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Directional etching of Si with perfect selectivity to SiO_2 using an ultraclean electron cyclotron resonance plasma

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Using a newly developed ultraclean electron cyclotron resonance plasma etcher, Si wafers masked by SiO_2 were etched with a chlorine plasma at pressures of 0.6–4.0 mTorr with a microwave power of 300–700 W. Ultraclean processing under a low ion energy condition at high pressures has revealed that there is an induction period during which time there is no SiO_2 etching. This is not observed with Si. During the induction period, perfectly selective etching for Si to SiO_2 has been achieved. Under this perfectly selective condition, anisotropic tenth micron patterns of polycrystalline silicon have been obtained with little undercut.

Highly selective dry etching is very important for ultralarge scale integration (ULSI) fabrication, as is anisotropic etching. As a candidate to realize both high selectivity and high anisotropy, electron cyclotron resonance (ECR) plasma etching is attractive because it is characterized by low ion energy for low damage, long mean free paths for high anisotropy, and a cathodeless discharge for low contamination.[1,2] However, so far perfect selectivity and high anisotropy have not been realized at the same time. Anisotropic etching has usually been performed by sidewall protection chemistries and/or rf biasing technique.[3–5] Such techniques should reduce selectivity, since the remaining impurities mask the intrinsic chemical properties of the materials surface and/or the kinetic energy of the incident ions is increased by rf bias. In order to perform highly selective etching, it is important that the intrinsic chemical reaction between the material surface and the plasma proceeds without native oxidation, chemical contamination, and plasma damage.

In the present work, an ultraclean ECR apparatus was newly developed, and selective etching characteristics for Si to SiO_2 were investigated. As a result of an ultraclean processing under a low ion energy condition, directional etching of Si with perfect selectivity to SiO_2 has been realized with a chlorine plasma.

The newly developed ultraclean ECR plasma apparatus is schematically shown in Fig. 1. Although the shapes of the plasma generating chamber and the etching chamber are similar to those of the conventional type,[1] the wafer is held vertically by an electrostatic chuck system[6] to minimize unexpected particle contamination of wafers. The chambers are made of 316L stainless steel, and the inside surfaces of the chambers were processed using an electromechanical polishing technique in order to make the chambers particle-free and outgas-free. An oil-free turbomolecular pump system is employed. An ultimate vacuum of about 5×10^{-9} Torr, measured by a Seiko MIC gauge, was obtained. All gases were supplied by an ultraclean gas delivery system, which was compactly constructed by the introduction of block valves and which is bakable for outgasing.[7] The etching wafer and the plasma generating chamber, which can be biased separately, were electrically floating in the present work. The wafer susceptor was cooled by water to avoid a temperature increase of the wafers due to the plasma exposure.

As an etching gas, highly purified chlorine was used at a flow rate of 3–50 sccm. The etching pressure was 0.6–4.0 mTorr, which was controlled by the gas flow rate and a variable conductance valve, and measured with an MKS Baratron guage. The microwave power used to generate plasma was 300–700 W.

The substrates used were *p*-type Si wafers of 3–8 Ω cm with mirror-polished (100) surfaces as well as polycrystalline silicon films deposited on SiO_2 films. To compare the

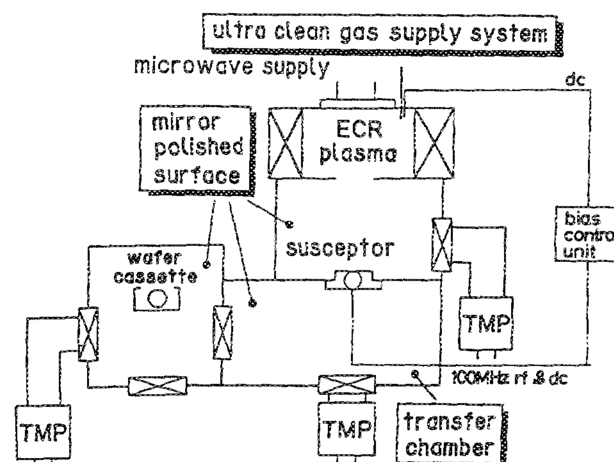

FIG. 1. Schematic diagram of the newly developed ultraclean ECR plasma etching system.

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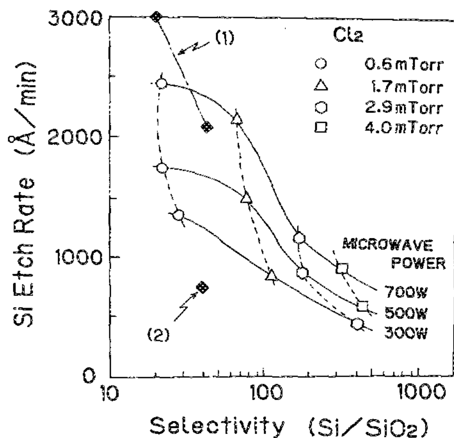

FIG. 2. Relationship between the etch rate of Si and the selectivity for Si to SiO_2 with microwave power and pressure as parameters. (○△○□) present results for Si(100). (1) Data by Ehata *et al.* (see Ref. 4) for polycrystalline silicon with a microwave power of 900 W and the rf bias of 10–20 W. (2) Data by Takashashi *et al.* (see Ref. 8) for Si with the microwave power of 400 W and floating bias, using a microwave mode transducer.

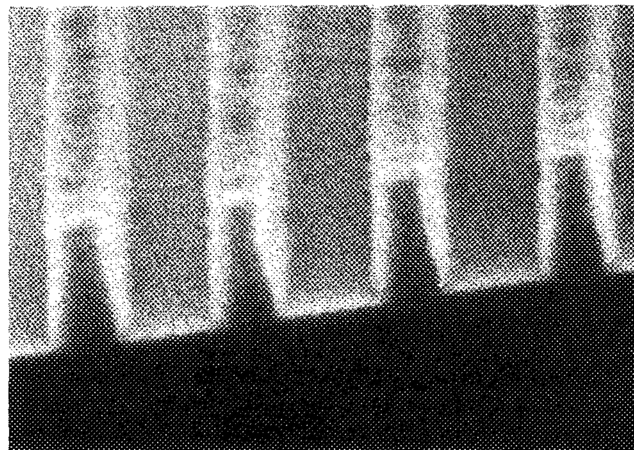

FIG. 4. Anisotropic etch profile of polycrystalline silicon masked by SiO_2 obtained under the perfect-selectivity condition with an etching pressure of 4.0 mTorr, a Cl_2 gas flow rate of 50 sccm, and a microwave power of 700 W.

etching characteristics of Si with those of SiO_2, the substrates were thermally oxidized and the oxide was locally removed. After cleaning the samples in a H_2SO_4-H_2O_2 solution, the native oxide on the surfaces was removed by etching in a dilute HF solution before plasma etching. The etched thickness of SiO_2 was determined by the difference before and after etching, using a Shimazu automatic ellipsometer. The etched thickness of Si was measured by a Tencor Alpha Step 200.

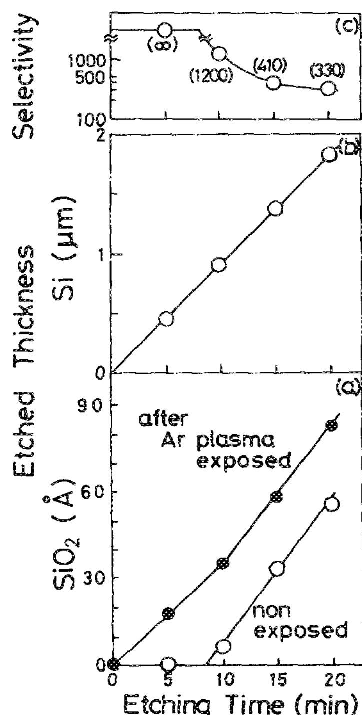

FIG. 3. Etching time dependence of the etched thickness of (a) SiO_2 and (b) Si, as well as (c) selectivity at 4.0 mTorr with a microwave power of 700 W. The closed circles in (a) show the results with Ar plasma pre-exposure for 1 min at 0.7 mTorr.

Figure 2 shows the characteristic relationship between the etch rate of Si and the selectivity for Si to SiO_2 with the microwave power and the pressure as parameters. The selectivity shown was calculated for the samples with etching times of 3, 10, 10, and 20 min for 0.6, 1.7, 2.9, and 4.0 mTorr, respectively. Although the selectivity depends on etching time as described below, a general tendency of the etching characteristics can be seen in the figure. There are etching conditions at higher pressures where the selectivity exceeds a few hundred, although the etch rate of Si decreases; a higher microwave power raises the Si etch rate with only a small decrease in the selectivity. Compared with reported data (closed symbols in Fig. 2) obtained using rf bias[4] and a microwave mode transducer[8] for etching enhancement, the present results obtained without these additional techniques have very good performance, especially high selectivity.

Under the condition with high selectivity at high pressures, an induction period was found only for SiO_2. Typical results are shown as open circles in Fig. 3. As the wafer is exposed to the chlorine plasma, the Si etch proceeds without any induction period. On the other hand, the SiO_2 does not etch for the first 8 min, and then starts at a constant rate. During this delay time, the Si is etched about 7000 Å with perfect selectivity. Figure 3 also shows that nominal selectivity decreases with time.

Generally in the higher pressure region, the radical etching process, which forms isotropic etch profiles, becomes dominant. However, under the etching condition with perfect selectivity, anisotropic etch profiles of polycrystalline silicon with tenth micron patterning are obtained, as shown in Fig. 4. This means that the ion incident process, not the radical etching, dominates the etching of Si in the present condition.

The effects of contamination on selectivity and the etching delay of SiO_2 were examined. It was found that the additions of CCl_4 (0.3 sccm) and of H_2(0.2 sccm) to Cl_2 (50 sccm) at 4.0 mTorr shorten the delay time to about 3 and 7

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min, respectively, from about 8 min in the pure Cl_2 case. On the other hand, the addition of O_2 (0.2 sccm) did not change the delay. These results suggest that the SiO_2 surface is deoxidized and the chemical reaction is enhanced by deoxidizing species such as C and H, although not by oxidizing species like O. The etching rate of Si was not influenced significantly by these additions.

Another factor affecting the SiO_2 etching is bombardment by ions with some kinetic energy. It is known that the ion energy is a few tens eV and higher at lower pressures in the ECR system.[4,9] It is considered that ions in this energy range are active enough not only to desorb the surface adsorbates but also to damage the surface layers.[10] Therefore, in order to investigate the effects of the ion bombardment on the SiO_2 etch, the samples were exposed to Ar plasma at a low pressure (0.7 mTorr) for 1 min, and then etched with chlorine plasma at a higher pressure (4.0 mTorr). The results are shown as closed circles in Fig. 3(a). The exposure of the wafer to the Ar plasma does not etch the SiO_2. After the exposure to the Ar plasma, SiO_2 is etched by the chlorine plasma without any time delay. The etch rate of SiO_2 is slightly less than the steady-state etch rate observed without Ar plasma exposure. The etching of Si was not affected by the Ar plasma exposure. From these results, it is concluded that the high-energy ion incidence enhances the following reaction of SiO_2 with chlorine plasma through the damage introduced onto the SiO_2 surface and/or the desorption of some surface adsorbates.

In conclusion, directional etching of Si with perfect selectivity to SiO_2 has been realized using a newly developed ultraclean ECR plasma etcher. Exposure to an ultraclean chlorine plasma has revealed an SiO_2 etching time delay and perfectly selective etching of Si. This perfectly selective etching is dominated by ion incidence, and anisotropic tenth micron patterning of polycrystalline silicon has been obtained with little undercut. It was found that the etching delay of SiO_2 is suppressed by deoxidizing impurity contamination such as CCl_4 and H_2 as well as by pre-exposure of lower pressure Ar plasma through damage introduced onto SiO_2 surface and/or desorption of some surface adsorbates.

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