

Etching Characteristics of SiO<sub>2</sub> in CHF<sub>3</sub> Gas Plasma\*

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The etching characteristics of SiO<sub>2</sub> have been investigated in the CHF<sub>3</sub> gas plasma using the planar type reactor with the 400 kHz rf power. The etch rate of SiO<sub>2</sub>, the SiO<sub>2</sub>/Si and SiO<sub>2</sub>/resist etch rate ratios, and the deterioration of photoresist films are studied with a variety of etching parameters. The etching characteristics depend strongly on the coupling mode. With the cathode coupling mode, the values of 300Å/min and of larger than 100 are obtained for the etch rate of SiO<sub>2</sub> and the SiO<sub>2</sub>/Si etch rate ratio, respectively. Only 8 is given for the SiO<sub>2</sub>/Si etch rate ratio with the anode one. The deterioration of photoresist films less occurs with the cathode coupling mode than with the anode one. The dependences of the etching characteristics on the rf current, gas pressure, gas flow rate, and the electrode separations are also studied some in detail with the cathode coupling mode. Possible explanations for some of the experimental results are discussed.

Key words: Plasma etching, SiO<sub>2</sub>, CHF<sub>3</sub> gas, Etching characteristics.

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### Introduction

The gas plasma etching in the planar type reactor offers the advantages and capabilities of the high resolution, anisotropic etching, the high etch rate, the high material selectivity, and the low electrical damage. These characteristics result from the admixture of the electric field effects with the chemical reactions between solid materials to be etched and reactive species in a glow discharge.

The gas plasma etching of  $\text{SiO}_2$  is one of the key techniques for the fine pattern definition in fabricating high density integrated circuits. Relating to this technique, many studies have been carried out (1-9), in which several kinds of etchant gases were tried to be used for etching  $\text{SiO}_2$ . Heinecke (3) and Lehmann (9) proposed the use of the  $\text{CHF}_3$  gas plasma for etching  $\text{SiO}_2$  mainly because of its high material selectivity. For the  $\text{CHF}_3$  gas plasma, however, only limited data are available on the etching characteristics of  $\text{SiO}_2$ .

In the planar type reactor, as stated above, the electric field is considered to affect the etching characteristics which, therefore, should depend strongly on the coupling mode of the wafer to be etched with the rf power. Consequently, the coupling mode is one of the important factors for etching materials in the planar type reactor, but we can find again only a few papers (10) which are concerned with this problem.

In this paper, some of the etching characteristics of  $\text{SiO}_2$  in the  $\text{CHF}_3$  gas plasma will be described. The etch rates of  $\text{SiO}_2$ , the  $\text{SiO}_2/\text{Si}$  and  $\text{SiO}_2/\text{resist}$  etch rate ratios, and the deterioration of photoresist films will be investigated with a variety of etching parameters, namely, the coupling mode, rf current, gas pressure, gas flow rate, and the electrode separation.

### Experimental

Fig. 1 shows schematically the planar type plasma reactor used in this study. The reactor is equipped with a stainless-steel chamber and teflon-coated, 160 mm diameter aluminum electrodes which are cooled by water to avoid the

temperature rise. The separation between the two electrodes  $d$  can be set at an arbitrary value in the range from 10 to 90 mm. In the following parts, the  $d$  was set at 40 mm unless otherwise noted. The rf power at 400 kHz can be applied either to the upper or to the lower electrode by changing the electrical connection as shown in Fig. 1. Either the anode or the cathode coupling mode can, therefore, be given without changing any factors in the configuration. In this paper, the anode and the cathode coupling mode mean that the rf power is applied, respectively, to the upper and to the lower electrode on which the wafer to be etched is placed. The rf current  $I_{rf}$  is measured instead of the rf power. The flow rate of CHF<sub>3</sub> gas  $Q$ , which was fixed at 24 sccm unless otherwise noted, is controlled with a thermal mass flow

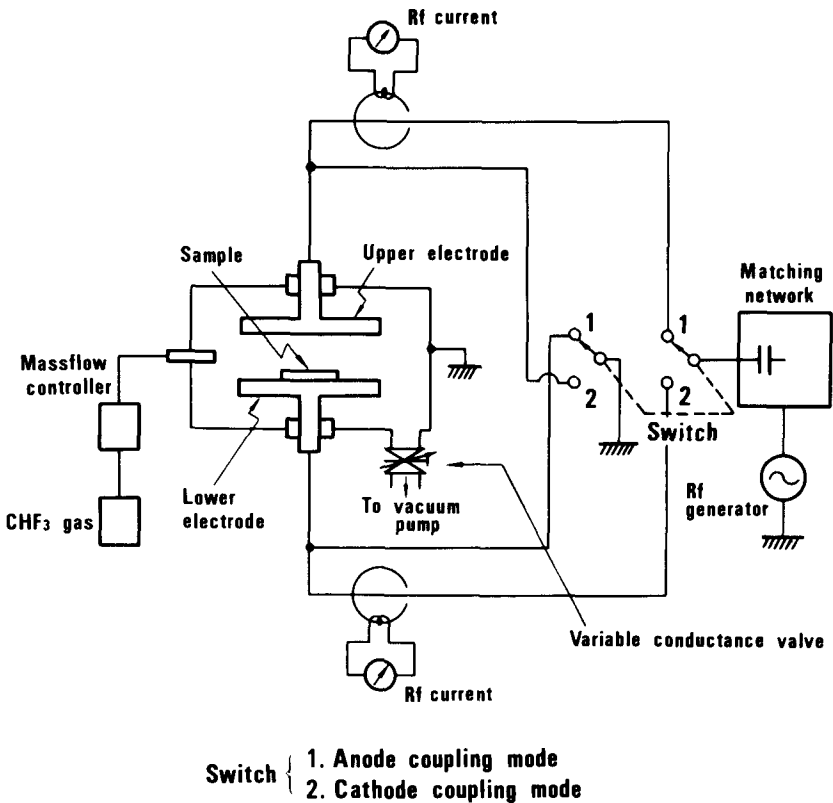


Fig. 1 Schematic diagram of the experimental plasma reactor.

controller. The gas pressure  $P$  in the chamber is adjusted independently of the gas flow rate with variable conductance valve in the exhaust line.

The sample, a 76 mm diameter wafer, had a structure which made it possible to measure the etched depths of both  $\text{SiO}_2$  and Si simultaneously. That is, within one wafer, there were both surfaces of  $\text{SiO}_2$  and Si exposed to the plasma. The positive-reacting photoresist, AZ-1370, was used for an etching mask. The wafer was baked at  $130^\circ\text{C}$  in  $\text{N}_2$  gas for 30 min after the resist definition. After the sample was placed on the lower electrode, the chamber was pumped down below 0.1 mTorr by using a diffusion pump, and then the  $\text{CHF}_3$  gas was introduced into the chamber. The etch time was usually 10 min. After etching, the sample was taken out of the chamber and divided into halves. One of them was treated in the  $\text{O}_2$  gas plasma in order to remove the photoresist film. If it could not be removed by this treatment, the sample was dipped successively in the  $\text{H}_2\text{O}_2$ - $\text{H}_2\text{SO}_4$  acid solution.

The etched depths of both  $\text{SiO}_2$  and Si were measured with a surface roughness gauge (Taly step) and were divided by the etch time to obtain their etch rates,  $E(\text{SiO}_2)$  and  $E(\text{Si})$ . The  $\text{SiO}_2/\text{Si}$  etch rate ratio,  $R(\text{SiO}_2/\text{Si})$ , was simply calculated to be the etch rate of  $\text{SiO}_2$  divided by that of Si,  $E(\text{SiO}_2)/E(\text{Si})$ . The thickness of the photoresist film was also measured with the Taly step before and after etching to obtain the etched thickness. Then the etch rate of the photoresist film,  $E(\text{resist})$ , and the  $\text{SiO}_2/\text{resist}$  etch rate ratio,  $R(\text{SiO}_2/\text{resist})$ , were calculated in the same way as described above. The degree of the deterioration of the photoresist film was observed through an optical microscope with another half of the sample.

## Results and Discussions

### Coupling mode dependence

The coupling mode dependences of the etching characteristics of both  $\text{SiO}_2$  and Si in the  $\text{CHF}_3$  gas plasma were investigated under various etching conditions. Fig. 2 shows the etch rates of both  $\text{SiO}_2$  and Si (A), and the  $\text{SiO}_2/\text{Si}$  etch rate ratio (B) as functions of the rf current with the cathode and the anode coupling mode. In the case of the cathode coupling mode, the etch rate of  $\text{SiO}_2$  increases with increasing rf current and reaches about 500 Å/min at the rf current of

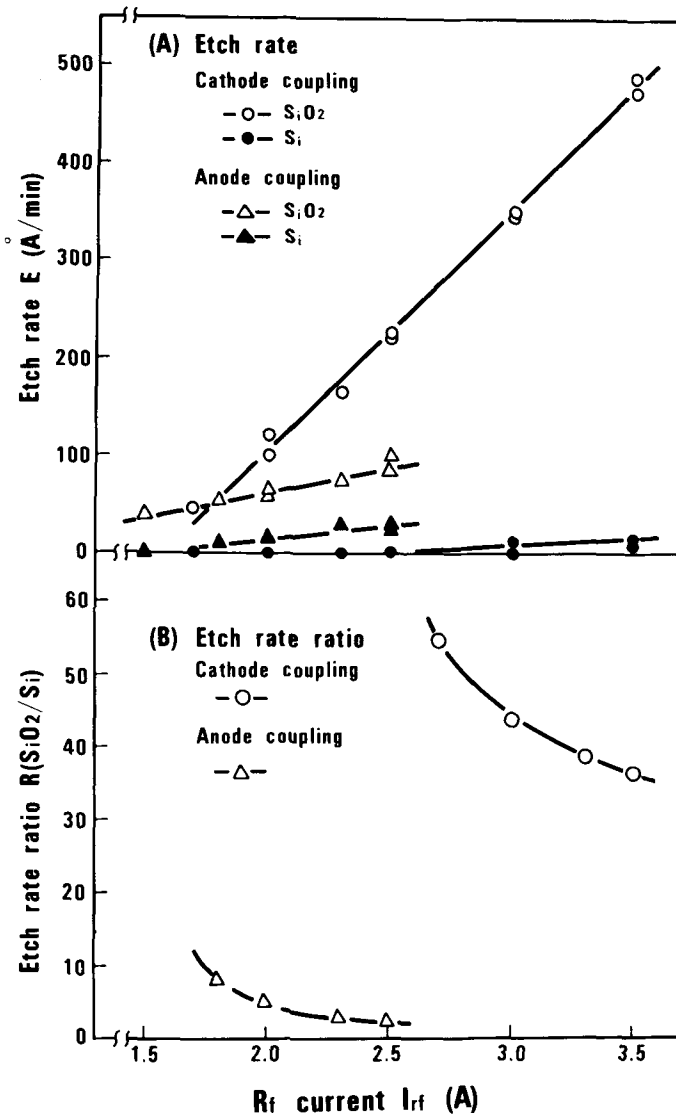


Fig. 2  $R_f$  current dependences of (A) the etch rates of  $\text{SiO}_2$  and Si and (B) the  $\text{SiO}_2/\text{Si}$  etch rate ratio for both coupling modes.  $P = 50$  mTorr.

3.5 A. The etch rate of Si is nearly zero in the range below 2.5 A. Above this current, Si begins to be etched but its etch rate reaches only 20 A/min even at 3.5 A. Therefore, the very high value of more than 30 is obtained for the  $\text{SiO}_2/\text{Si}$  etch rate ratio as shown in Fig. 2(B). The etch rate of Si in the range below 2.5 A is too small for us to calculate the  $\text{SiO}_2/\text{Si}$  etch rate ratio. In the case of the anode coupling mode, on the other hand, both  $\text{SiO}_2$  and Si start to be etched at the relatively low rf current as shown in Fig. 2(A), and their etch rates increase with increasing rf current. However, on the whole, the etch rate of  $\text{SiO}_2$  is lower in comparison with that for the cathode coupling mode and reaches 100 A/min at 2.5 A. The etch rate of Si is not insignificantly low even in the range below 2.5 A. Therefore, the low  $\text{SiO}_2/\text{Si}$  etch rate ratio of less than 8 is obtained (Fig. 2(B)).

The etch rates of both  $\text{SiO}_2$  and Si and the  $\text{SiO}_2/\text{Si}$  etch rate ratio are shown in Fig. 3(A) and (B), respectively, as a function of the  $\text{CHF}_3$  gas pressure for both coupling modes. The  $\text{SiO}_2/\text{Si}$  etch rate ratio for the cathode coupling mode was not again calculated in the range of the gas pressure below 80 mTorr because the etched depth of Si was too small to be measured. The cathode coupling mode gives the relatively high etch rate of  $\text{SiO}_2$  which first increases with increasing gas pressure, then decreases after reaching the maximum rate of about 300 A/min around 80 mTorr. The etch rate of Si is nearly zero in the range below 70 mTorr. Above this pressure the etching of Si occurs but the rate is as small as 15 A/min even at the gas pressure of 100 mTorr. The  $\text{SiO}_2/\text{Si}$  etch rate ratio, therefore, has a very high value. In the case of the anode coupling mode, on the other hand, the etch rate of  $\text{SiO}_2$  is comparatively small in the range below 80 mTorr but continuously increases with the increase of the gas pressure in the higher range. The etch rate of Si is not as low as that with the cathode coupling mode and also increases with increasing pressure. Therefore, only a low value of less than 3 is obtained for the  $\text{SiO}_2/\text{Si}$  etch rate ratio.

Fig. 4 illustrates the cross-sectional SEM image of a  $\text{SiO}_2$  pattern that was formed by etching in  $\text{CHF}_3$  in the cathode coupling mode using a photoresist mask. The pattern size of  $\text{SiO}_2$  is about 1  $\mu\text{m}$  wide. It is shown that the sidewalls of the etched  $\text{SiO}_2$  are practically vertical and that an almost ideal pattern transfer is obtained from the mask into the  $\text{SiO}_2$  layer.

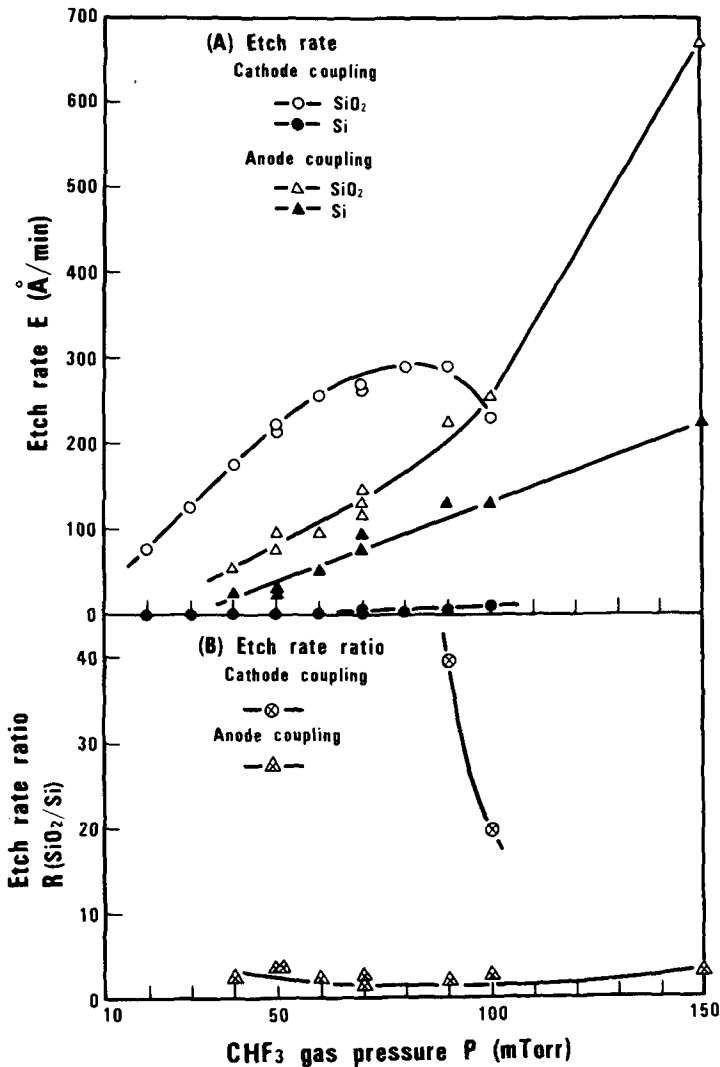


Fig. 3 Pressure dependences of (A) the etch rates of SiO<sub>2</sub> and Si and (B) the SiO<sub>2</sub>/Si etch rate ratio for both coupling modes.  $I_{rf} = 2.5$  A.

From the results described above, it has become clear that the etching characteristics of SiO<sub>2</sub> depend strongly on the coupling mode, and that the cathode coupling mode is

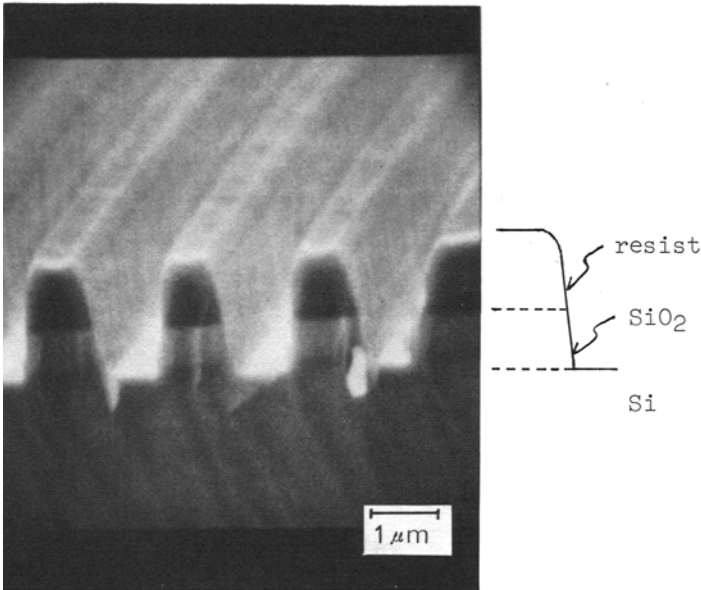


Fig. 4 Cross-sectional SEM image of  $\text{SiO}_2$  pattern with resist.

preferable to the anode mode to obtain high values for both the etch rate of  $\text{SiO}_2$  and the  $\text{SiO}_2/\text{Si}$  etch rate ratio. This fact suggests that the physical sputtering effect due to charged species is one of the key factors for etching  $\text{SiO}_2$  in the planar type plasma reactor as Coburn et al. believe (11).

In the etching of Si, however, the chemical reactions between Si and F radicals  $\text{F}^*$  are generally considered to play a main role. The life time of  $\text{F}^*$  is also supposed to be long. The high  $\text{SiO}_2/\text{Si}$  etch rate ratio obtained in the  $\text{CHF}_3$  gas plasma results primarily from the extremely low etch rate of Si, which might be caused by a low concentration of  $\text{F}^*$ . The low concentration of  $\text{F}^*$  in a  $\text{CHF}_3$  plasma probably result from the existence of  $\text{F}^*$  scavenging species such as hydrogen atoms or ions.

#### Etching Characteristics with Cathode Coupling Mode



The cathode coupling mode has been shown, in the previous section, to be preferable to that of the anode coupling mode for the selective etching of SiO<sub>2</sub> on Si. The etching characteristics of SiO<sub>2</sub> and Si with the cathode coupling mode, therefore, were investigated in more detail under various etching conditions.

The rf current dependences have already been described in the previous section (Fig. 2). The electrode separation of 20 mm gives almost the same characteristics as that of 40 mm did in Fig. 2.

Fig. 5 shows the pressure dependences of the etch rates of SiO<sub>2</sub>, Si and photoresist (A) and the SiO<sub>2</sub>/Si and SiO<sub>2</sub>/resist etch rate ratios (B). The data for 2.5 A are replotted from Fig. 3. In the range below 70 mTorr, as pointed out in Fig. 3, the etch rates of SiO<sub>2</sub> increase almost linearly as the pressure increases, while the etch rates of Si are nearly zero with the rf currents of 2 and 2.5 A, which makes the SiO<sub>2</sub>/Si etch rate ratio very large. In the case of 3 A, the etch rate of Si is also small and almost constant at about 15 Å/min up to the pressure of 70 mTorr and tends to increase with increasing pressure from this value. This results in the SiO<sub>2</sub>/Si etch rate ratio that has a maximum value around 60 mTorr as shown in Fig. 5(B). The scattering of the data above this pressure results from a variation in the etch rate of Si. The increase in the etch rate of SiO<sub>2</sub> begins to decrease gradually in the range from 50 to 70 mTorr, and then the etch rates decrease rapidly after passing the maximum values. The maximum value shifts to higher pressures as the rf current increases. The decrease in the etch rate is caused by the deposition of polymer which masks the surface of the wafer. Furthermore, in this region, the reproducibility is so poor that the data scatter in the range between the two dotted lines for each curve. This is considered to result from a relatively large variation in the rate of polymer deposition produced by small fluctuations in the discharge conditions. The etch rates of photoresist films are also small but increase with the pressure increased and then decrease slowly after reaching the maximum rate at about 60 mTorr. The SiO<sub>2</sub>/resist etch rate ratio tends to increase with the pressure increased.

The dependence of the etch rates of both SiO<sub>2</sub> and Si on the gas flow rate is shown in Fig. 6. The etch rate of SiO<sub>2</sub> increases with increasing flow rate in the range below 10 sccm

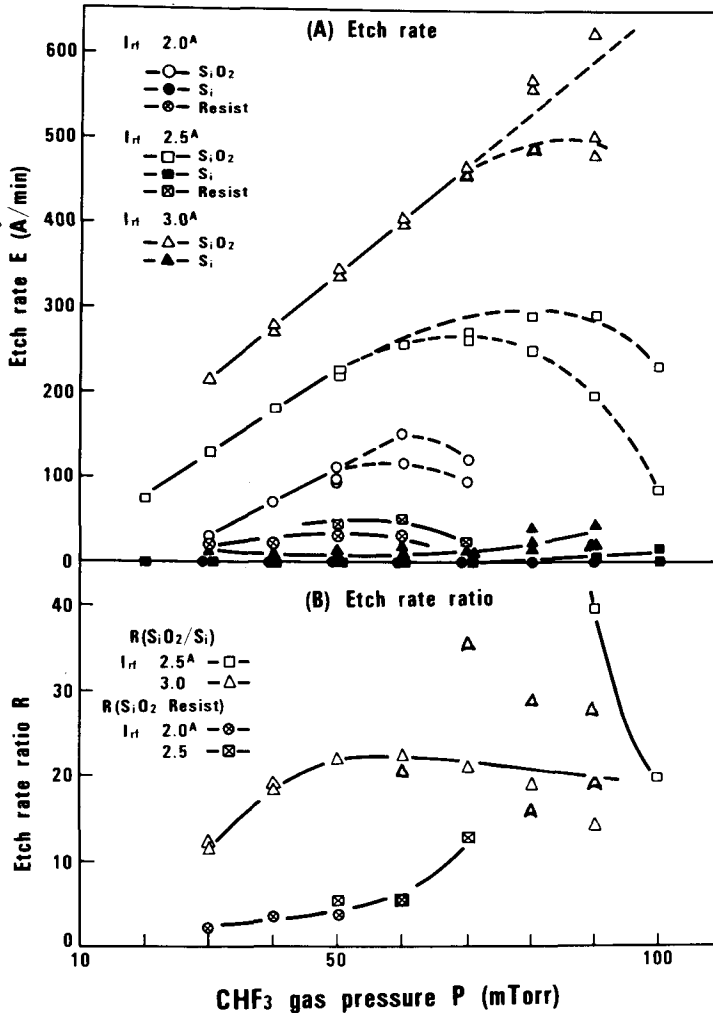


Fig. 5 Pressure dependences of (A) the etch rates of SiO<sub>2</sub>, Si and resist and (B) the SiO<sub>2</sub>/Si and SiO<sub>2</sub>/resist etch rate ratios.

and is kept constant in the higher range. That is, under the conditions of this experiment, the etching of SiO<sub>2</sub> is limited by the supply rate of the etchant gas in range of the gas flow rate below 10 sccm, and above this value it is limited by the reaction rate. In the case of the gas pressure of 60

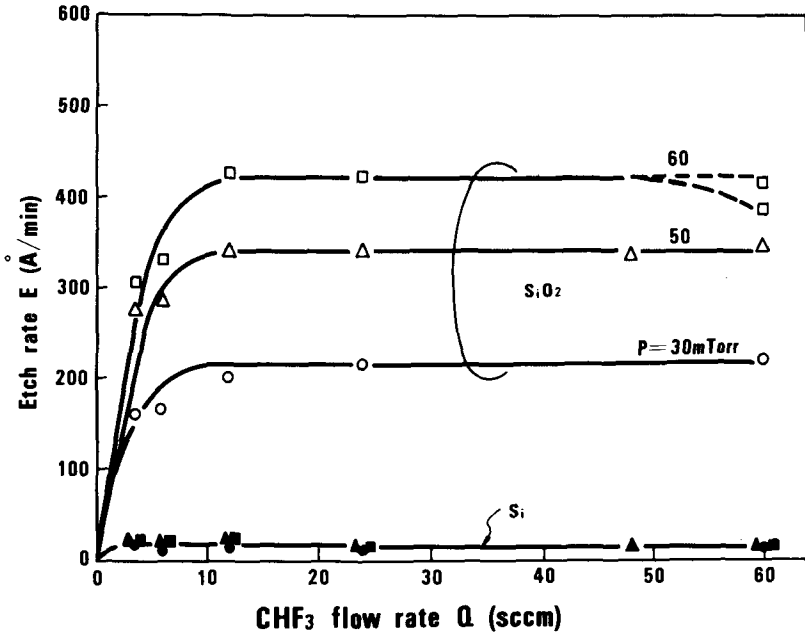


Fig. 6 Etch rates of SiO<sub>2</sub> and Si as the functions of the gas flow rate.  $I_{rf} = 3$  A.

mTorr, the etch rate of SiO<sub>2</sub> tends to decrease and scatter around 60 sccm. This is also caused by the polymer deposition masking the surface. The etch rates of Si are too small (10 ~ 30 A/min) for us to discuss about the mechanism limiting them.

Fig. 7 shows the dependences of the etch rates of both SiO<sub>2</sub> and Si on the electrode separation. The etch rate of SiO<sub>2</sub> decreases slowly with an increase in the electrode separation. This reduction might be caused by the decrease in the plasma density which results from the electric field divergence due to the increase in the electrode separation. The etch rates of Si are small but show somewhat similar dependences to those of SiO<sub>2</sub>.

#### Deterioration of Photoresist Film

Table I summarizes the results of the deterioration of

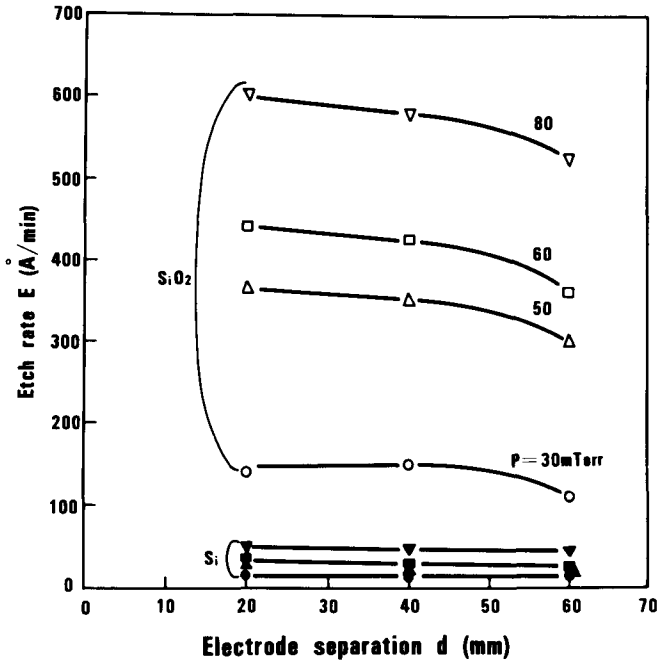


Fig. 7 Etch rates of SiO<sub>2</sub> and Si as the functions of the electrode separation.  $I_{rf} = 3$  A.

AZ-photoresist films on SiO<sub>2</sub> after etching for 10 min under various etching conditions. The samples were postbaked in N<sub>2</sub> gas for 30 min at the temperature of 130°C. In this table, the degree of deterioration is classified by 4 kinds of symbols, from a circle to a double X. The circle indicates "no deterioration", and the double X does "hard deterioration" which means that the photoresist film can not be removed by the treatments both in the O<sub>2</sub> plasma and in the acid solution. It is found from Table I that the deterioration of the photoresist film is lighter with the cathode coupling mode than with the anode one under the same etching condition. The deterioration becomes lighter as the rf current or the gas pressure decreases.

The typical aspects of the deterioration of the photoresist film on SiO<sub>2</sub> are shown in Fig. 8 for the cathode (A) and the anode (B) coupling mode. The sample were etched in

Table I Degree of deterioration of photoresist films on SiO<sub>2</sub>.

Gas pressure	Coupling mode		Cathode coupling		Anode coupling	
	RF current	2.0A	2.5A	3.0A	2.0A	2.5A
20 mflorr		o				
30		o	o	o		
40		o	o	Δ, o	o	Δ
50		o	o	Δ	o	Δ
60		o	o	Δ	Δ, o	Δ
70		o	Δ, o	Δ	Δ	Δ
80		o	Δ	Δ	Δ	Δ
90		o	Δ	Δ	Δ	x
100		o	Δ		Δ	x
130					Δ	
150					x	xx

	O <sub>2</sub> plasma	acid solution
o	good removal	good removal
Δ	good removal	good removal
x	residue	good removal
xx	no removal	no removal

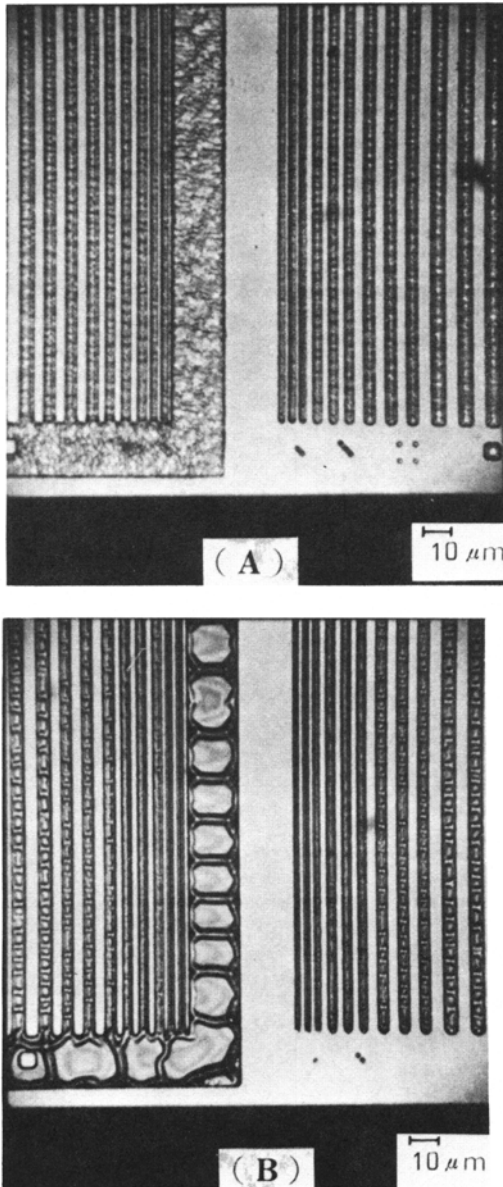


Fig. 8 Photographs of the deterioration of photoresist films on SiO<sub>2</sub> after etching with the cathode (A) and the anode (B) coupling mode.

the period of 10 min, with the rf current of 3 A at the pressure of 60 mTorr for the cathode coupling mode, and with 2.5 A at 50 mTorr for the anode one. In Fig. 8, we can find some differences in the aspect between two coupling modes. With the cathode coupling mode, the deterioration of the photoresist film seems to be caused by the ion sputtering which causes the direct hardening of the photoresist film due to the physical bombardment. With the anode coupling mode, however, the deterioration seems to result from the photoresist film being softened by the temperature rise of a surface of the wafer, which is followed by a hardening due to rise in the temperature. Therefore, the deformation of the photoresist relief is smaller with the cathode coupling mode than with the anode one for the same degree of deterioration.

### Conclusions

In this paper, the etching characteristics of SiO<sub>2</sub> have been investigated by using CHF<sub>3</sub> as the etchant gas and the planar type plasma reactor. This study has clarified that the cathode coupling mode is preferable to the anode one to obtain high values for the etch rate of SiO<sub>2</sub> and for both of the SiO<sub>2</sub>/Si and the SiO<sub>2</sub>/resist etch rate ratio. The typical data obtained in the cathode coupling mode are 250 A/min and more than 100 for the etch rate of SiO<sub>2</sub> and the SiO<sub>2</sub>/Si etch rate ratio, respectively. The etching of SiO<sub>2</sub> in the CHF<sub>3</sub> gas plasma with the cathode coupling mode is capable of a good transfer from the mask to the etched pattern. The cathode coupling mode also brings about the lighter deterioration of photoresist films.

The etching mechanism is not yet clear, but it has been shown that the sputtering effects due to ions play an important role in the etching of SiO<sub>2</sub>. It is also believed that the additional scavenging species for fluorine radicals, which are localized near the cathode surface, suppress the concentration of fluorine radicals in the region close to the cathode. This results in the extremely low etch rate of Si for the cathode coupling mode.

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