Self-limited layer-by-layer etching of Si by alternated chlorine adsorption and Ar⁺ ion irradiation

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We report the observation of self-limited layer-by-layer etching of Si by alternated chlorine adsorption and low energy Ar⁺ ion irradiation using an ultraclean electron-cyclotron-resonance plasma apparatus. The etch rate per cycle increased with the chlorine supplying time and saturated to a constant value of about 1/2 atomic layer per cycle for Si(100) and 1/3 for Si(111), which was independent of the chlorine partial pressure in the range of 1.3–6.7 mPa. These results indicate that etching was determined by self-limited adsorption of chlorine. Moreover, the chlorine adsorption rate was found to be described by a Langmuir-type equation with an adsorption rate constant $k=83$ and 110 $(Pa\ s)^{-1}$ for Si(100) and Si(111), respectively.

Silicon layer-by-layer processing with atomic order precision is extremely important for the fabrication of novel semiconductor devices. A self-limited mechanism usually gives a constant and stable value of process parameters automatically determined by the thermodynamical saturation condition. Therefore, the mechanism is essential to precision as well as to uniformity in thickness control by the layer-by-layer process with a large margin of process conditions. Layer-by-layer deposition of Si by Langmuir-type self-limited adsorption of SiH_4 was recently achieved by flash heating chemical vapor deposition.[1] An effort for digital etching of Si carried out at $-110\,°C$ was reported, where the etch rate depended on the exposure of substrates to a supplied fluorinated plasma.[2] Therefore, no self-limited mechanism has yet been reported in Si etching prior to the present work. In the present letter, chlorine adsorption on Si in combination with alternated irradiation of low energy Ar⁺ ions has been investigated and a self-limited mechanism has been found in layer-by-layer etching at room temperature.

Ultraclean electron cyclotron resonance (ECR) plasma processing with chlorine was applied in order to suppress contamination.[3] The details of the ECR apparatus were described elsewhere.[3] The substrates used were n-type Si(100) and (111) wafers with patterned thermal SiO_2 films on the surface as a mask. Wafers were wet cleaned in a H_2SO_4-H_2O_2 solution, dipped in diluted HF, and rinsed with deionized (DI) water just before loading into the ECR apparatus. The wafer susceptor was cooled with water. The Ar⁺ ion was cyclically irradiated onto the wafer by opening and closing the shutter in front of the wafer. The substrate temperature was 25 °C just before etching, and during the layer-by-layer etching it was elevated up to ~100 °C, which was much lower than that in the case of continuous Ar⁺ ion irradiation,[4] where it was 25–~200 °C. The shutter was operated within a moving time less than 0.05 s by high pressure air and a set of vacuum-seal mechanism. Chlorine gas was supplied continuously or

synchronously with the shutter motion into the etching chamber, which was separated by a plate with a 100 mm$^\phi$ window from the ECR plasma generating chamber where Ar gas was introduced. Energy of Ar⁺ ions measured by an electrostatic analyzer[5] at the wafer position was ~10 eV at the peak and the tail extended for ~ ±8 eV at 0.35 Pa in the present condition.

Figure 1 shows the dependence of the average etch rate per cycle (R_{pc}) on the chlorine partial pressure (p_{cl}) with cyclicly opening and closing the shutter in continuous chlorine supply, where R_{pc} is defined as the total etched depth divided by the number of cycles. Without chlorine introduction [(●) and (▲) in Fig. 1], Ar⁺ ion irradiation scarcely etches Si. On the other hand, it does etch Si with chlorine introduction [(○) and (△) in Fig. 1], and R_{pc} in continuous chlorine supply has a linear relation to p_{cl}. R_{pc0} defined as the R_{pc} value extrapolated to $p_{cl}=0$ is finite, larger than those (●) and (▲) without chlorine introduction, and almost independent of the shutter opening time (t_{open}). Moreover, $[R_{pc}-R_{pc0}]$ is nearly proportional to t_{open}. These results indicate that R_{pc0} is mainly determined
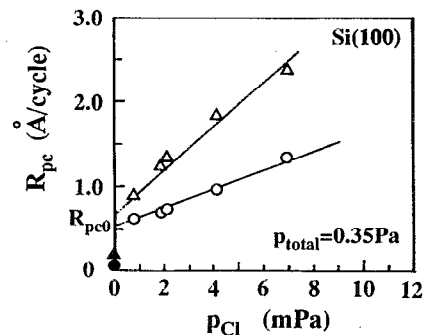

FIG. 1. Dependence of the etch rate per cycle (R_{pc}) on the chlorine partial pressure (p_{cl}) with continuous chlorine supply. The shutter closing time is 20 s and the shutter opening time is 0.2 (○) and 0.5 (△) s. (●) and (▲) indicate the data without chlorine supply.
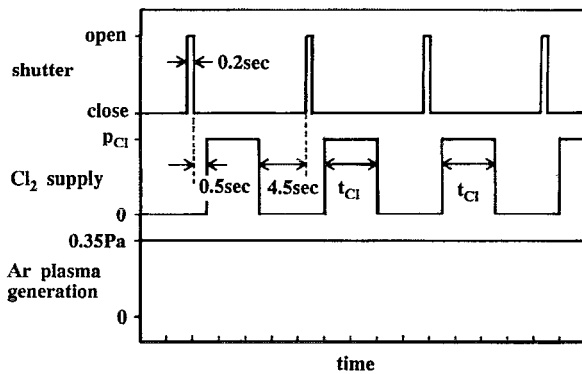
FIG. 2. Typical time sequence for the layer-by-layer etching process with synchronous chlorine gas supply. The shutter opening time was 0.2 s. Time necessary for chlorine gas introduction or substitution in the etching chamber was typically 0.5 s.

by saturated chlorine adsorption during the shutter closing time, while $[R_{pc} - R_{pc0}]$ is determined mainly by fresh chlorine adsorption during the shutter opening time. Therefore, suppression of chlorine supply onto the wafer surface during the shutter opening time is necessary for self-limited layer-by-layer etching.

Considering the above results, the layer-by-layer etching process with synchronous chlorine gas supply was determined. The typical time sequence is shown in Fig. 2. The chlorine supply was controlled synchronously with the shutter by a mass flow controller and stop valves. Time necessary for chlorine gas introduction or substitution in the etching chamber after the valves were switched on or off was typically 0.5 s. It was also confirmed from the ion current variation experiments that Ar^+ ions bombarding onto the surface during a shutter opening time of 0.2 s at a total pressure of 0.35 Pa are sufficient for layer-by-layer etching using the present ECR apparatus.

Figure 3 shows the dependence of R_{pc} on the synchronous chlorine supplying time (t_{cl}) for (a) Si(100) and (b) Si(111). R_{pc} increases with t_{cl} and saturates to a constant value of about 1/2 atomic layer per cycle (AL/C) for Si(100) [Fig. 3(a)] and about 1/3 AL/C for Si(111) [Fig. 3(b)] independently of the chlorine partial pressure studied. These results indicate that self-limited adsorption and etching occurs by using chlorine gas and Ar^+ ion exposure. The above saturation values may suggest that 2 and 3 adsorbed chlorine atoms may be necessary to etch one Si atom on an average for Si(100) and for Si(111), respectively, if the density of the adsorbed chlorine atoms is assumed to be the same as that of the surface Si atoms, because of the size of Cl and Si atoms. Further investigation is necessary and in progress about the Si crystal orientation dependence.

The time necessary for saturation depends on the chlorine partial pressure and is longer for Si(100) than for Si(111), as shown in Fig. 3. Assuming a simple Langmuir-type adsorption without desorption with a rate constant k, the layer-by-layer etch rate per cycle is given by

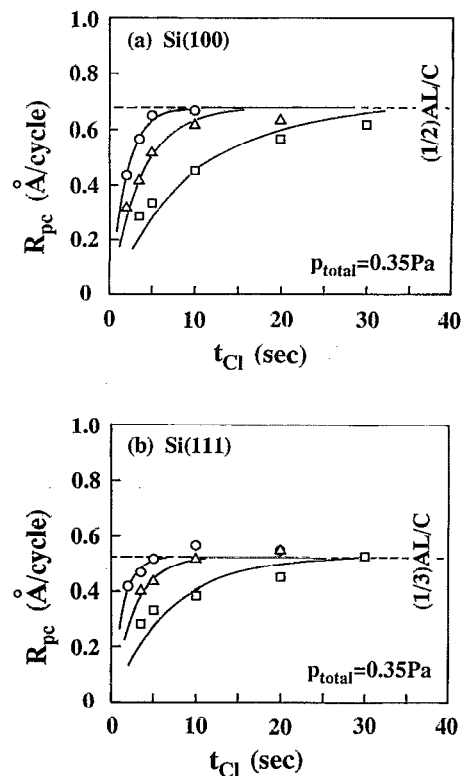$$R_{pc} = \text{constant} \ [1 - \exp(-kp_{cl}t_{cl})], \qquad (1)$$

FIG. 3. Dependence of the etch rate per cycle (R_{pc}) on the synchronous chlorine supplying time (t_{cl}) for (a) Si(100) and (b) Si(111). The solid curves are calculated from Eq. (1) using $k = 83$ and 110 (Pa s)$^{-1}$ for (100) and (111), respectively. $p_{cl} = 1.3$ (□), 3.3 (△), and 6.7 (○) mPa.

where it is also assumed that all the adsorbed chlorine atoms contribute to etching in a single opening of the shutter. The solid curves in Fig. 3 are calculated from Eq. (1) using $k = 83$ and 110 (Pa s)$^{-1}$ for Si(100) and Si(111), respectively. The calculated values are in excellent agreement with the experimental ones.

Figure 4 shows the etched profile of a Si substrate by the present method. Very fine patterns can be fabricated with almost no undercut by this technique. This indicates that the ion induced reaction is dominant and the chlorine radical etching is negligible in this layer-by-layer etching.

In conclusion, self-limited layer-by-layer etching of Si at room temperature has been realized by alternated chlorine adsorption and low energy Ar^+ ion irradiation using an ultraclean ECR apparatus. In the present method, etching has been determined by chlorine adsorption and the
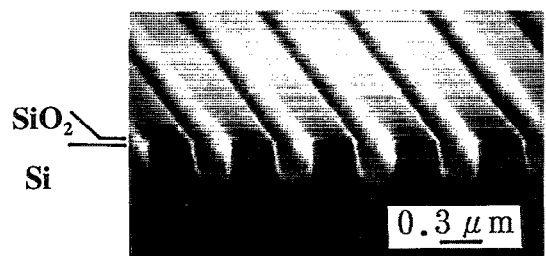

FIG. 4. Layer-by-layer etched profile of a Si substrate. Mask material is SiO₂ patterned by electron beam lithography.

saturated etch rate per cycle has been 1/2 atomic layer per cycle for Si(100) and 1/3 for Si(111). Furthermore, the chlorine adsorption rate has been described by a Langmuir-type equation with a rate constant $k=83$ and 110 $(Pa\ s)^{-1}$ for Si(100) and Si(111), respectively.

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