THE ROLE OF HIGHLY EXCITED, LONG-LIVED N_2^* IN CF_4-NO ETCH PLASMAS

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ABSTRACT

The differences in formation of the main products COF_2 and F in CF_4-NO as compared to CF_4-O_2 mixtures can be ascribed to the intermediate production of metastable nitrogen molecules N_2^* which transfer energy to COF_2, dissociating it into CO and F. The chemical physics of the NO-CF_4 plasma will be discussed as a function of concentration, pressure and residence time. The consequences for practical etching will be indicated.

1. INTRODUCTION

Isotropic plasma etching of Si, Mo, Ta, Mo-silicides etc., with the aid of atomic fluorine is rapidly growing to maturity. This holds both for the application and for the understanding of the plasma reactions[1,2]. Briefly, the atomic fluorine is produced by a plasma in a mixture of a gaseous fluorine compound like CF_4, SF_6 etc. and a gaseous oxidant. The etch recipes are developed by optimizing the values of parameters like oxidant concentration, r.f. power, pressure etc.. The insight into the mechanisms of the plasma reactions leading to the final etch results has been obtained by studying the products in the effluent of the plasma, mostly with the aid of mass spectrometry. This means that the knowledge of the precise plasma reactions is indirect. Nevertheless, it has been established that such an approach to these problems yields useful, although simplified, insight into the important reaction paths leading to the etch results.

It is the object of this paper firstly to give a survey of recent results obtained with CF_4-O_2 and CF_4-NO mixtures, secondly to discuss the influence of pressure and residence time on the etch results, and thirdly to relate these results to the simplified plasma reactions established by earlier work.

2. EXPERIMENTAL

Two reactors were used in our experiments: one reactor was a barrel etcher type Dionex 2100T-11018 SCA, the other was a microwave effluent reactor. Briefly, the latter equipment consisted of a microwave cavity enclosing an alumina tube; the gas mixture to be studied was discharged at 2450 MHz in a volume of about 1 cm^3 enclosed by the cavity; the effluent of this discharge was pumped into an etch reactor with a volume of about 10^4 cm^3. A more detailed description of the microwave effluent reactor has been given previously[3]. The influence of residence time was investigated by changing the pumping speed with an iris diaphragm, while keeping the reactor pressure unchanged by adjustment of the gas flow. For a total pressure of 13.5 Pa in the microwave effluent reactor we varied the plasma residence time between 10 and 50 mseconds; thus the residence time in the reactor was about four orders of magnitude higher. The pressure p was changed by changing the flow; the change in residence time τ due to the change in pumping speed could be neglected. In both reactors a power of 150 W was used throughout the experiments.

3. RESULTS

3.A. A summary of previous results[4)]

Our previous results, which pertain to τ = 45 msec and p = 13.5 Pa, can be summarized by the following set of simplified reactions:

The plasma dissociates CF_4, O_2 and NO according to

$$CF_4 \xrightarrow{e} CF_3 + F \qquad (1)$$

$$O_2 \xrightarrow{e} O(^3P) + O(^1D) \qquad (2)$$

$$NO \xrightarrow{e} N(^4S) + O(^3P) \qquad (3)$$

The production of atomic fluorine as well as the etch rate of Si in the effluent show a maximum as a function of the oxidant concentration. Up to the maximum the O_2 and NO are consumed quantitatively by the simplified reaction

$$CF_3 + O \xrightarrow{e} COF_2 + F \qquad (4)$$

For the CF_4-NO mixture additional production of atomic fluorine occurs via the set of reactions:

$$N(^4S) + N(^4S) \xrightarrow{M,W} N_2^* \qquad (5)$$

$$N_2^* + COF_2 \longrightarrow N_2 + CO + 2F, \qquad (6)$$

where M or W are a third molecule or a wall, respectively.
At the pressure and residence time used, reactions (5) and (6) are also quantitative; this means that excited N_2^* consumes just half of the COF_2 produced by reaction (4) and causes an increase in the atomic fluorine concentration by a factor of 1½. Reaction (6) requires about 7 eV, a quantity easily supplied by the higher excited states of the N_2 molecule resulting from reaction (5). Qualitative consequences of this set of reactions for etching of Si in a barrel reaction with a patterned resist on top of it are depicted in Figures 1 and 2.

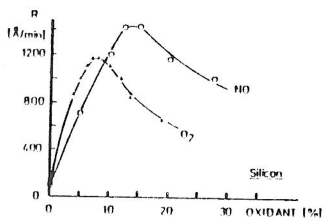

Fig. 1. Etch rate R of Si in the effluent of CF_4-oxidant plasmas as a function of oxidant content.

Figure 1 shows the etch rates of Si, R(Si), as a function of oxidant concentration. It can be seen that the CF_4-NO mixture gives rise to a higher etch rate at the maximum than the CF_4-O_2

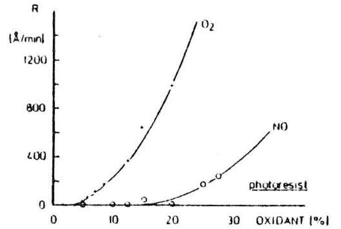

Fig. 2. The same as Fig. 1 for the etch rate of the photoresist.

mixture. Figure 2 shows that this is accompanied by a much lower resist erosion. The selectivity S of Si with respect to resist R, at the respective maxima, is about 6 for CF_4-O_2 and about 30 for CF_4-NO mixtures. The better selectivity of the CF_4-NO mixture is due to the reaction of the CO produced by reaction (6) with a slight excess of atomic oxygen produced at this maximum,

$$CO + O \longrightarrow CO_2 \qquad (7)$$

so that it cannot react with the resist.

3.B. Results for the microwave effluent reactor

3.B.1. Influence of plasma residence time at constant p

The results depicted in Figures 3A and 3B for a total pressure of 13.5 Pa show that the amount of CF_4 decomposed increased with plasma residence time. Naturally this entails an increasing percentage of gaseous oxidant consumed to form atomic fluorine. In agreement with the higher decomposition of CF_4 the etch rate of Si also increases. The Si etch rate maximum quantitatively shifts with the maximum of CF_4 decomposition.

An additional effect of longer plasma residence times is a slight increase in the relative COF_2 percentage for CF_4-NO mixtures. This is not observed for CF_4-O_2 mixtures.

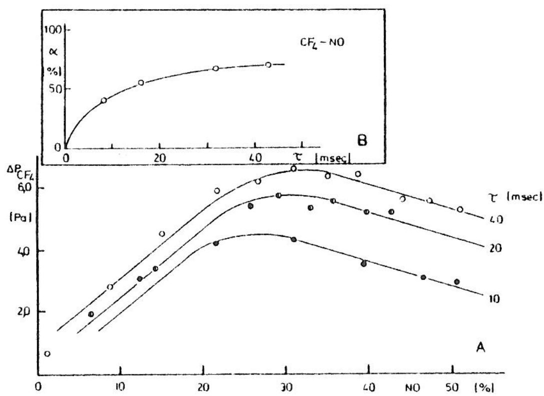

Fig. 3. A. Consumption of CF_4 in CF_4-NO plasmas as a function of NO content for the plasma residence time indicated.

B. Maximum conversion of CF_4 in % in CF_4-NO plasmas as a function of residence time.

3.B.2. Influence of total pressure at constant τ .

Increase of pressure in the range 13.5 to 133 Pa at constant τ causes a relative decrease of the decomposition of CF_4 and of the etch rate maximum. At the same time its position shifts to lower oxidant percentages. At the lower end of the pressure range the absolute amounts of CF_4 decomposed and the absolute Si etch rate increase with pressure.

3.C. Results for the barrel reactor

In the barrel reactor, the position of the maximum conversion of CF_4 (or etch rate of Si, etc.) is rather insensitive to both changes in residence time and in pressure. For the same pressure and residence time ranges as used for the microwave effluent reactor, the shift was of the order of one percent in the concentration of oxidant.

3.D. Summary of some differences between the two reactors

Typical differences between our microwave effluent reactor and a barrel reactor are:

1) the frequencies used: 2.45 GHz c.q. 13.56 MHz.
2) the ratio between the power densities P.D. in the effluent and the barrel reactor is about 10^4.
3) the plasma residence time τ in the effluent reactor is about 10^{-4} of that in the barrel reactor.
4) in the barrel reactor the etch products may be decomposed again in the plasma.

3.E. Summary of similarities of the two reactors

The product formation in both of the reactors corresponds to that described in Section 3.A.

4. DISCUSSION

Earlier and new results can be explained, without any additional reactions, by the set of reactions given in section 3.A., except the slight increase in relative COF_2 percentage for CF_4-NO mixtures with increasing τ . The latter observation is easily explained by assuming that this is due to a back reaction of CO, formed by reaction (6) with F according to

$$CO + 2F \longrightarrow COF_2 \qquad (8)$$

That this indeed occurs is confirmed by a similar increase in COF_2 induced by adding CO to plasmas in CF_4-O_2 mixtures. Comparison of conditions used for microwave effluent reactor and barrel reactor could indicate that the amount of conversion is higher in the case of the barrel reactor because the plasma residence times there are about a factor of 10^4 higher than in the microwave effluent reactor. However, this is not observed, which means that the 10^4 times higher power density in the plasma of the effluent reactor, possibly combined with the higher frequency, plays the dominating role in the conversion. This is in agreement with the relative insensitivity of the position of the maximum conversion (or etch rate) to residence time changes in the barrel reactor.

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