

Rate Determining Process and Loading Effects in Si Etching with HCl Gas

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1. Introduction

In nanoscale electronics, surface damages and size fluctuations introduced by patterning processes might disturb the device operation. HCl gas etching, traditionally employed as an in-situ cleaning prior to Si epitaxial growth, can be effective for removal of process-induced damage and size fluctuation in Si-based nanostructures because HCl etches Si surface chemically without giving damages to the crystal and results in atomically flat surface. Since there are only limited studies on application of HCl gas etching for Si nanostructures [1-4] and systematic study on slow rate HCl etching is missing, slow rate etching of Si with HCl gas was investigated.

2. Results and Discussion

Etching was performed in a horizontal cold-wall reactor with an inductive heating system at atmospheric pressure. The samples were heated in H₂ ambient and subsequently HCl (< 0.3%, diluted in 3 slm H₂) was introduced.

Figure 1 shows the atomic force microscope images of (100) and (110) Si on insulator (SOI) substrates after etching with 0.12% HCl at 1050°C for 3 min. A small RMS roughness of 0.08 nm was obtained on (100) and step structure appeared on (110). The step height on (110) corresponds to mainly 2 (1–4) atomic layers, and RMS roughness on a terrace was 0.07 nm, indicating very smooth surface. Figures 2 and 3 show plots of the etch depth vs. time and the HCl concentration vs. etch rate on SOI (100) measured by spectroscopic ellipsometry, respectively. Slow-rate etching below 3 nm/min was achievable. The etch depth did not depend on the crystal face, (100) and (110) (Fig. 4).

The Si etching by HCl consists of successive processes; (1) gas phase HCl diffusion through a stagnant layer, (2) surface reaction of $2\text{HCl} + \text{Si} \rightarrow \text{SiCl}_2 + \text{H}_2$, (3) surface diffusion of SiCl₂, (4) desorption of SiCl₂, and (5) gas phase diffusion of SiCl₂ through the stagnant layer, as shown in Fig. 5 [5]. The temperature dependence of the etch rate is very small (activation energy < 10 kcal/mol) in the range of 1000–1100°C at 0.12% HCl (Fig. 6). This indicates that the etching-limiting regime should be controlled by mass transport ((1) or (5)) because the activation energies of etch rate in the surface-kinetics-limiting regime ((2)–(4)) on (100) Si are reported as 51–95 kcal/mol [6-9]. Since the etch rate is not proportional to the HCl concentration (Fig. 3), *i.e.* partial pressure, the HCl supply is not the limiting factor. If the gas phase diffusion of reaction product SiCl₂ limits the etching, the etch rate should be proportional to the SiCl₂ equilibrium pressure $P_{\text{eq}}(\text{SiCl}_2)$, as reported for high-rate HCl gas etching > 250 nm/min (at atmospheric pressure, 1123–1323°C, and HCl fraction > 1%) [5]. Figure 7 shows the relationship between the etch rate and $P_{\text{eq}}(\text{SiCl}_2)$ calculated by a method of [5] and the thermochemical data of [10]. This proportional relation indi-

cates that SiCl₂ diffusion is the dominant rate-limiting step of slow-rate HCl gas etching at atmospheric pressure and 1000–1100°C. In addition, the face-independent etching (Fig. 4) supports the diffusion-limiting model. The small temperature dependence of etch rate is probably due to the small temperature dependence of both $P_{\text{eq}}(\text{SiCl}_2)$ (Fig. 8) and the diffusion coefficient in gas phase.

The gas phase diffusion of SiCl₂ should strongly depend on the area and density of exposed Si at the surface. Thus, we investigated the loading effect by etching SiO₂/Si samples with line-and-space patterns (Fig. 9) at 1050°C with 0.12% HCl for 5 minutes. Under the present condition, HCl etches blanket Si by ~20 nm and hardly etches SiO₂. Figure 10 shows the etched Si depth profile measured by an optical profiler. In the case of the pattern with a constant Si (opening of SiO₂ mask) width of 10 μm and varied SiO₂ mask widths of 10-500 μm (type-A), significant etching acceleration was observed with increase in SiO₂ width. On the other hand, in the case of patterns with the same Si and SiO₂ widths (type-B), the etched depth at the center of exposed Si was almost constant (~50 nm) regardless of the pattern width and acceleration was observed near the Si-SiO₂ boundary. Because SiCl₂ is not generated on the masked area, the SiCl₂ pressure is low near the Si-SiO₂ boundary or in the case of sparse patterns. Therefore, diffusion of SiCl₂ is enhanced and etching is accelerated to keep the surface SiCl₂ pressure at the equilibrium value.

To evaluate validity of the diffusion model, the etching acceleration on stripe patterns was simulated by solving 2D stationary diffusion equation for SiCl₂. The temperature distribution in the gas and the mass transport by the gas flow were neglected for simplicity. The simulation domain and boundary conditions were set up as shown in Fig. 12. The stagnant layer thickness δ was 9.6 mm, calculated from the etch rate vs. $P_{\text{eq}}(\text{SiCl}_2)$ plot (Fig. 7) and SiCl₂-H₂ diffusion coefficient $5.7 \times 10^{-4} \text{ m}^2/\text{s}$ [11]. Note that the simulated etching acceleration results are insensitive to δ because the size of patterns are sufficiently smaller than δ . The experimental and simulation results are compared in Fig. 13 (a) and (b) for type-A and type-B patterns, respectively. From calculation results, acceleration of the etch rate is observed with increase in SiO₂ mask width for type-A pattern. For type-B pattern, the etch rate at the center of Si is independent of pattern width and that at the Si edge was accelerated. Despite the simplified model, the simulated results qualitatively agree with experimental data very well, supporting the diffusion-limited model.

3. Conclusions

By experimental and simulation studies, it was confirmed that SiCl₂ gaseous diffusion is the rate determining step of HCl gas etching at atmospheric pressure and at 1000–1100°C. Intensive investigation on the etching load-

ing effects revealed that they can be described well by the pattern-dependent SiCl_2 diffusion model. To weaken the loading effects, the process pressure or temperature should be lowered because etching dynamics will move to the surface-kinetics regime under those conditions.

References

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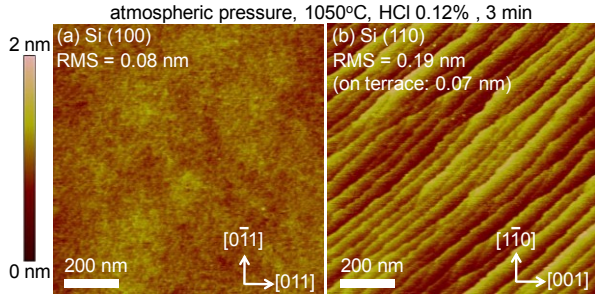


Fig. 1 Atomic force microscope images of SOI (a) (100) and (b) (110) substrates etched with HCl gas.

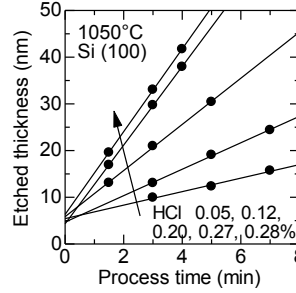


Fig. 2 Etch depth vs. etch time in HCl etching of Si (100)

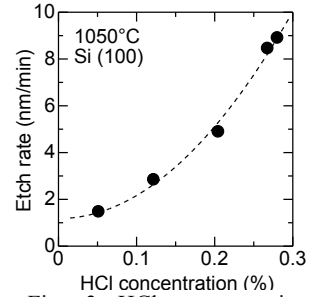


Fig. 3 HCl concentration dependence of etch rate.

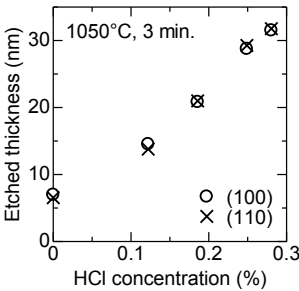


Fig. 4 Etched depth of Si (100) and (110) faces vs HCl concentration.

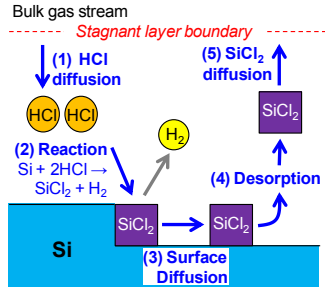


Fig. 5 Schematics of reaction of Si etching with HCl [5]

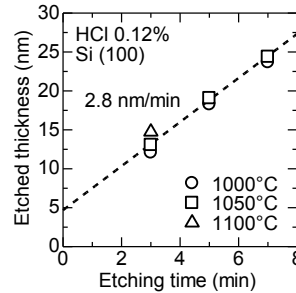


Fig. 6 Etched thickness at different process temperatures.

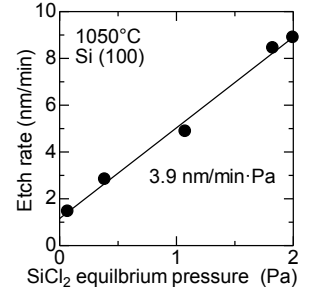


Fig. 7 Etch rate vs. SiCl_2 equilibrium pressure.

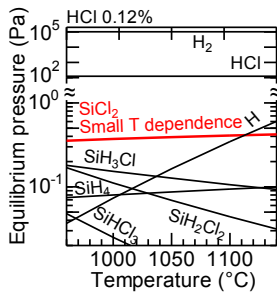


Fig. 8 Gas phase equilibria of H-Cl-Si system calculated with thermochemical data.

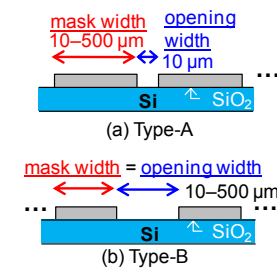


Fig. 9 Schematics of Si- SiO_2 patterns for loading-effect study.

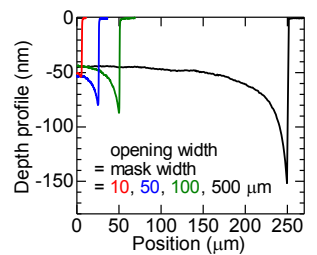
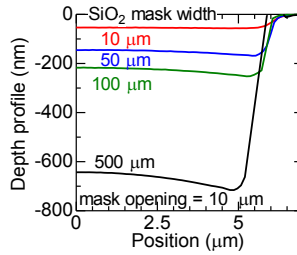


Fig. 10 Etched depth profile of Si with SiO_2 mask patterns of (a) type-A and (b) type-B. Position zero is the center of mask opening.

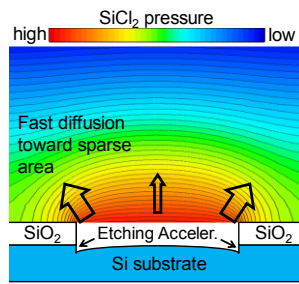


Fig. 11 Explanation of loading effect by pattern-dependent diffusion of SiCl_2

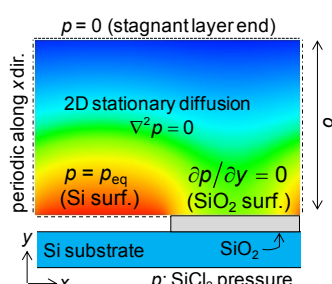


Fig. 12 Schematic of simulation domain and boundary conditions for SiCl_2 diffusion simulation.

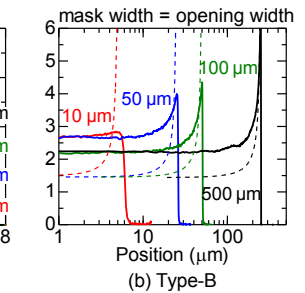
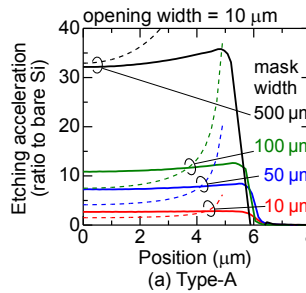


Fig. 13 Experimental (solid) and simulation (dashed) results of etching loading effects in line- and space-patterns of (a) type-A and (b) type-B. Position zero is the center of mask opening. The horizontal axis in (b) is logarithmic for easier view.