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Etch mechanism in the reactive ion etching of silicon nitride

J. Dulak,^{a)} B. J. Howard, and Ch. Steinbrüchel

Materials Engineering Department and Center for Integrated Electronics, Rensselaer Polytechnic Institute, Troy, New York 12180

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Reactive ion etching of silicon nitride with CHF_3/O_2 plasmas has been studied in a hexode reactor and compared to silicon dioxide etching. Measurements of etch rates as a function of gas composition and pressure were combined with Langmuir probe data for the ion flux to the substrate to give etch yields (number of substrate atoms removed per bombarding ion). At low oxygen content, the etch yields of both materials are about 2 atoms/ion and are essentially independent of pressure between 10 and 60 mTorr. At higher oxygen content, the etch yield is considerably larger for silicon nitride, and for both materials the etch yields increase with increasing pressure. From these results it can be concluded that in a CHF_3/O_2 plasma at low oxygen content, the etch mechanism is mostly direct reactive ion etching for both silicon nitride and silicon oxide. On the other hand, at higher oxygen content the etching is ion enhanced for both materials, but to a much greater extent in the case of silicon nitride.

I. INTRODUCTION

Silicon nitride (Si_3N_4) is a frequently used material in microelectronics technology. Its main applications are as a passivation layer and as an oxidation mask.¹ There have also been proposals to use Si_3N_4 together with SiO_2 as a multi-layer gate dielectric.² In all of these applications Si_3N_4 needs to be patterned, for which operation the preferred technique now is dry etching in a plasma.

Si_3N_4 is generally etched in a fluorocarbon plasma, i.e., with a fluorine-based plasma chemistry.³ The main difficulty in etching Si_3N_4 is to achieve anisotropic etching with good selectivity relative to SiO_2 . The best selectivity is obtained in a barrel reactor⁴ or an afterglow geometry⁵ with an F-atom-rich plasma, but this leads to isotropic etching. On the other hand, anisotropic patterning can only be done by reactive ion etching in an F-atom-poor, unsaturate-rich plasma, where Si_3N_4 and SiO_2 etch at comparable rates.^{3,6-8} To circumvent these problems, a two-step process has been implemented, in which during most of the etch anisotropic plasma conditions are used but the etch is completed under conditions giving high selectivity.⁹ The plasma etching of Si_3N_4 is sometimes said to be intermediate between SiO_2 and Si,^{3,10} but the underlying reasons for the similarities and differences between the behavior of Si_3N_4 and SiO_2 have not been identified. The details of the etching of Si_3N_4 also depend on whether the material was deposited by low-pressure chemical vapor deposition (LPCVD) or by a plasma-enhanced process.³

In this work we reexamine the reactive ion etching of Si_3N_4 and SiO_2 in CHF_3/O_2 plasmas but, with the help of Langmuir probe data, we focus on comparing etch yield, rather than etch rates. This will allow us to clarify the etch mechanisms involved. In particular, we will be able to show to what extent direct reactive ion etching on the one hand and ion-enhanced chemical etching on the other hand are

II. EXPERIMENTAL DETAILS

All our experiments were performed in an Applied Materials AME-8130 hexode reactor loaded with 23 Si wafers and one Si_3N_4 or SiO_2 wafer to be etched. Standard plasma conditions were 100 sccm of total gas flow and 1000 W of radio frequency (rf) power, with the gas pressure variable from 10 to 60 mTorr. Two gas mixtures were investigated: $\text{CHF}_3/10\% \text{O}_2$ and $\text{CHF}_3/20\% \text{O}_2$ by flow. (Under these conditions, etching of the Si was very small, thus representing a minimal load on the plasma). The substrates were thermal SiO_2 ($\sim 5000 \text{ \AA}$, grown with O_2 and H_2 at 1000°C) and LPCVD Si_3N_4 ($\sim 1500 \text{ \AA}$, grown with NH_3 and SiH_2Cl_2 at 780°C). Etch rates were measured interferometrically on a substrate wafer in the top position on a hexagonal face, whereas Langmuir probe data were taken over a substrate wafer in the second position from the top.

The Langmuir probe was L shaped, with the active part consisting of a tungsten wire of 0.5 mm diam and 10 mm length, and was mounted on a flange over one of the wafer-holding hexagon faces. The probe could be moved parallel as well as perpendicular to the substrate wafer surface. The sheath edge above the wafer was located from the probe position giving maximum ion current. Ion density, electron temperature, and ion flux to the substrate wafer were determined as described previously.¹¹

The etch yield Y , i.e., the number of substrate atoms removed per bombarding ion, was calculated from the etch rate R_e and the ion flux f_i by

$$Y = \frac{R_e \rho N}{M f_i}, \quad (1)$$

where ρ is the density of the substrate film (3.4 g/cm^3 for Si_3N_4 and 2.3 g/cm^3 for SiO_2), N is the number of atoms per molecular unit ($N = 7$ for Si_3N_4 and $N = 3$ for SiO_2), and M is the molecular weight of the substrate material. The ion

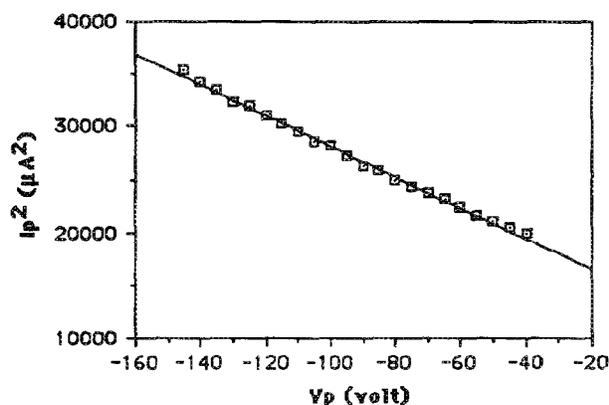


FIG. 1. Plot of square of probe current I_p^2 vs probe voltage V_p in the ion saturation regime, where I_p is due to collected ions. Slope of curve is proportional to N_i^2 .

$$f_i = N_i (kT_e/m_i)^{1/2}, \quad (2)$$

where N_i is the ion density, T_e the electron temperature, and m_i the mass of a CHF_2^+ ion.

III. RESULTS

In Figs. 1 and 2 we give an example of Langmuir probe data for the ion current and the electron current to the probe. One can see that the square of the ion current is a linear function of the probe voltage V_p as is expected in a low-density plasma.¹² From this curve the ion density N_i can readily be deduced.¹¹ Also, the natural logarithm of the net electron current I_e (probe current minus ion current) is a linear function of the probe voltage over about two orders of magnitude, so that an electron temperature T_e can be associated with the electron energy distribution. (Note that we have always observed a slight s shape in the $\ln I_e$ versus V_p curves). Typical figures obtained for the ion density and the electron temperature were $N_i = 8 \times 10^9 \text{ cm}^{-3}$ and $T_e = 4.5 \text{ eV}$ under the given plasma conditions.

Figures 3 and 4 display etch rates versus pressure. We point out that in pure CHF_3 neither Si_3N_4 nor SiO_2 etched.

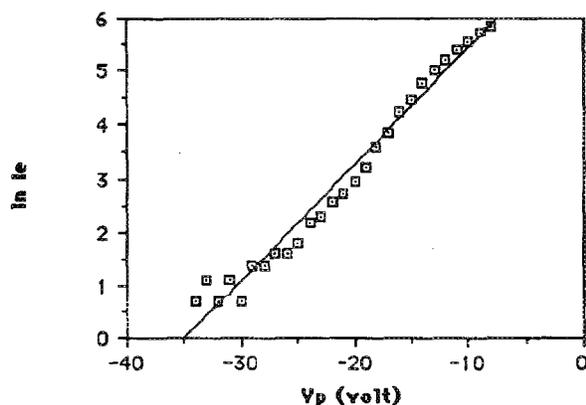


FIG. 2. Natural logarithm of electron current I_e vs probe voltage V_p . Slope

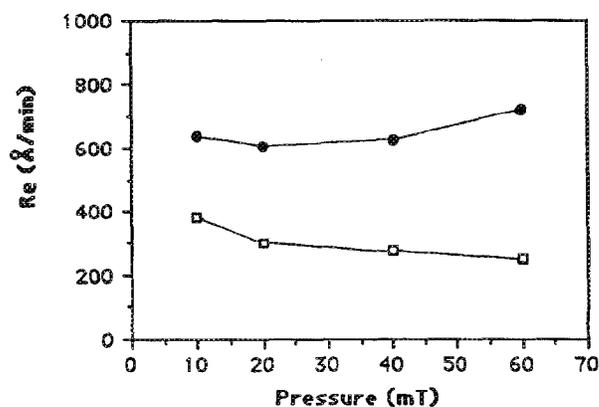


FIG. 3. Etch rates for Si_3N_4 vs pressure. \square : CHF_3 -10% O_2 ; \bullet : CHF_3 -20% O_2 .

Furthermore, for Si_3N_4 at 40 and 60 mTorr of CHF_3 /10% O_2 the etch rate slowed down noticeably over time (cf. Ref. 8), so that in those two cases the initial etch rates were used in Fig. 3. In all other cases the etch rates were constant in time. Figures 5 and 6 present etch yields corresponding to the etch rates of Figs. 3 and 4.

IV. DISCUSSION

For the purpose of discussing the above results we mention first that increasing the O_2 content in an CHF_3/O_2 plasma decreases the amount of fluorocarbon unsaturates but increases the amount of free F atoms in the plasma, whereas increasing the pressure has the opposite effect, i.e., it increases the amount of unsaturates.³ It is then remarkable that neither O_2 content nor pressure have a significant effect on the etch rate of SiO_2 (Fig. 4), but an increased O_2 content leads to an increase in the etch rate of Si_3N_4 by a factor 2 or more (Fig. 3).

The significance of these results becomes clearer if one focuses on the etch yields. At 10% O_2 the etch yield decreases slightly with increasing pressure for Si_3N_4 and remains practically constant for SiO_2 (Fig. 5). At 20% O_2 the

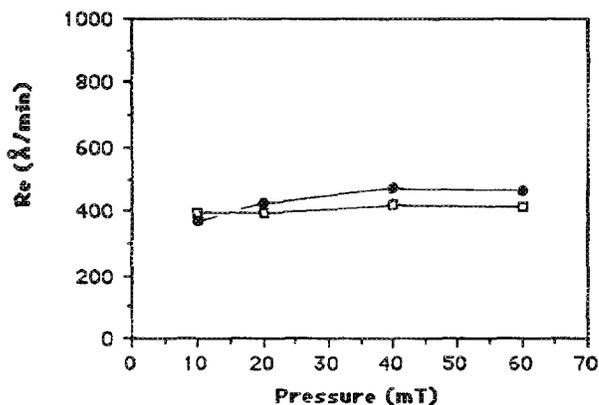


FIG. 4. Etch rates for SiO_2 vs pressure. \square : CHF_3 -10% O_2 ; \bullet : CHF_3 -20%

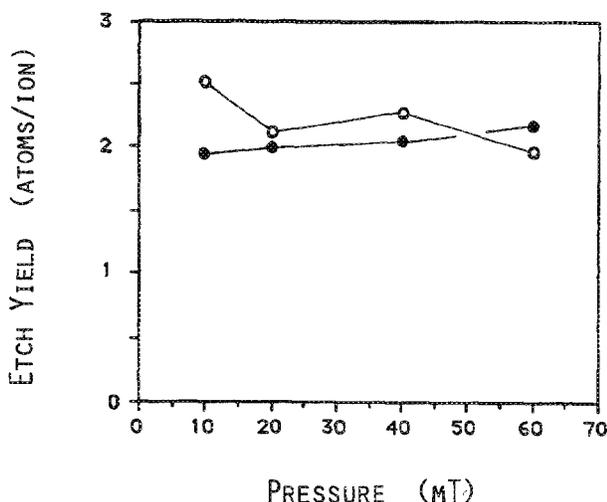
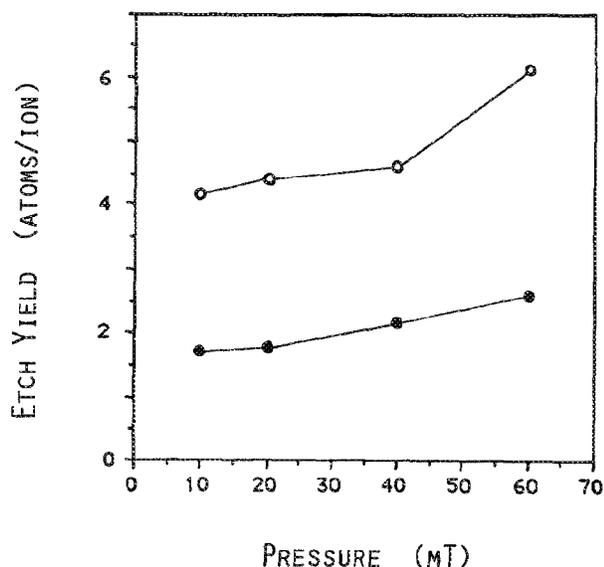


Fig. 5. Etch yields vs pressure with CHF₃-10% O₂. ○: Si₃N₄; ●: SiO₂.

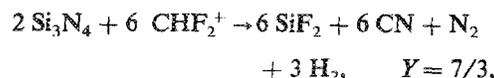
etch yield for Si₃N₄ is higher by a factor 2 or more than at 10% O₂ and increases markedly with increasing pressure. On the other hand, at 20% O₂ the etch yield for SiO₂ is slightly lower than at 10% O₂, and it increases only slightly with increasing pressure (Fig. 6). Thus, the etch yield of SiO₂ is largely unaffected by the presence of unsaturates in a CHF₃-based plasma as long as there is etching, in agreement with previous results,^{12,13} whereas the etch yield of Si₃N₄ is strongly enhanced under conditions of reduced unsaturates (and probably somewhat increased F atom content).

We interpret these results as indicating that for Si₃N₄ at 10 % O₂ and for SiO₂ at 10% O₂ and to a large extent also at 20% O₂, the etching depends only on the ions in the plasma. More specifically, ions may react directly with the substrate which, for a fixed reaction probability, leads to a constant etch yield independent of neutral reactants present. The increased yield for Si₃N₄ with 20% O₂ may be ascribed to the

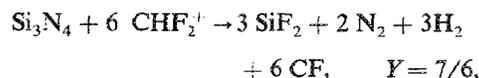
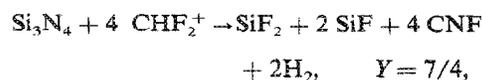
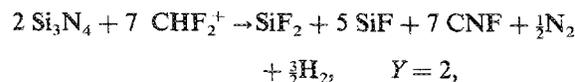


fact that under those conditions the etching of Si₃N₄ does become ion enhanced and, apparently, ion-enhanced chemical etching requires a much smaller concentration of neutral reactants in the case of Si₃N₄ than in the case of SiO₂. This is consistent with the previous observation that the etching of SiO₂ is strongly ion enhanced only with an excess of F atoms present in the plasma.¹⁴

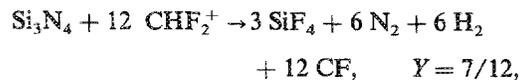
In order to show that the above mechanism of direct reactive ion etching is plausible, we need to demonstrate that chemical reactions between plasma ions and the substrate give reasonable etch yields. Thus we note first that energetic molecular ions will dissociate into highly reactive atoms upon impinging onto the substrate.¹⁵ In addition, mass spectrometry and optical emission spectroscopy studies revealed that the important etch products with Si₃N₄ are SiF₂, N₂, and CN (as a radical or as a fragment of CNF).^{16,17} (Clarke *et al.*¹⁶ also observed SiF in the plasma but argued that this was a gas phase reaction product from SiF₂ and not a true etch product). It is then clear that the most efficient ion reaction from the point of view of the etch yield is



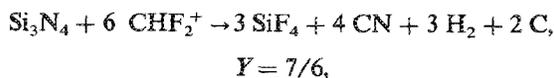
where Si and C are removed in the form of SiF₂ and CN. Other possible reactions such as



lead to lower etch yields. Furthermore, reactions producing SiF₄ directly also give lower yields, for example



or else they leave carbon on the substrate, for example



in which case the etch reaction would soon be suppressed. Of course, it is not possible to decide at this point which of the first four reactions for the etching of Si₃N₄ are the most important ones, but it is evident that the expected yields are consistent with the ones measured at 10% O₂ content. One should keep in mind, though, that here as well as in other etching situations involving ion bombardment of the substrate, there is always a small contribution to the overall etching from simple physical sputtering.

For SiO₂ the etch yields measured here are somewhat higher than those found in a previous study.¹² This is probably due to the fact that in the present experiment the ion

($V_{ac} \approx 150$ V),¹² where the reaction probability of the ions may well have been less than 1 and the contribution by sputtering to the overall etching smaller. But for SiO₂ also, the numerical values of the etch yields are consistent with plausible ion reaction mechanisms and with observed etch products.¹³ The pressure dependence of the etch yield of SiO₂ at 20% O₂ indicates that at that composition there is a slight ion-enhanced component to the overall etching.

V. CONCLUSIONS

The above results suggest to us that in a CHF₃/O₂ plasma at low O₂ content, the etch mechanism for both Si₃N₄ and SiO₂ is mostly direct reactive ion etching, with ions themselves being the main reactants. On the other hand, at higher O₂ content the etching is quite strongly ion-enhanced for Si₃N₄ but only slightly ion-enhanced for SiO₂. Thus it is with respect to etch yields or, equivalently, with respect to the degree of ion enhancement under conditions of low concentration of unsaturate species that the etching of Si₃N₄ in a fluorocarbon plasma can be said to be intermediate between SiO₂ and Si. The strongest evidence for this general picture is that etch yields are practically independent of pressure at low O₂ content for both materials but increase to different degrees with increasing pressure at higher O₂ content. In addition, the numerical values of the etch yields at low O₂

content can be rationalized on the basis of plausible ion-substrate chemical reactions.

- ^{a)} Present address: IBM East Fishkill, Hopewell Junction, NY 12533-0999
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