

Significant Effect of OH inside Silicon Chemical Oxides on AHF(Anhydrous Hydrofluoric Acid) Etching

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It is demonstrated for the first time that the etching of Si chemical oxides by AHF is controlled by the amount of Si-OH bonds incorporated in the oxides. It is found that the etching rate is in proportion to the amount of Si-OH bonds, which is monitored by TDS (Thermal Desorption Spectroscopy). This result can be understood by the model that H₂O formed by Si-OH bonds in the chemical oxide initiates the ionization of the HF molecule and, as a result, the generated HF₂⁻ ion reacts with SiO₂. Moreover, it is found that in-situ annealing around 100-200 °C is effective in removing residual fluorine at the Si surface after the etching.

1. INTRODUCTION

Recently, more attention has been paid on the control of Si surface condition just prior to the gate oxidation from the viewpoint of the oxide reliability, because it has been reported that the quality of the native oxides affects the structure of SiO₂^{1,2)}. Therefore, the establishment of an in-situ SiO₂ etching technique is strongly required. One of the promising techniques is to use Anhydrous Hydrofluoric Acid (AHF) vapor as the etchant^{3,4)}. However, the etching mechanism of SiO₂ by AHF has not been fully understood yet, in spite that the etching behavior has been reported to be significantly different between the native oxides and the thermal oxides⁴⁾. It has also been pointed out⁴⁾ that one possible problem in the AHF etching is residual fluorine (F) at the Si surface after the etching, which could degrade the reliability of gate oxides.

This paper demonstrates, for the first time, that the etching rate of Si chemical oxides by AHF is controlled by the amount of Si-OH bonds incorporated in the oxides. Moreover, it is found that in-situ heating around 100-200 °C is really effective in removing residual fluorine at the Si surface after the etching, whereas the fluorine removal has been difficult by ex-situ etching after the exposure to the air⁴⁾.

2. EXPERIMENTS

In order to clarify the relationship between the etching rate by AHF and the film quality of Si chemical oxides, it is necessary to combine a technique for monitoring the surface reaction with one for evaluating the oxide quality. In-situ XPS (X-ray Photoelectron Spectroscopy), where an AHF etching chamber is connected with the XPS chamber, was used to measure the etching rate of ultra thin native oxides. Also, TDS (Thermal Desorption Spectroscopy) was used to

evaluate the quality of Si chemical oxides with emphasis on the bonding state of water in the chemical oxides. It is shown later that water plays a quite important role in the etching rate of the chemical oxides.

XPS spectra were recorded using an Ulbac-Phi 5500 spectrometer. Mg-K α radiation was irradiated at the incident angle 45° and photoelectrons were collected in the take-off angle 15°. The oxide thickness d (nm) is given by the integrated photoelectron intensity of chemically shifted Si2p spectrum I_{SiO_2} and that of metallic Si signal I_{Si} as follows⁵⁾:

$$d = \Lambda_{SiO_2} \sin \alpha \cdot \ln \left(k \frac{I_{SiO_2}}{I_{Si}} + 1 \right) \quad (1)$$

where Λ_{SiO_2} is the escape depth of Si2p photoelectron from SiO₂ (2.5nm), α is the take-off angle (15°). The value of $k = 2.086$ estimated by the atomic density of Si and SiO₂.

Desorption experiments were performed using the UHV-TDS apparatus. The sample were heated directly from the back through a quartz rod with an external infrared lamp. The base pressure was less than 1×10^{-9} Torr with a working pressure of approximately 4×10^{-9} Torr at room temperature. The gas components desorbed from the sample surfaces were detected by a double-focused mass spectrometer. The ions with mass number of 18, which correspond to H₂O, were detected.

The wafers used in this study were polished, (100), p-type silicon wafers with resistivity 4.5~6.0 $\Omega \cdot \text{cm}$. They were dipped in diluted HF, and rinsed in deionized water. After these treatments, the wafers were briefly oxidized by two chemical solutions, either a mixed solution of HCl, H₂O₂ and H₂O (1:1:1) or O₃ water. After the chemical oxidation, the wafers were introduced into In-situ XPS vacuum chamber. The base pressure in the etching, transport and analyzing chambers were below 10^{-7} Torr, about 10^{-9} Torr

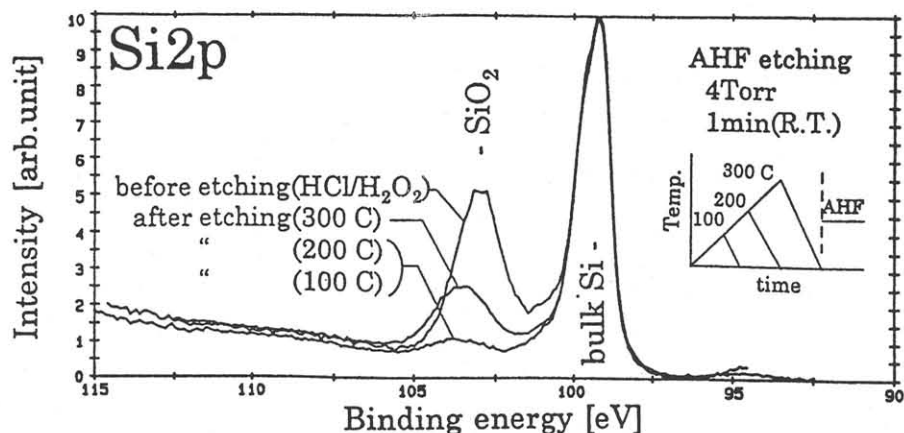
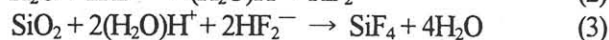
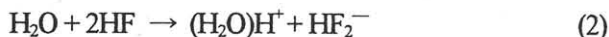


Fig.1 Si2p XPS spectra collected from anhydrous HF (AHF) gas-cleaned Si surfaces. After pre-annealing at various temperatures in vacuum, chemical oxide was treated by AHF (4 Torr, 1 min) gas at room temperature.

and about 10^{-10} Torr, respectively. In order to intentional control the amount of water in the chemical oxides, in-situ annealing in the XPS vacuum chamber was carried out.

3. RESULTS AND DISCUSSION

It has already been reported⁴⁾ that AHF vapor can etch Si chemical oxides even at its low pressure. The etching is believed⁴⁾ to be initiated by H₂O physisorbed at the chemical oxide surface and proceed in the following reactions.



However, it has not been examined yet whether physisorbed H₂O is a trigger to ionize HF or not. Although H₂O is considered to play an important role in the AHF etching, the origin of H₂O to initiate the reaction has not been clarified yet. Therefore, in order to quantitatively examine the role of water in Si chemical oxides on the AHF etching, we studied the etching rate of the chemical oxides by AHF, varying the annealing temperature before the etching, which is expected to change the amount of H₂O inside the chemical oxides. The AHF etching was carried out just after the annealing without exposure to air, so as to avoid any change in the quality of the chemical oxides after the annealing.

Fig.1 shows the Si2p XPS spectra for the Si surface, where the chemical oxide was formed by a mixed solution of HCl, H₂O₂ and H₂O (1:1:1), before and after the exposure to AHF. The in-situ annealing temperature was varied from 100 to 300 °C. It is clearly shown that the etching is significantly retarded by the annealing at 300 °C, while the etching rate is the same for the annealing temperatures of 100 and 200 °C.

TDS analysis was used to examine the change in the chemical oxide associated with the annealing. Fig.2 shows the TDS spectrum of H₂O taken from the same chemical oxide. It is found that there is a peak at around 200-300 °C, which has been assigned to Si-OH bonds inside the oxides⁷⁾, while the

signal corresponding to physisorbed H₂O, which has been reported to be observed around 180 °C⁸⁾, is absent. This result means that the change in the etching rate between 200 and 300 °C shown in Fig.1 can originate in the release of -OH bonds, not in the release of physisorbed H₂O.

The total amount of Si-OH bonds in the oxides can be determined by integrating the TDS spectra over temperature. Fig.3 shows the correlation between the amount of Si-OH bonds and the etching rate. In order to confirm that the etching rate is not determined by the other physical parameters of the chemical oxide such as the network structure, but is determined by the OH concentration, the result for the chemical oxide formed by O₃ water is also plotted in Fig.3. It is found that the etching rate is roughly proportional to the amount of Si-OH bonds, demonstrating that the etching rate is controlled by the amount of Si-OH bonds in the oxides.

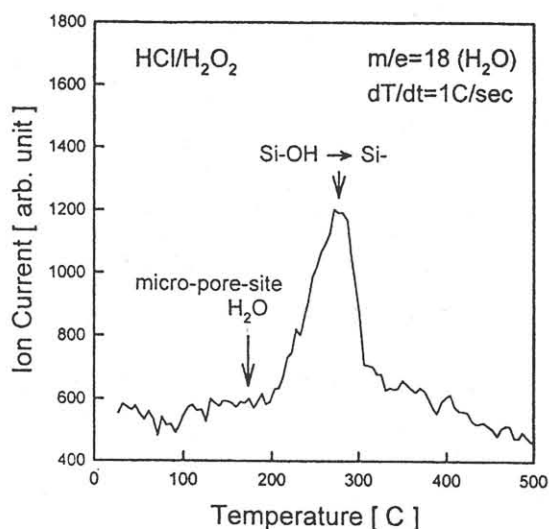


Fig.2 TDS spectra of 18 m/e (H₂O) obtained from chemical oxide (SC2:HCl/H₂O₂/H₂O). Linear heating rate of 1°C/sec was used. H₂O spectrum had a broad peak at 270°C (Si-OH).

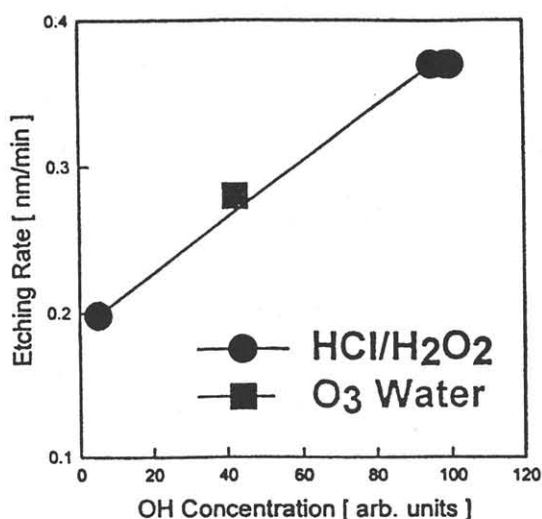
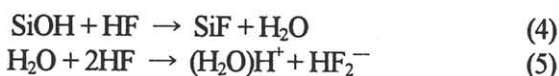


Fig.3 Relationship between the OH concentration and the etching rate.

This result can be understood by considering that H₂O formed by Si-OH bonds in the chemical oxide initiates the ionization of the HF molecule and, as a result, the generated HF₂⁻ ion reacts with SiO₂. The keynote reactions are as follow:



It has been revealed from the above experimental results that the limiting parameter for the AHF etching of the chemical oxides is the amount of Si-OH bonds inside the oxides, not the amount of physisorbed H₂O, which has been suggested in the previous work⁴⁾.

In addition, it is also found that residual fluorine at the Si surface after the AHF etching can be removed by in-situ annealing around 100-200 °C just after the etching. Fig.4 shows the normalized F1s signal intensity of in-situ XPS after the etching as a function of the annealing temperature in vacuum. It is observed here that in-situ annealing around 100-200 °C removes terminating fluorine from the silicon surface significantly. This result is in good contrast with the ex-situ annealing after the exposure to the air, which has been previously reported to be unable to remove fluorine at Si surface, even if the substrate temperature is raised up to 630 °C⁴⁾. The removal of fluorine by in-situ annealing is attributable to the thermal desorption of the physisorbed fluorine-related species left at the surface after the etching. On the other hand, since fluorine at surface can be incorporated into the oxide network after exposure to air, ex-situ etching is considered to be ineffective in the removal of fluorine.

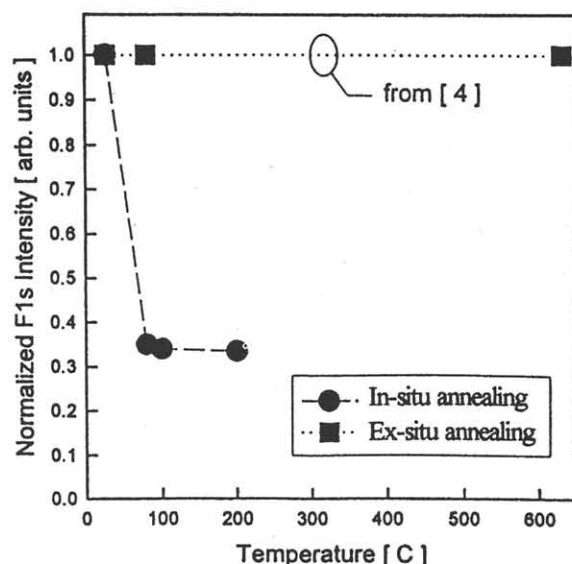


Fig.4 Normalized F1s signal intensity from fluorine-terminated surfaces plotted against the annealing temperature in vacuum.

4. CONCLUSION

It was demonstrated, for the first time, that the etching of Si chemical oxides by AHF is controlled by the amount of Si-OH bonds incorporated into the oxides. It was also found that in-situ annealing can effectively remove residual fluorine after the AHF etching even at low temperature. These new findings are quite important in terms of the process control of AHF etching for the removal of Si native oxides prior to the gate oxidation.

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