PLASMA ETCHING OF Si BY CF_4: STEADY STATE AND TRANSIENT STUDIES OF PLASMA CONSTITUENTS

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ABSTRACT

Si wafers have been etched in a d.c. plasma under CF_4, and the plasma constituents were studied mass spectrometrically. The half-times of transient responses resulting from small stepwise changes of the applied voltage as well as the corresponding total changes of the signals were interpreted in terms of a relatively simple overall mechanism which is also consistent with ESCA results on partially etched Si surfaces as obtained by other workers.

1. INTRODUCTION

Transient responses to step-wise perturbations of a reaction system have been studied in several laboratories in order to elucidate the underlying mechanism(s) (1,2,3). From early relaxation studies on plasma chemical systems in this laboratory and from Mauer and Logan's preliminary transient study of the CF_4 plasma etching of Si, it is clear that the response of such systems can be rather complex, involving gas pressure and cell current instabilities which are caused by the rapid fragmentation of the gas present and which in turn affect the ensuing etching process in an intricate way (4).

In the present study, d.c. plasma etching of Si by CF_4 has been studied using relatively small perturbations of the reaction systems, such that the instabilities mentioned above are reduced, or are avoided entirely, at the cost of dealing with relatively small responses. As a consequence, the unavoidable experimental errors must be given careful attention in planning this work and in evaluating the results.

2. EXPERIMENTAL

The plasma chemical cell and its connection to a medium resolution mass spectrometer have been described elsewhere (5). The Si sample consisted of a thin wafer of 0.25 cm^2 surface area, and 0.055 cm thickness, placed on the cathode approximately 0.2 cm from the aperture connecting the plasma cell and the differential pumping region (see Fig. (1) of Ref. (5)), while the total cathode surface area was 2.0 cm^2. The cell currents were approximately 1, 2, and 3 mA at applied voltages of 700, 800, and 900 V, respectively. The flow rate and pressure of CF_4 were about 0.16 cm^3(STP)/sec and 0.10 Torr.

Several methods were explored in order to obtain very reproducible perturbations of the plasma etching process. Step-wise changes of the gas composition and the addition of small pulses of reactive gases, such as O_2, to the gas flow proved to lead to somewhat erratic results. The ignition of a plasma, especially in the presence of Si samples which had not been recently etched led to fairly reproducible but complicated transients, which will be discussed in some more detail, below. The simplest and most reproducible results were obtained by step-wise increases of the applied voltage from 700 to 800, and to 900 V, as well as step-wise decreases in this range, as illustrated in Figure (1), and were therefore given most attention in this study. Cell pressure and current variations were common in the initial steps, on igniting the plasma. As a result, the apparent half times, $t_{1/2}$, the total changes in the response and sometimes even the direction of this change produced in these initial steps could not be trusted or be used to elucidate the plasma chemical mechanism; the interdependence of these quantities and of the plasma composition is too complex in this case.

Blank experiments were performed and it was found that the side walls of the plasma cell, containing small amounts of SiO_2 in a matrix of Al_2O_3 were not quite resistant to CF_4 plasma attack, but the corrections required were only about 2% for the SiF_3^+. For some species studied, such as $C_2F_5^+$ the signal transient responses found in blank experiments were relatively large; this is to be expected since they originated from the fragmentation and subsequent chemical changes involving the supporting gas, CF_4. Interestingly, the initial steps of series of blank transients led to maxima in the $C_2F_5^+$ signals. This suggests that the cell wall react, initially, but are becoming nearly inert after a few seconds of plasma exposure - a situation analogous to that encountered in some catalytic transient studies (6). This effect is absent in subsequent transient experiments.

As in the earlier studies, it was necessary to recognize, and under certain conditions to correct for, the fragmentation of species in the mass spectrometer ion source (5).

In view of these error considerations and blank corrections, it was decided to develop a uniform protocol for the series of transients performed, as exemplified below, in Table (1), in order to recognize various potential systematic errors and data trends.

3. RESULTS AND DISCUSSION

From Table (1)(a) it is seen that the average half times for the CF_3^+ and $C_2F_5^+$ signals agree rather well; the average differences between half times obtained in corresponding voltage steps agree even more closely in many such series, that is to within 0.03 or 0.04 sec.. Differences of 0.10 or 0.15 sec between averages can be considered significant, except when dealing with very small total changes in the signals (see Table (1)(b)).

The close agreement of the CF^+ and $C_2F_5^+$ signals probably means that CF or CF^+ combines with excess CF_4 in the plasma; from the relative signal height one would infer that the equilibrium is in favor of the C_2F_5 or $C_2F_5^+$.

Next, one notes from Table (1)(a) that the CF_3^+ appears first on the scene, upon increasing the plasma voltage; it is followed by CF_2^+, and then by CF^+. Clearly, the relaxation method used is capable of giving important information on the mechanism. The same sequence of $t_{1/2}$'s is found after step-wise decreases of the applied voltage. As one might expect, CF_3^+ and CF_2^+ decrease, while CF^+ increases on raising the voltage, indicating that the first two species are predominantly reactants, supplying F when new Si-F bonds are being formed. Also, the F^+ and SiF_3^+ signals have essentially the same average $t_{1/2}$'s in most series; the experimental errors of the average $t_{1/2}$'s for the rather small F^+ signals are of course somewhat larger than most others.

Interestingly, when the voltage is increased, the F^+ signals decrease, while those of SiF_3^+ always increase. Presumably the layer of intermediate and final products formed on the surface of the Si sample during etching is tilled by the more energetic ions impacting on the surface, such that the SiF_4 formed can escape far more easily. The F needed to form SiF_4 is probably supplied at a somewhat higher rate, but not sufficiently fast to keep up with the demand. In agreement with this, the SiF_4 etching yield at higher voltages is distinctly larger, per voltage increment, than the one at lower voltages.

The average of the SiF_3^+ half times is somewhat larger than those of the CF_3^+ and CF_2^+ species, indicating that the F supplied by the fragmentation of these species is used in forming SiF_4, or other Si-F species, but only after some delay, possibly due to its role in other chemical steps.

Some additional insight concerning other species existing in the plasma is available from these transient measurements. For example, $C_2F_4^+$ signals were found to be probably unrelated to the mass spectrometric cracking pattern which yielded $C_2F_5^+$ signals - the half times are significantly different. $C_2F_4^+$ is present in rather small amounts, and thus not very important to the overall mechanism.

Several species, notably COF_2^+ and COF^+, present only at the 1 or 2% level, relative to SiF_3^+, were found from blank experiments to be entirely due to plasma attack on the cell walls, while a small amount of CHF_2 present could be partially attributed to this source.

Several experiments were performed to gain more information concerning the role of the deposition layers. For one, in a number of experiments, the Si sample was discharge cleaned by a 5 minute exposure to an Ar plasma, at 900 V and 0.5 Torr, between successive transient experiments, but the effect of this treatment was small. Also, varying the time between successive transient measurements revealed that the plasma induced defects in the sample surface and/or the deposition layers changed considerably, during these rest periods. This finding supported the decision to use mostly small stepwise changes in the applied voltage to arrive at the above conclusions.

By way of summary, it appears that the reaction scheme

$$CF_4 \xrightleftharpoons[+F]{-F} CF_3 \xrightleftharpoons[+F]{-F} CF_2 \xrightleftharpoons[+F]{-F} CF$$

$$CF + CF_4 \rightleftharpoons C_2F_5$$

$$2F + Si \longrightarrow SiF_2$$

$$2F + SiF_2 \longrightarrow SiF_4 \uparrow$$

accounts rather well for the experimental observations. Small amounts of SiF and SiF_3 are presumably present as well, but SiF_2 appears to be the prevalent intermediate species, according to detailed XPS measurements by Chuang (7). In addition to the neutrals, small amounts of ionic species are probably present.

ACKNOWLEDGMENT

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(a) Half Times, $t_{1/2}$ (sec)

Applied Voltage Step	$\frac{m}{e}$ =19 F^+	85 SiF_3^+	31 CF^+	119 C_2F_5	100 $C_2F_4^+$	50 CF_2^+	69 CF_3^+	19 F^+	85 SiF_3^+
0 to 700	1.38	1.41	1.01	1.01	1.42	0.71	0.56	1.18	1.48
700 to 800	1.39	1.15	1.23	1.35	1.41	0.93	0.74	1.48	1.38
800 to 900	1.36	1.26	1.21	1.48	1.64	1.48	0.87	1.48	1.26
900 to 800	1.47	1.36	1.58	1.63	2.01	1.07	0.96	1.55	1.72
800 to 700	1.08	1.48	1.61	1.64	1.48	1.04	0.89	1.36	1.60
700 to 0	1.41	1.58	1.55	1.51	1.84	1.35	0.78	1.33	1.66
Average	1.35	1.37	1.37	1.44	1.63	1.10	0.80	1.40	1.52

(b) Corresponding Mass Spectrometric Signal Changes

0 to 700	-13.7	+ 79	+143	+362	+11.2	- 43	-970	- 9.8	+ 70
700 to 800	- 4.2	+113	+ 65	+254	+ 7.5	- 18	-884	- 6.7	+113
800 to 900	- 3.7	+137	+ 71	+314	+ 9.0	- 19	-410	-10.9	+140
900 to 800	+ 4.0	-146	- 87	-346	- 9.9	+ 14	+313	+11.1	-151
800 to 700	+ 2.8	-114	- 54	-213	- 6.0	+ 13	+205	+ 7.3	- 97
700 to 0	+ 5.1	- 87	- 72	-223	- 9.3	+ 13	+205	+ 7.6	- 90
Average Magnitudes	5.4	113	82	286	8.8	+20	498	8.9	107

Table (1)(a) Half times, $t_{1/2}$, in seconds, obtained in a typical series of transient experiments, by step-wise changes of the applied voltage, for the mass-to-charge ratios, $\frac{m}{e}$, as indicated, together with the corresponding species. Successive transients for the same m/e were obtained every 20 seconds, while the changeover to another m/e required about 250 seconds.
(b) Corresponding total changes of the mass spectrometric signals during each transient experiment. All values are on a relative scale but are corrected for changes of the instrumental sensitivity using an internal reference peak.

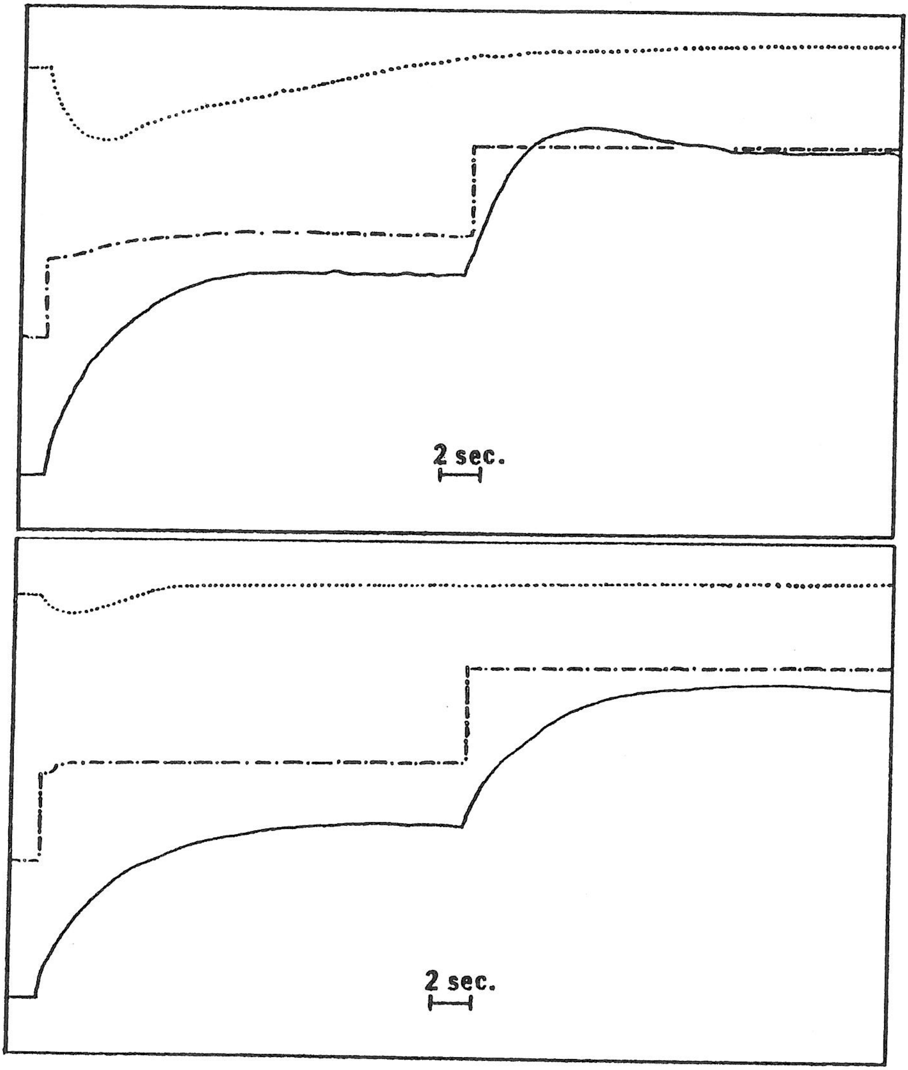

Fig. (1)(a) Top: Transients obtained on a Si sample which had not been etched recently. (---) Pressure (-•-) cell current, and (—) SiF_3^+ mass spectrometric signal ($\frac{m}{e}$ = 85) as a function of time. The pressure minimum corresponds to a drop of about 6%, while the cell current increases from 0 to 0.70 mA in the first transient, and to 1.60 mA in the second. The SiF_3^+ signal starts at zero, and is shown on an arbitrary scale.
(b)-Bottom: Similar results for a Si sample which had been etched for a few minutes and then been at rest for 20 sec.