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Microwave Plasma Etching of Silicon with CF_4, F_2 and SF_6

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Silicon is etched in CF_4, F_2 and SF_6 microwave plasma. Also, it is etched with a sulfur plate positioned outside F_2 plasma. The etched surfaces are analyzed with x-ray photoemission spectroscopy. The Si etching mechanism is discussed in terms of the experimental results. Adsorption of hydrocarbon compounds and oxygen onto the Si surface prevents Si etching. Sulfur atoms inhibit surface oxidation and promote Si etching. One of the reasons a high etch rate of Si can be achieved by SF_6 plasma is that sulfur atoms contained in SF_6 inhibit surface oxidation.

I. Introduction

Plasma etching is a key technology for fabrication of semiconductor integrated circuits. However, it is becoming difficult for conventional plasma etching techniques to satisfy production process requirements, as packing density of integrated circuits increases.

The microwave plasma etching technique which was developed by the authors allows submicron pattern delineation with minimal surface damage and contamination.[1-3] Studies on the etching mechanism are required for further improvement and development of this technique.

In this study, silicon is etched in CF_4, F_2 and SF_6 microwave plasma, and the etched surface is analyzed with x-ray photoemission spectroscopy (XPS). Then, the silicon etching mechanism is discussed in terms of the experimental results.

II. Experiments

An apparatus used in the experiments is schematically shown in Fig. 1.[4] The reaction and the transfer chamber were evacuated with turbo-molecular pumps down to 2.7×10^{-4} Pa and 4.0×10^{-6} Pa, respectively. An ion pump was employed to evacuate the surface analysis chamber in which a pressure was kept around 6.7×10^{-8} Pa.

Silicon sample ((100) p-type 14-20 Ωcm) was etched in CF_4, F_2 and SF_6 microwave plasma. After evacuation, each gas was introduced into the reaction chamber at pressures between 5.3×10^{-2} Pa and 6.7×10^{-2} Pa. Corresponding flow rates of these gases were 5-6, 8-10 and 2-3 sccm, respectively. The sample was etched for 10-20 minutes at an input power of 130-200 W. The method for generating the microwave plasma is the same as reported previously.[3] Either a quartz or an alumina discharge tube was used for generating the plasma. The inpurity concentration in the quartz was less than 20 ppm, and that in the alumina was 1%.

In order to clarify the effect of sulfur atoms in Si etching, Si was etched with a sulfur plate positioned outside F_2 plasma. The sulfur plate was made by heating (120°C) and melting crystal granular sulfur (of 99.9999% purity) in a stainless steel vessel in air.

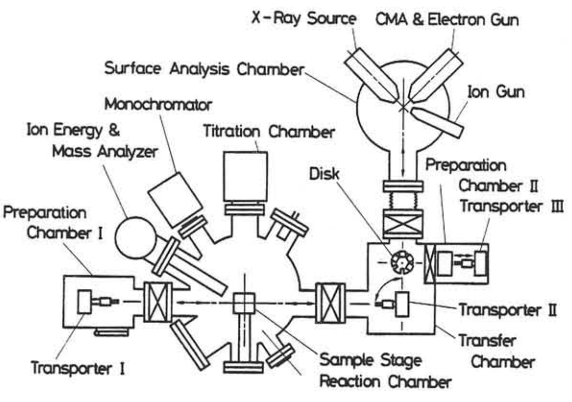

Fig. 1 Schematic diagram of microwave plasma etching and surface analysis system.

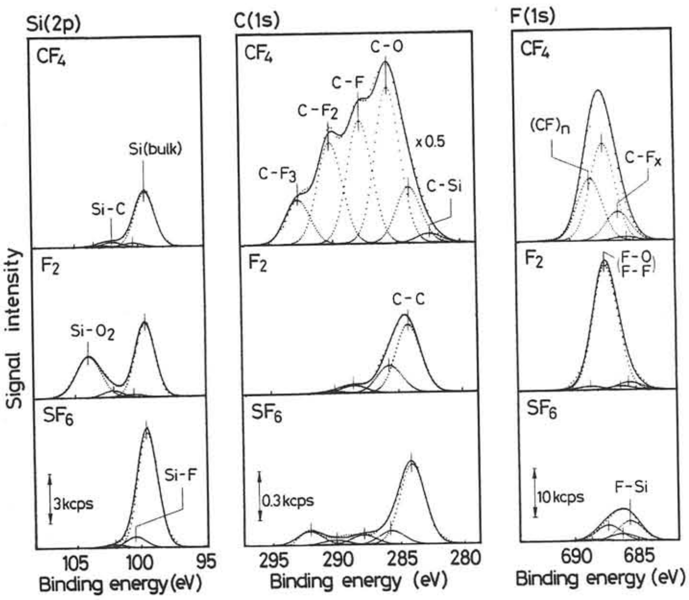

Fig. 2 Si(2p), C(1s) and F(1s) XPS spectra of Si surface etched in CF_4, F_2 and SF_6 microwave plasma with a quartz discharge tube. Each spectrum is deconvoluted into peaks representing chemical bonds related to the spectrum.

For XPS analysis, the etched sample was transferred in ultra-high vacuum to the surface analysis chamber. The MgKα line at 1253.6 eV was used as the exciting x-ray, and the pass energy of a cylindrical mirror type analyzer (CMA) was 50 eV. The CMA resolution was about 1.7 eV. The CMA was calibrated with the Si(2p) peak at 99.4 eV.

Fluorine atom concentration in the plasma was measured with gas phase titration and spectroscopic methods. The former method was reported previously.[5] In the latter method, after a small amount of Ar (2% of the discharge pressure) was added into the discharge, the ratio between emission intensities of excited F and Ar atoms was measured.[6] Wavelengths used for these observations were 685.6 nm for the F atom and 750.4 nm for the Ar atom. The emission spectra were observed with a monochromator through a quartz window.

III. Results

Silicon was etched at 6.7 x 10^{-2} Pa in CF_4, F_2 and SF_6 microwave plasma by using the quartz discharge tube. Figure 2 shows Si(2p), C(1s) and F(1s) XPS spectra of the etched surface. A large amount of CF_n compound is adsorbed onto the surface etched in CF_4 plasma. The SiO_2 peak is observed for the surface etched in F_2 plasma. On the other hand, the C(1s) and the F(1s) peak intensities are rather small, and no SiO_2 peaks are observed for the surface etched in SF_6 plasma.

The dependence of Si etch rate on the F_2 flow rate is shown in Fig. 3. Here, the quartz and the alumina discharge tubes are employed. When the alumina discharge tube is used, the Si etch rate is more than 4 times as large as that obtained with the quartz discharge tube.

The XPS measurement was carried out to explain the large difference between the Si etch rates in Fig. 3. Figure 4 shows Si(2p) and O(1s) spectra of Si etched in F_2 plasma by using the alumina (A) and the quartz (B) discharge tubes. The amount of O atom adsorbed onto the surface is considerably reduced when the alumina discharge

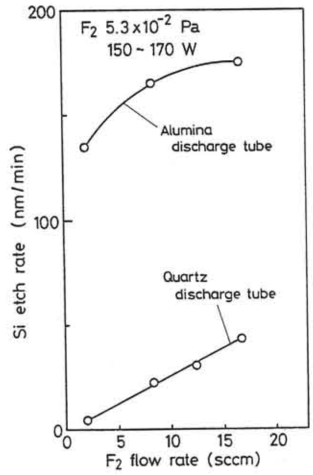

Fig. 3 Dependence of Si etch rate on F_2 flow rate. Alumina and quartz discharge tubes are used in etching.

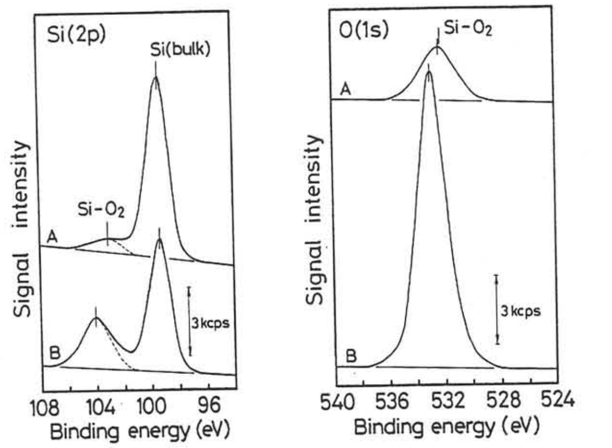

Fig. 4 Si(2p) and O(1s) XPS spectra of Si surface etched in F_2 plasma by using alumina (A) and quartz (B) discharge tubes.

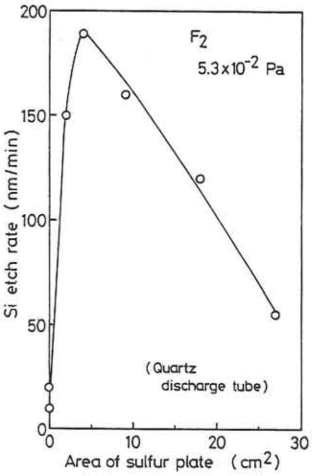

Fig. 5 Dependence of Si etch rate on the area of sulfur plate.

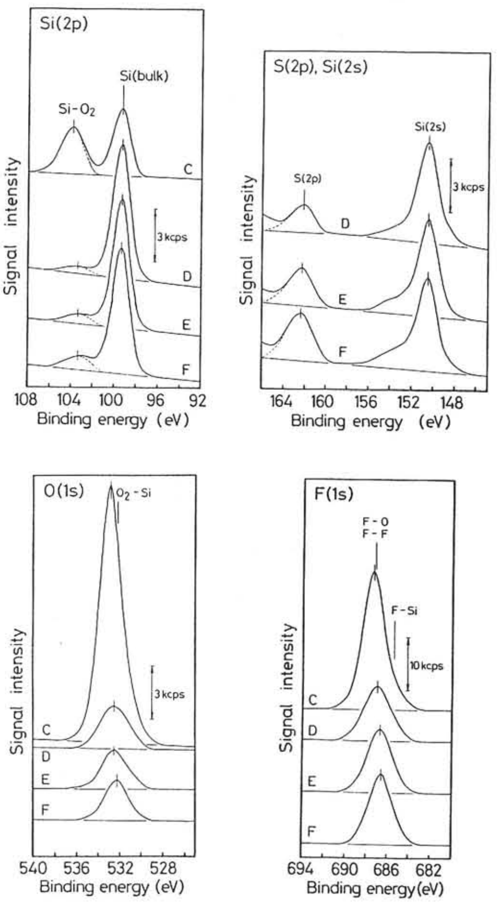

Fig. 6 Changes in Si(2p), S(2p), O(1s) and F(1s) XPS spectra with the increase in the area of sulfur plate. A quartz discharge tube is used in etching. The sulfur plate has the different area in the spectra C-F: C: 0 cm^2, D: 3 cm^2, E: 9 cm^2 and F: 27 cm^2.

tube is used. The SiO_2 peak height decreases rapidly at the same time.

For investigating the role of S atoms contained in SF_6, Si was etched with a sulfur plate positioned outside F_2 plasma. The quartz discharge tube was used in the etching. The dependence of Si etch rate on the area of the sulfur plate is shown in Fig. 5. The Si etch rate increases rapidly with an increase in the plate area, and then, decreases rather slowly. Especially, the etch rate at 4 cm^2 is about 10 times as large as that obtained without the sulfur plate.

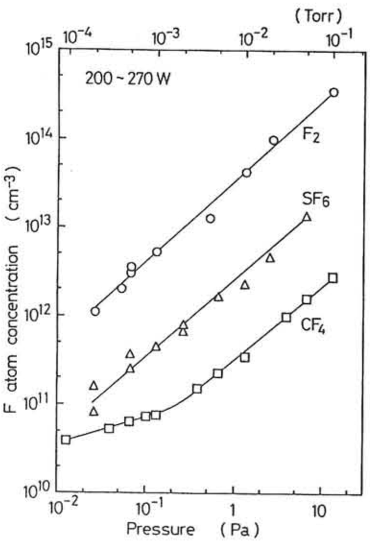

Fig. 7 Pressure dependences of F atom concentration in CF_4, F_2 and SF_6 plasma.

Figure 6 shows the chemical change in the etched Si surface caused by the sulfur plate, which has a different area with respect to spectra C-F: C: 0 cm^2, D: 3 cm^2, E: 9 cm^2 and F: 27 cm^2. The amount of O atom adsorbed onto the surface decreases rapidly from C to D. The SiO_2 peak height is reduced at the same time. In addition, the S(2p) peak intensity increases and the F(1s) peak shifts towards the lower binding energy position as the area of the sulfur plate is increased.

Fluorine atom concentration in plasma was measured with the method mentioned in the preceding section. The pressure dependences of the F atom concentration are shown in Fig. 7. For example, the concentrations for CF_4, F_2 and SF_6 plasma are about 7×10^{10}, 3×10^{12} and 3×10^{11} cm^{-3}, respectively, at 6.7×10^{-2} Pa.

IV. Discussion

Many atomic or molecular species are adsorbed onto the etched Si surface. If we use a model in which these adsorbed surface species make a thin surface layer stoichiometrically different from

Table I Comparison of CF_4, F_2 and SF_6 microwave plasma etching of silicon.

Etching gas	Surface layer thickness (nm)	Number of atoms			Etch rate (nm/min)
		$Si(SiO_2)$	Carbon	Fluorine	
CF_4	1.3	1.0 (0.02)	21.3 (0.43)	23.8 (0.48)	8
F_2	0.9	8.8 (0.26)	1.3 (0.04)	11.4 (0.34)	20
SF_6	0.2	0 (0)	1.7 (0.19)	3.1 (0.35)	250

Number of atoms is a relative value.
The figures in parentheses are relative atomic densities in each surface layer.

the bulk material, surface layer thickness and the number of atoms in the layer can be estimated from XPS spectra obtained.[4)]

The values calculated from the spectra shown in Fig. 2 are summarized in Table I, along with the corresponding Si etch rates. The etch rate by CF_4 plasma is about one-thirtieth as large as that by SF_6 plasma. One of the reasons only small etch rate can be obtained by CF_4 plasma is in the thick surface layer consisting mainly of CF_n compounds (Fig. 2). These compounds prevent Si etching due to surface recombination reactions with F atoms impinging to the surface.[6)] Another reason is in the low F atom concentration in the plasma (Fig. 7).

It is expected, from the F atom concentration, that the highest Si etch rate would be obtained by F_2 plasma. However, the measured etch rate is much lower than that by SF_6 plasma. As shown in Fig. 2, the largest difference between the surfaces etched in F_2 and SF_6 plasma is in surface oxidation: the relative density of Si bonded to O atoms is 0.26 with respect to the surface etched in F_2 plasma (Table I).

As shown in Fig. 4, surface oxidation is considerably reduced by using the alumina discharge tube, which is not subject to etching by fluorine-containing plasma.[7)] This indicates that surface oxidation by F_2 plasma (Fig. 2) is caused mainly by O atoms resulting from etching of the quartz discharge tube. The etch rate obtained with the alumina discharge tube is much larger than that obtained with the quartz one (Fig. 3). It is concluded, therefore, that surface oxidation strongly inhibits Si etching.

When a small sulfur plate is placed in the reaction chamber and Si is etched in F_2 plasma, the etch rate increases rapidly from 20 nm/min to 180 nm/min (Fig. 5). According to the above discussion, the main reason for this increase in the etch rate is a reduction of surface oxidation (Fig. 6). Sulfur atoms from the sulfur plate seem to have roles of decreasing O atom concentration in the plasma and removing O atoms from the Si surface. It is concluded that S atoms have inhibitive action towards the surface oxidation and promote Si etching. One of the reasons a high etch rate of Si can be achieved by SF_6 plasma is that S atoms contained in SF_6 prevent surface oxidation. Other reasons are relatively high F atom concentration in the plasma (Fig. 8) and little formation of CF_n compounds on the surface.

V. Conclusion

Silicon is etched in CF_4, F_2 and SF_6 microwave plasma. In addition, it is etched with a sulfur plate positioned outside F_2 plasma. Then, the etched surface is analyzed with XPS. The Si etching mechanism is discussed in terms of these experimental results. As a result, it is shown that adsorption of hydrocarbon compounds and oxygen onto the Si surface prevents Si etching. It is also revealed that S atoms have an important role of preventing surface oxidation and promoting Si etching. One of the reasons a high etch rate can be obtained by SF_6 plasma is that S atoms contained in SF_6 inhibit surface oxidation.

References
1) K. Suzuki et al., Proceedings of the International Ion Engineering Congress (Institute of Electrical Engineers of Japan, Kyoto, 1983), pp. 1645.
2) S. Nishimatsu et al., Proceedings of the 1982 Dry Process Symposium (Institute of Electrical Engineers of Japan, Tokyo, 1982), pp. 11.
3) K. Suzuki et al., J. Electrochem. Soc. 126, 1024(1979).
4) K. Ninomiya et al. (to be published).
5) K. Ninomiya et al., Jpn. J. Appl. Phys. 22, 139(1983).
6) K. Suzuki et al., J. Electrochem. Soc. 129, 2764(1982).
7) J. W. Coburn and M. Chen, J. Vac. Sci. Technol. 18, 353(1981).