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Layer-by-Layer Etching of Si by Self-Limited Adsorption of Chlorine with Alternated Irradiation of Low Energy Ar^+ Ions

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Self-limited layer-by-layer etching of Si was achieved 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 $(Pa \cdot sec)^{-1}$ for Si(100) and Si(111), respectively.

1. INTRODUCTION

Layer-by-layer processing of Si with atomic order precision is extremely important for fabrication of novel Si-based semiconductor devices. In order to obtain precision as well as uniformity in thickness control by layer-by-layer process, a self-limited mechanism is essential, because it usually gives constant and stable process automatically determined by the thermodynamical saturation condition. Thus, the mechanism results in a large margin of process conditions.

Layer-by-layer deposition of Si by Langmuir-type self-limited adsorption of SiH_4 was recently achieved using 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 realized in Si etching prior to the present work. In the present paper, 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.

2. EXPERIMENTAL

Ultraclean electron cyclotron resonance (ECR) plasma apparatus, schematically shown in Fig. 1, was applied in order to suppress contamination.[3] The majority part of the ECR apparatus is the same as was 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 DI water just before loading into the ECR apparatus. The wafer susceptor was cooled with water. Ar^+ ions were cyclically irradiated onto the wafer by opening and closing the shutter in front of the wafer. The shutter was operated within a moving time less than 0.05 sec 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 100mm$^{\phi}$ window from the ECR plasma generating chamber where Ar gas was introduced. Pressure during process was monitored by Baratron gauge. Energy of Ar^+ ions measured by an electrostatic analyzer[4] at

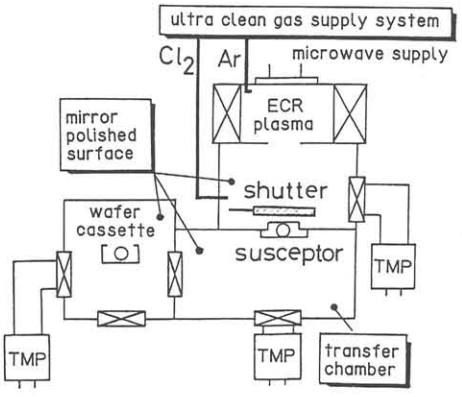

Fig. 1. Schematics of an ultraclean ECR plasma apparatus. TMP : Turbo molecular pumping system with magnetic bearing.

the wafer position was extended around several eV at 0.35 Pa. The etched surface was evaluated by a scanning electron microscope (SEM) and a scanning tunneling microscope (STM).

3. RESULTS & DISCUSSION

(Continuous Chlorine Supply) Since in layer-by-layer deposition of silicon the reaction gas (SiH_4) was continuously supplied and decomposed by msec-order flash light,[1] continuous chlorine supply with cyclic opening and closing the shutter was investigated firstly in this study. Figure 2 shows the dependence of the average etch rate per cycle($\mathbf{R_{pc}}$) on the chlorine partial pressure($\mathbf{p_{Cl}}$), where $\mathbf{R_{pc}}$ is defined as the total etched depth divided by the number of cycles. Without chlorine introduction (● and ▲ in Fig. 2), Ar^+ ion irradiation scarcely etches Si. On the other hand, it does etch Si with chlorine introduction (○ and △ in Fig. 2), and $\mathbf{R_{pc}}$ in continuous chlorine supply has a linear relation to $\mathbf{p_{Cl}}$. $\mathbf{R_{pc0}}$ defined as the $\mathbf{R_{pc}}$ value extrapolated to $\mathbf{p_{Cl}}$=0 is finite, larger than those(● and ▲) without chlorine introduction, and almost independent of the shutter opening time($\mathbf{t_{open}}$). Moreover, [$\mathbf{R_{pc}}$-$\mathbf{R_{pc0}}$] is nearly proportional to $\mathbf{t_{open}}$. These results indicate that $\mathbf{R_{pc0}}$ is mainly determined by saturated chlorine adsorption during the shutter closing time, while [$\mathbf{R_{pc}}$-$\mathbf{R_{pc0}}$] 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. Otherwise, a higher shutter speed with a higher ion current density becomes necessary, which is beyond the ability of the apparatus at present.

(Synchronous Chlorine Supply) Considering the above results, layer-by-layer etching process with synchronous chlorine gas supply was determined. The typical time sequence is shown in Fig. 3. 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 sec. It was also confirmed from the ion current variation experiment that Ar^+ ions bombarding onto the surface during a shutter opening time of 0.2 sec at a total pressure of 0.35 Pa are sufficient for layer-by-layer etching using the present ECR apparatus.

Figure 4 shows the dependence of $\mathbf{R_{pc}}$ on the synchronous chlorine supplying time($\mathbf{t_{Cl}}$) for (a) Si(100) and (b) Si(111). $\mathbf{R_{pc}}$ increases with $\mathbf{t_{Cl}}$ and saturates to a constant value of about 1/2 atomic layer per cycle(AL/C) for Si(100) (Fig. 4(a)) and about 1/3 AL/C for Si(111) (Fig. 4(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 adsorbed chlorine atoms are necessary to etch one Si atom on an average for Si(100) and 3 chlorine atoms for Si(111), if the density of the adsorbed chlorine atoms is assumed to be the same as that of the surface Si atoms.

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. 4. Assuming a simple Langmuir-type adsorption without desorption with a rate constant **k**, the layer-by-layer etch rate per cycle is given by

$$\mathbf{R_{pc}} = \mathbf{const.}\ (1 - \exp(-\mathbf{k}\,\mathbf{p_{Cl}}\,\mathbf{t_{Cl}})) \quad (1)$$

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. 4 are calculated from Eq. (1) using **k**= 83 and 110 $(Pa \cdot sec)^{-1}$ for Si(100) and Si(111), respectively. The calculated values are in excellent agreement with the experimental ones.

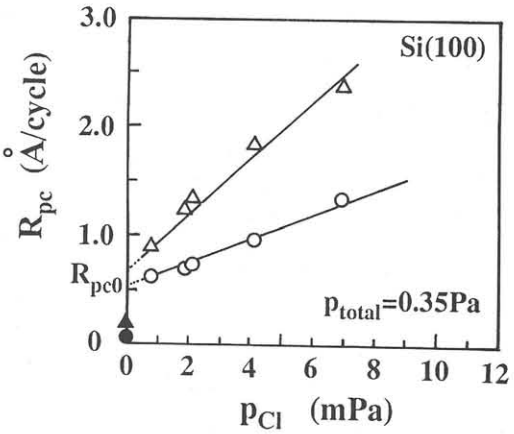

Fig. 2. Dependence of the etch rate per cycle ($\mathbf{R_{pc}}$) on the chlorine partial pressure($\mathbf{p_{Cl}}$) with continuous chlorine supply. The shutter closing time is 20 sec and the shutter opening time is 0.2(○) and 0.5(△) sec. ● and ▲ indicate the data without chlorine supply.

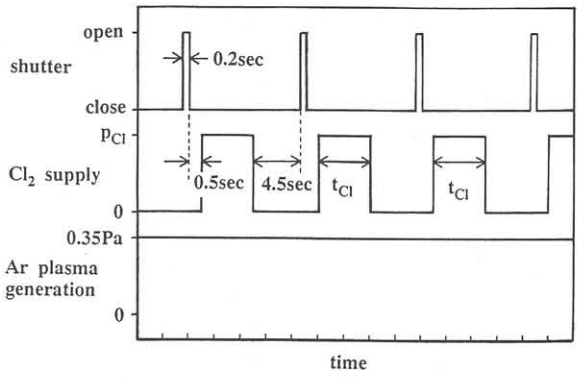

Fig. 3. Typical time sequence for the layer-by-layer etching process with synchronous chlorine gas supply.

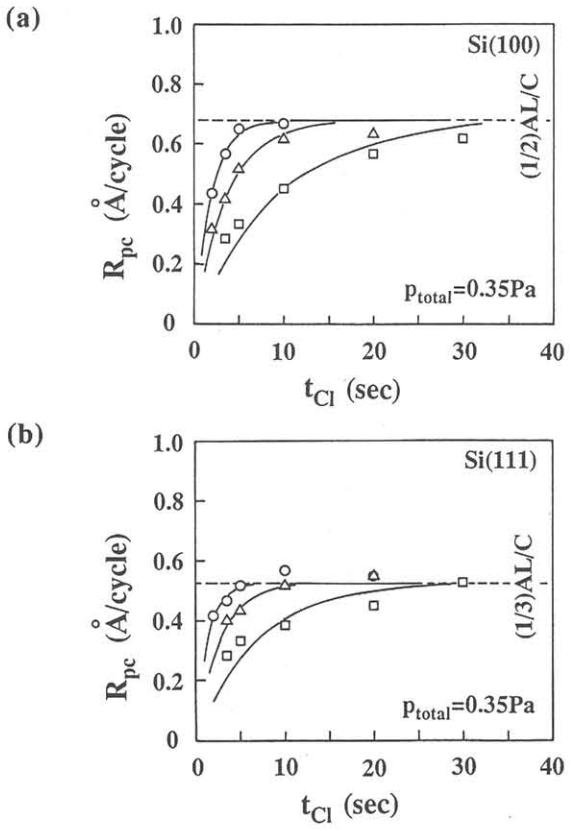

Fig. 4. Dependence of the etch rate per cycle (R_{pc}) on the synchronous chlorine supplying time(t_{Cl}) for (a) Si(100) and (b) Si(111). The solid curves are calculated from Eq. (1) using k=83 and 110 $(Pa \cdot sec)^{-1}$ for (100) and (111), respectively. p_{Cl} = 1.3(□), 3.3(△), and 6.7(○) mPa.

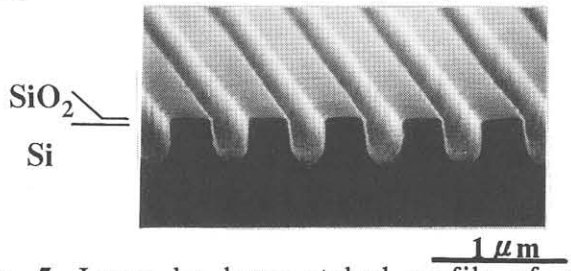

Fig. 5. Layer-by-layer etched profile of a Si substrate. Mask material is SiO_2 patterned by electron beam lithography.

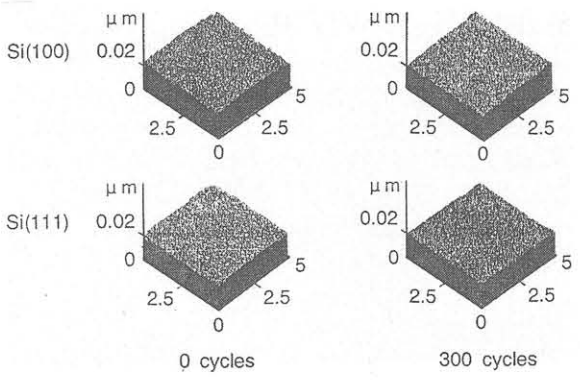

Fig. 6. STM surface profiles of the layer-by-layer etched Si surfaces.

Figure 5 shows the etched cross section of a Si substrate by the present method. A very fine pattern can be fabricated with almost no undercut by this technique. This indicates that the ion induced reaction is dominant in this layer-by-layer etching.

Figure 6 shows the STM surface profiles of the etched Si surfaces. The surface roughness after 300 cycle layer-by-layer etching is almost the same as that of the initial Si substrate before etching.

4. CONCLUSIONS

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 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 $(Pa \cdot sec)^{-1}$ for Si(100) and Si(111), respectively. This self-limited layer-by-layer etching method has a high potential to fabricate new Si-based devices with ultrafine patterns.

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