

Characteristics of Plasmaless Dry Etching of Silicon-Related Materials Using Chlorine Trifluoride Gas

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Silicon substrates and thermally grown oxide films were exposed to ClF_3 gas at various temperatures between room temperature and 600°C . Above room temperature, the activation energy of the silicon etch rate is 0.18 eV. The activation energy of SiO_2 etch rate below 400°C is estimated to be 0.12 ± 0.01 eV. The obtained etch selectivity of silicon with respect to the SiO_2 is 100–300 between room temperature and 400°C . An enhanced etch rate is observed for the n-type silicon with low resistivity near room temperature. The ClF_3 gas, which has appropriate vapor pressure, has useful properties not only for *in-situ* cleaning but also for micromachining of silicon-related materials.

1. Introduction

Recently, reactive halogen compounds have been used to etch silicon during micromachining without plasma. An angular-rate sensor was fabricated with the assistance of spontaneous etching of silicon by XeF_2 .^(1,2) It was also demonstrated that the ratio of the etch rate of silicon with respect to that of SiO_2 using BrF_3 is 3,000,⁽³⁾ which is much higher than that of any wet etch process or plasma-induced dry etch process. It is reported, moreover, that an electrostatic micromotor was fabricated using spontaneous etching of silicon by ClF_3 (chlorine trifluoride) gas.⁽⁴⁾ These halogen compounds can etch silicon spontaneously at room temperature without plasma, but rarely attack quartz, thermally grown oxide, aluminum, or positive type-photoresist at temperatures close to room temperature. The highly selective etch phenomenon is due to a chemical reaction. The

isotropic etch property is often useful for etching the area behind the mask material during micromachining. Studies of the application of chemical dry etching to micro-machining have recently been initiated.

We have been investigating in ClF_3 gas,⁽⁵⁻⁷⁾ which has very similar chemical properties to XeF_2 and BrF_3 . ClF_3 gas has a suitable vapor pressure (1.5 atom at 20°C) in comparison with the very low vapor pressures of XeF_2 and BrF_3 gases (4.5 and 7 Torr, respectively). The flow rate of ClF_3 can be controlled, therefore, by a conventional mass flow controller. ClF_3 gas is already popular for *in-situ* cleaning of silicon-related CVD (chemical vapor deposition) apparatus over the past ten years. We also believe that ClF_3 gas is highly advantageous in terms of contributing to the "greenhouse effect" because ClF_3 gas can be easily trapped and decomposed in a scrubber or by soda lime.

Our research group reported previously the influence of temperature and uv light illumination on the etch rate of silicon⁽⁸⁾ and silicon nitrides⁽⁹⁾ at temperatures under 150°C. Basic etch properties of the oxide have not yet been clarified. In this study, the etch rates of silicon and silicon dioxide are investigated at various temperatures. The resistivity dependence of the silicon etch rate is also shown.

2. Experimental Procedure

(100)-oriented p-type single crystalline silicon substrates with resistivity of 30–60 Ω cm were used in this study. The substrates were boiled in an alkali solution of NH_4OH , H_2O_2 , and H_2O (1:1:6) for 10 min, rinsed with flowing deionized water for 3 min, and dipped into the diluted HF solution for 1 min to remove the native oxide. The substrates were rinsed again for 3 min and blown dry in nitrogen. After the chemical pretreatments, silicon dioxide films were thermally grown in dry oxygen ambient at 1,000°C on the substrates. The grown oxide was patterned by a photolithography technique.

The substrate was, subsequently mounted onto a resistive heater made of GLC (glass-like carbon) in a reaction chamber made of stainless steel as shown in Fig. 1. The GLC heater was heated by electrical power, and was resistive to ClF_3 gas up to 650°C at least. The copper electrodes were water-cooled to prevent their corrosion. The substrate temperature was measured using an infrared pyrometer, which was previously calibrated by thermocouple measurements.

After evacuating the reaction chamber, Ar gas was introduced at a pressure of up to 1.5 Torr, and the substrate was heated. ClF_3 gas of 99.9 % purity and Ar gas were introduced into the reaction chamber at the flow rates of 20 sccm and 10 sccm, respectively, and the total pressure was maintained at 1.5 Torr by evacuating the chamber with a multistage dry pump. The partial pressure of the ClF_3 gas was 1 Torr. After the dry etching, the substrate was taken out of the reaction chamber, and the oxide film was partially removed with a buffered HF solution. The etch rates of the silicon and the oxide were estimated from the etched depth of silicon and the residual thickness of the oxide film, respectively which were measured with a surface profiler.

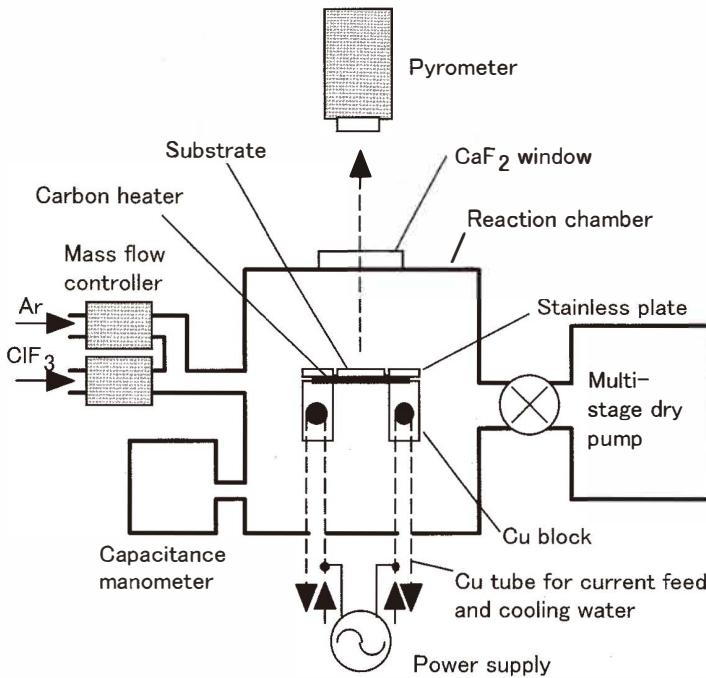


Fig. 1. Schematic diagram of the etching system with a cold wall chamber.

3. Experimental Results and Discussion

The silicon substrates and thermally grown oxide films were exposed to the ClF₃ gas at various substrate temperatures ranging from room temperature to 650°C. The temperature dependence of the etch rate is shown by solid circles in Fig. 2. Previously obtained data⁽⁶⁾ for a relatively low-temperature region are also shown as open circles in this figure. The etch rate of silicon varies complexly with temperature. The activation energy of the etch rate has a negative value near room temperature, because the reaction is limited by the adsorption of ClF₃ gas.⁽⁵⁾ At high temperatures, the activation energy is about 0.18 eV, which is consistent with that reported previously.^(5,6) In the high-temperature region, the etch rate exhibits a complex dependence on the ClF₃ pressure above 2 Torr. Below room temperature, the etch rate of silicon is proportional to the ClF₃ pressure up to 10 Torr at least.⁽⁶⁾

The etch rate of the oxide is much lower than that of silicon as shown in Fig. 2, and its activation energy is estimated to be 0.12±0.01 eV below 400°C. An activation energy larger than 0.3 eV is observed over 400°C. The significance of the activation energy is not understood, because the mechanism of oxide etching has not been investigated. The *in-*

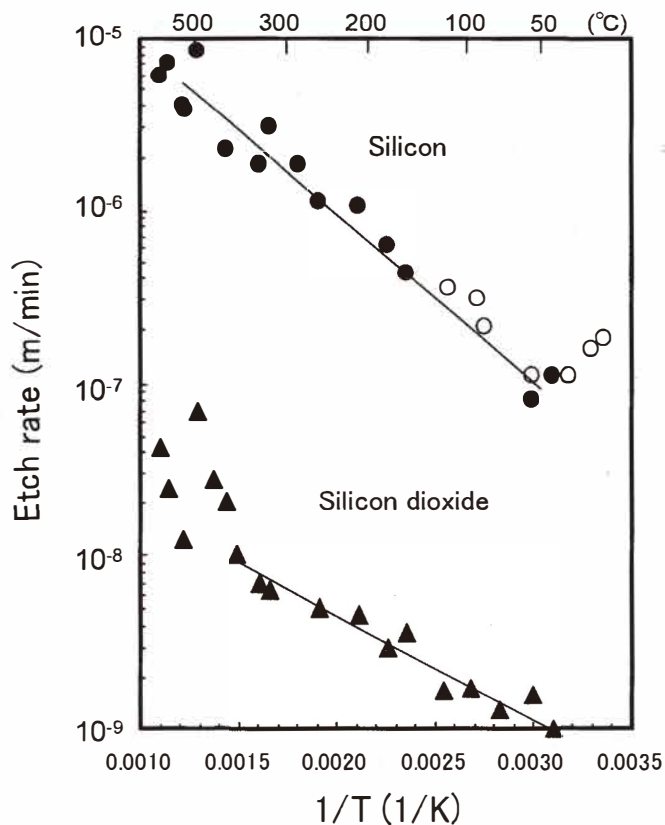


Fig. 2. Dependence of etch rates of crystalline silicon (circles) and silicon dioxide (triangles) on temperature using ClF_3 gas at a partial pressure of 1 Torr. The data shown by open circles is from ref. (6).

situ cleaning of quartz tubes in CVD apparatus is usually carried out at temperatures between 400 and 600°C. According to the data in Fig. 2, the process temperature should be around 400°C to obtain the maximum etch rate selectivity with respect to the oxide, the value of which is about 300. The selectivity higher than 100 is obtained near room temperature. Ueda and Kuribayashi reported that the selectivity is about 300 using 5% ClF_3 under atmospheric pressure at room temperature.⁽⁴⁾ Considering this value is much more than 100, the activation energy of the etch rate of oxide will be constant around room temperature, although that of silicon dramatically varies around 50°C. They also reported that the Cr mask has a selectivity four times as large as that of the oxide. If a selectivity larger than 1,000 is required, the use of a Cr mask may be more suitable than the use of oxide films.

The crystalline silicon substrates with various electrical resistivities were exposed to ClF_3 gas. Figure 3 shows the dependence of the etch rate of crystalline silicon, where the pressure of ClF_3 gas was 0.2 Torr and the substrate temperature was 60°C . The lightly doped polycrystalline film was used only for a sample with the highest resistivity. From this figure, it is found that the etch rate increases only for n-type silicon with resistivity below about $0.1 \Omega \text{ cm}$. The selective etch process is difficult, however, using the resistivity dependence of the etch rate, because the change of the etch rate is not so large. The enhanced etch rate of n+ silicon has also been observed in the etching by XeF_2 .⁽¹⁰⁾ Generally, the etch reaction between silicon and halogen requires electron extraction from the substrate because halogen atoms have a large electronegativity. A sufficient supply of electrons can assist the etch reaction. A model of the surface electric-field-induced reaction was also proposed,⁽¹⁰⁾ but its quantitative validity is still unclear.

Figure 4 shows a cross-sectional SEM (scanning electron microscope) image of crystalline silicon etched by ClF_3 gas near room temperature using a mask of patterned SiO_2 . The silicon was etched almost isotropically, but the mask oxide was not damaged. The ratio of the undercut with respect to the etched depth is 1.2–1.3. This value, not unity, implies that the reaction would be limited by the supply of the reactant. When lateral etching is required, this value should be taken into consideration.

We have also applied ClF_3 gas to highly selective etching of gate polycrystalline silicon films using aluminum electrodes as the mask in MOS (metal oxide semiconductor) capacitors.⁽¹¹⁾ The Al thickness was about 200 nm and the thickness of etched polycrystal-

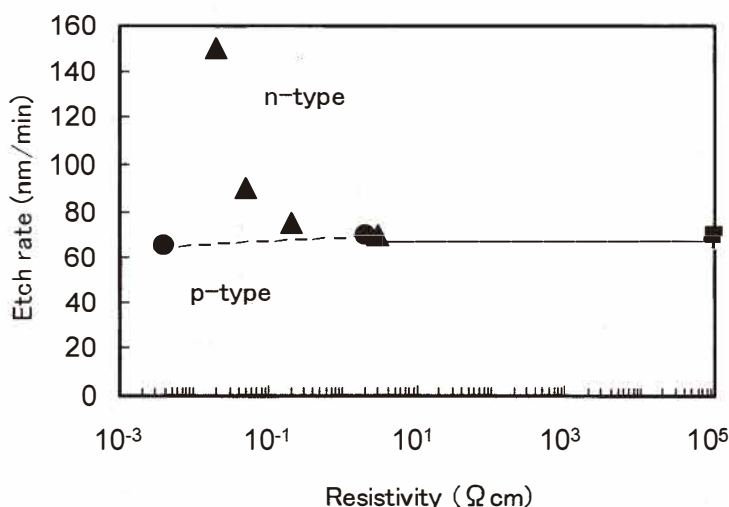


Fig. 3. Dependence of etch rate of crystalline silicon on its resistivity using ClF_3 gas under 0.2 Torr at 60°C . Boron-doped (circles) and phosphorus-doped (triangles) single crystalline silicon substrates were used. A lightly doped polycrystalline silicon film was used for the highest resistivity.

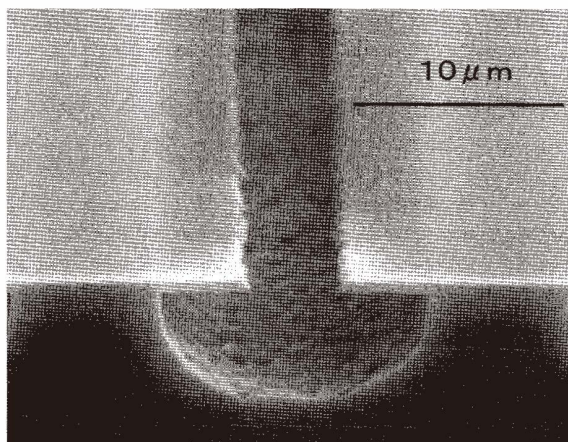


Fig. 4. Cross-sectional SEM image of crystalline silicon etched by ClF_3 gas at a temperature close to room temperature using a mask of patterned SiO_2 .

line silicon films was 150 nm. The thin oxide films of 10 nm thickness functioned as etch stoppers. The obtained capacitance-voltage characteristic of the fabricated capacitors shows that there is no damage induced by the etch process if there is no any subsequent high-temperature anneal.

Plasmaless dry etching is useful for highly selective etching of silicon-related materials. Mask materials other than the oxide should be investigated for realizing enhanced selectivity. On the other hand, the ClF_3 gas can rapidly etch W, Ta, and TaN.⁽¹²⁾ The etch characteristics of sacrificial materials should be discussed for obtaining new ideas for micro machining processes.

4. Conclusions

Silicon substrates and thermally grown oxide films were exposed to ClF_3 gas at various temperatures between room temperature and 600°C. Above near room temperature, the activation energy of the silicon etch rate is 0.18 eV. The activation energy of the SiO_2 etch rate below 400°C is estimated to be 0.12 ± 0.01 eV, which is reported for the first time. The etch selectivity of silicon with respect to SiO_2 is 100–300 between room temperature and 400°C. The maximum selectivity is obtained around 400°C in this experiment. An enhanced etch rate is observed for the n-type silicon with low resistivity at room temperature. Although the etch rate of silicon is lower than the reported value for BrF_3 near room temperature, ClF_3 gas has useful properties not only for *in-situ* cleaning but also for micromachining of silicon-related materials.

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References

- 1 R. Toda, K. Minami and M. Esashi: International Conf. on Solid-State Sensors and Actuators (1997) p. 671.
- 2 J-J Choi, K. Minami and M. Esashi: T. IEE Japan **118-E** (1998) 437. (in Japanese)
- 3 X. Q. Wang, X. Yang, K. Walsh and Y-C Tai: Technical Digest, 1997 Int. Conf. on Solid-State Sensors and Actuators (Transducers '97), (Chicago, 1997) Vol. 2, p. 1505.
- 4 T. Ueda and K. Kuribayashi: Seimitsu-Kogakkai-shi **66** (2000) 871. (in Japanese)
- 5 D. E. Ibotson, J. A. Mucha, D. L. Flamm and J. M. Cook: J. Appl. Phys. **56** (1984) 2939.
- 6 Y. Saito, O. Yamaoka and A. Yoshida: J. Vac. Sci. & Tech. **B9** (1991) 2503.
- 7 Y. Saito: Recent Research Development in Electrochemistry 1, ed. S. G. Pandalai (Transworld Research Network, Trivandrum, 1998) p. 191.
- 8 Y. Saito, O. Yamaoka and A. Yoshida: Applied Physics Letters **56** (1990) 1119.
- 9 Y. Saito, M. Hirabaru and A. Yoshida: IEICE of Japan Trans. on Electron. **E75** (1992) 834.
- 10 H. F. Winters and D. Haarer: Phys. Rev. **B36** (1987) 6613.
- 11 Y. Saito and K. Tokuda: Jpn. J. Appl. Phys. **41** (2002). In print.
- 12 D. E. Ibotson, J. A. Mucha, D. L. Flamm and J. M. Cook: Appl. Phys. Lett. **46** (1985) 794.

About the Author



Yoji Saito was born in Tokyo, Japan, in 1959. He received B.S., M.S., and doctoral degrees in electrical engineering from Keio University, Japan, in 1982, 1984, and 1987, respectively. He joined Toyohashi University of Technology, Japan, as a research associate in 1987. He started an assistant professor at Seikei University in 1992. He was a visiting researcher at North Carolina State University, U. S. A., from 1998 to 1999. He has been working as a professor in Seikei University since 2001. His research interests focus on the etching process and the growth of ultrathin dielectric films for semiconductor devices, using remote plasma and vacuum ultraviolet light. He received the 50th annual award from the Tokai branch of the Institute of Electronics, Information, and Communication Engineers for his achievement in the study on vacuum-ultraviolet-light-induced process in 1989. He is a member of the Japan Society of Applied Physics, the Institute of Electronics, Information, and Communication Engineers, Materials Science Society of Japan, and Japanese Society for Synchrotron Radiation Research.