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# Etch mechanism in the reactive ion etching of silicon nitride

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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 multilayer 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 reactor[4] or an afterglow geometry[5] 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 yields 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: $CHF_3$/10% $O_2$ and $CHF_3$/20% $O_2$ 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 Å, grown with $O_2$ and $H_2$ at 1000 °C) and LPCVD $Si_3N_4$ ($\sim$1500 Å, 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

$$Y = \frac{R_e \rho N}{M f_i}, \tag{1}$$

where $\rho$ 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

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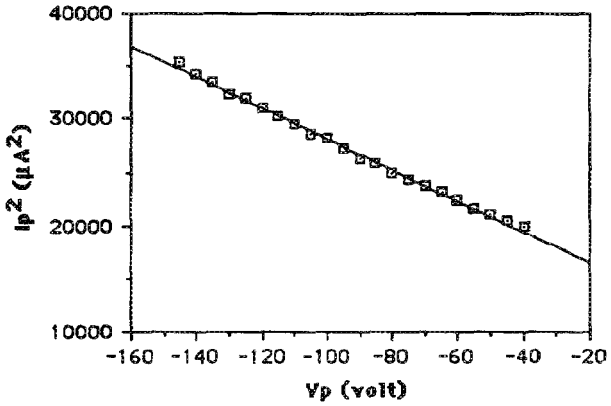


FIG. 1. Plot of square of probe current $I_p^2$ vs probe voltage $V_p$ in the ion saturation regime, where $I_p$ is due to collected ions. Slope of curve is proportional to $N_i^2$.

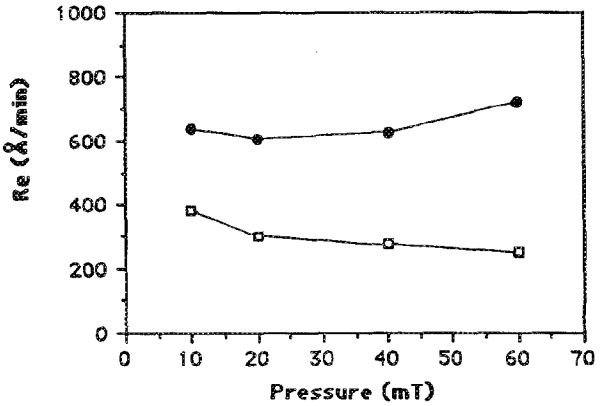


FIG. 3. Etch rates for $Si_3N_4$ vs pressure. □: $CHF_3$-10% $O_2$; ●: $CHF_3$-20% $O_2$.

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

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 $N_i = 8\times10^9$ cm$^{-3}$ and $T_e = 4.5$ 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. 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

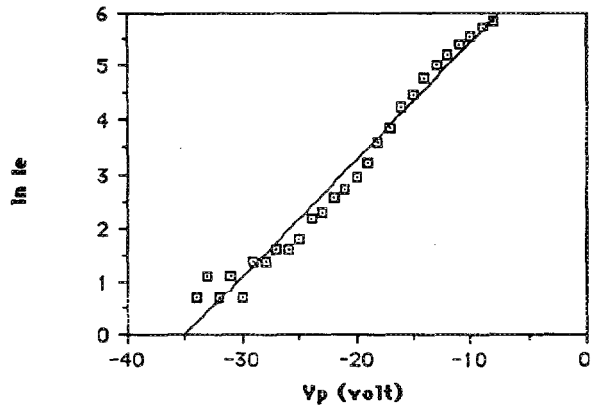


FIG. 2. Natural logarithm of electron current $I_e$ vs probe voltage $V_p$. Slope

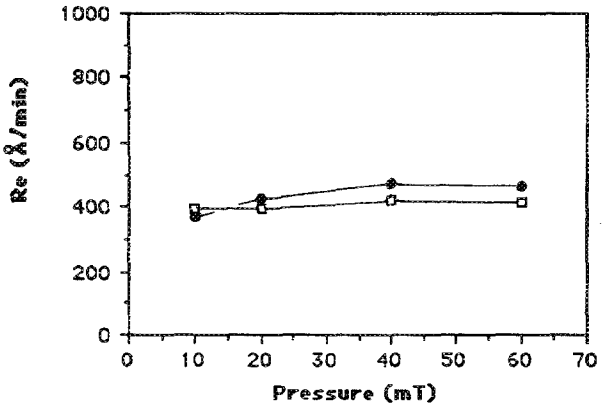


FIG. 4. Etch rates for $SiO_2$ vs pressure. □: $CHF_3$-10% $O_2$; ●: $CHF_3$-20%

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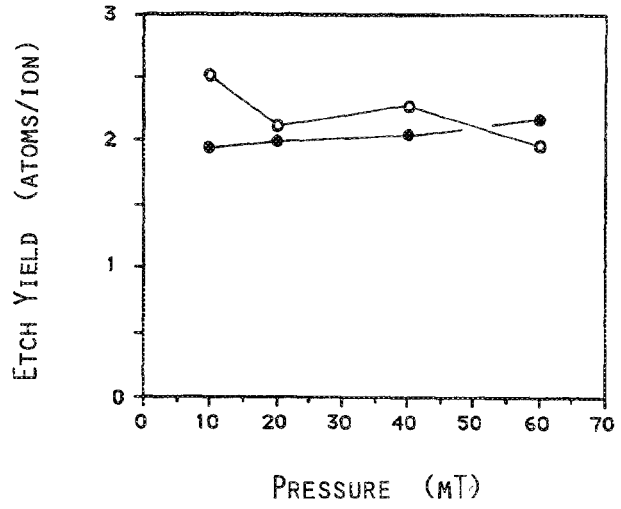
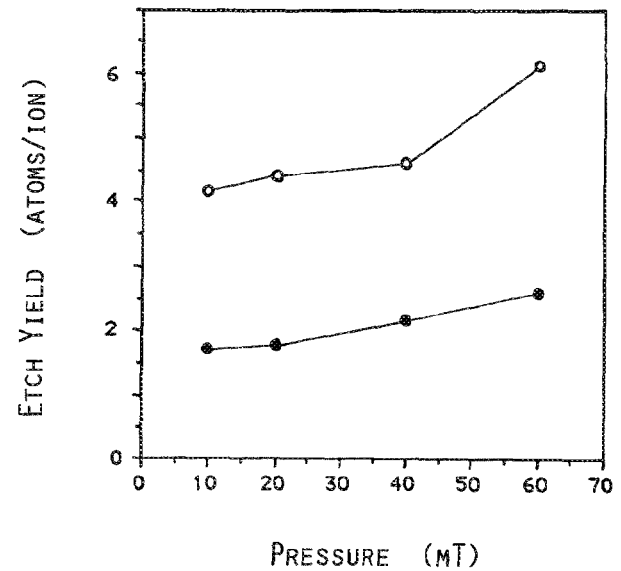



FIG. 5. Etch yields vs pressure with $CHF_3$-10% $O_2$. ○: $Si_3N_4$; ●: $SiO_2$.

etch yield for $Si_3N_4$ is higher by a factor 2 or more than at 10% $O_2$ and increases markedly with increasing pressure. On the other hand, at 20% $O_2$ the etch yield for $SiO_2$ is slightly lower than at 10% $O_2$, and it increases only slightly with increasing pressure (Fig. 6). Thus, the etch yield of $SiO_2$ is largely unaffected by the presence of unsaturates in a $CHF_3$-based plasma as long as there is etching, in agreement with previous results,[12,13] whereas the etch yield of $Si_3N_4$ is strongly enhanced under conditions of reduced unsaturates (and probably somewhat increased F atom content).

We interpret these results as indicating that for $Si_3N_4$ at 10 % $O_2$ and for $SiO_2$ at 10% $O_2$ and to a large extent also at 20% $O_2$, 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 $Si_3N_4$ with 20% $O_2$ may be ascribed to the




fact that under those conditions the etching of $Si_3N_4$ does become ion enhanced and, apparently, ion-enhanced chemical etching requires a much smaller concentration of neutral reactants in the case of $Si_3N_4$ than in the case of $SiO_2$. This is consistent with the previous observation that the etching of $SiO_2$ 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 $Si_3N_4$ are $SiF_2$, $N_2$, 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 $SiF_2$ 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

$$2\,Si_3N_4 + 6\,CHF_2^+ \rightarrow 6\,SiF_2 + 6\,CN + N_2 + 3\,H_2, \qquad Y = 7/3,$$

where Si and C are removed in the form of $SiF_2$ and CN. Other possible reactions such as

$$2\,Si_3N_4 + 7\,CHF_2^+ \rightarrow SiF_2 + 5\,SiF + 7\,CNF + \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2, \qquad Y = 2,$$

$$Si_3N_4 + 4\,CHF_2^+ \rightarrow SiF_2 + 2\,SiF + 4\,CNF + 2H_2, \qquad Y = 7/4,$$

$$Si_3N_4 + 6\,CHF_2^+ \rightarrow 3\,SiF_2 + 2\,N_2 + 3H_2 + 6\,CF, \qquad Y = 7/6,$$

lead to lower etch yields. Furthermore, reactions producing $SiF_4$ directly also give lower yields, for example

$$Si_3N_4 + 12\,CHF_2^+ \rightarrow 3\,SiF_4 + 6\,N_2 + 6\,H_2 + 12\,CF, \qquad Y = 7/12,$$

or else they leave carbon on the substrate, for example

$$Si_3N_4 + 6\,CHF_2^+ \rightarrow 3\,SiF_4 + 4\,CN + 3\,H_2 + 2\,C, \qquad Y = 7/6,$$

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 $Si_3N_4$ are the most important ones, but it is evident that the expected yields are consistent with the ones measured at 10% $O_2$ 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 $SiO_2$ 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

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($V_{dc} \approx 150$ 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 $SiO_2$ 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 $SiO_2$ at 20% $O_2$ 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 $CHF_3/O_2$ plasma at low $O_2$ content, the etch mechanism for both $Si_3N_4$ and $SiO_2$ is mostly direct reactive ion etching, with ions themselves being the main reactants. On the other hand, at higher $O_2$ content the etching is quite strongly ion-enhanced for $Si_3N_4$ but only slightly ion-enhanced for $SiO_2$. 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 $Si_3N_4$ in a fluorocarbon plasma can be said to be intermediate between $SiO_2$ and Si. The strongest evidence for this general picture is that etch yields are practically independent of pressure at low $O_2$ content for both materials but increase to different degrees with increasing pressure at higher $O_2$ content. In addition, the numerical values of the etch yields at low $O_2$ content can be rationalized on the basis of plausible ion-substrate chemical reactions.

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[1] C. J. Mogab, in *VLSI Technology*, ed. by S. M. Sze (McGraw-Hill, New York, 1983), p. 337.
[2] C. G. Sodini, S. S. Wontedt, and T. W. Ekstedt, IEEE Trans. Electron Devices **ED-29**, 1662 (1982).
[3] D. L. Flamm, in *Plasma Etching: An Introduction*, edited by D. M. Manos and D. L. Flamm (Academic, San Diego, 1989), p. 165.
[4] F. H. M. Sanders, J. Dieleman, H. J. B. Peters, and J. A. M. Sanders, J. Electrochem. Soc. **129**, 2559 (1982).
[5] N. Hayasaka, H. Okano, and Y. Horiike, Solid. State Technol. **4**, 127 (1988).
[6] H. W. Lehmann and R. Widmer, J. Vac. Sci. Technol. **15**, 319 (1978).
[7] S. Matsuo, J. Vac. Sci. Technol. **17**, 587 (1980).
[8] T. C. Mele, J. Nulman, and J. P. Krusius, J. Vac. Sci. Technol. B **2**, 684 (1984).
[9] H. J. Stocker, J. Vac. Sci. Technol. A **7**, 1145 (1989).
[10] P. E. Riley and D. A. Hanson, J. Vac. Sci. Technol. B **7**, 1352 (1989).
[11] Ch. Steinbrüchel, J. Electrochem. Soc. **130**, 648 (1983).
[12] Ch. Steinbrüchel, J. Vac. Sci. Technol. A **8**, 1663 (1990).
[13] Ch. Steinbrüchel, H. W. Lehmann, and K. Frick, J. Electrochem. Soc. **132**, 180 (1985).
[14] Ch. Steinbrüchel and B. J. Curtis, Mat. Res. Soc. Symp. Proc. **76**, 179 (1987).
[15] Ch. Steinbrüchel, J. Vac. Sci. Technol. B **2**, 38 (1984).
[16] P. E. Clarke, D. Field, A. J. Hydes, D. F. Klemperer, and M.J. Seakins, J. Vac. Sci. Technol. B **3**, 1614 (1985).
[17] D. Field, D. F. Klemperer, and I. T. Wade, J. Vac. Sci. Technol. B **6**, 551 (1988).

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