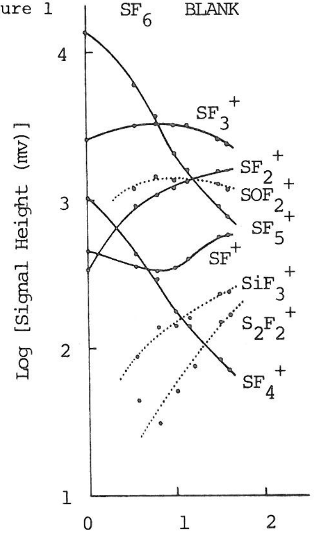


Figure 2

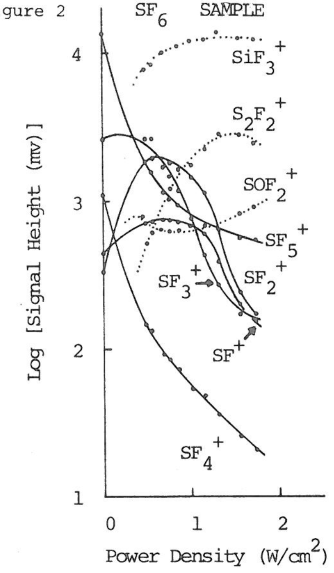
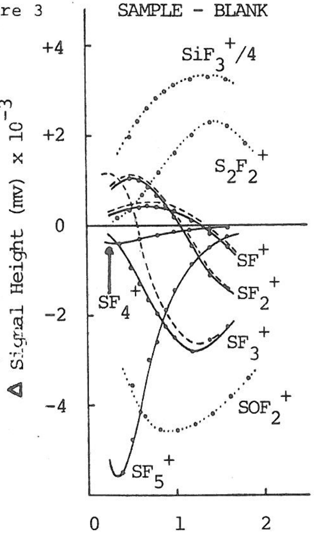


Figure 3



Figures 1 and 2 - Log Mass Spectrometer Signal Height vs. Power Density for SF_6 Blank (Fig. 1) and SF_6/Si (Fig. 2) Experiments.

Figure 3 - Δ Mass Spectrometer Signal Height vs. Power Density for Sample (Fig. 2) - Blank (Fig. 1). Dashed curves show the cracking pattern corrections for the SF_x fragments (see text).