

Native Oxide Growth Rate of Si Surface with Various Flatness

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Effect of Si surface flatness on the native oxide growth rate is investigated. The flatness was varied by treating the Si wafers in a HF aqua solution of various concentrations. A wafer treated with a HF aqua solution of a higher concentration had a rough surface. However, no apparent relation between the native oxide growth rate and the flatness was observed. This is because the number of fluorine atoms remaining on the surface increases as the HF concentration increases and these fluorine atoms suppress the native oxide growth. The result indicates that both hydrogen and fluorine termination are relevant to control the native oxide growth.

1. Introduction

Control of native oxide growth on Si surfaces is becoming a very important factor in submicron ULSI fabrication. This is because the native oxide films degrade the electrical characteristics of thin SiO₂ gate films and metal-Si Ohmic contacts. Several techniques utilizing hydrogen-termination of Si surfaces, such as diluted HF and pH-modified buffered-HF treatments, have been reported to suppress the native oxide growth^{1)~10)}. These processes are well known to successfully passivate the Si (111) surface by obtaining hydrogen-terminated atomically flat surface. However, the wafers mostly used in ULSI fabrications are Si (100). It is generally difficult to obtain an atomically flat Si (100) surface compared with Si (111) surface. Reportedly, nearly flat surface can be obtained using HF/H₂O₂ aqua solution treatment¹¹⁾, but the surface still has some microscopic defects (such as steps) even using this technique. Moreover, the actual processed wafers have rough surfaces due to damage from dry-etching or poly-Si surfaces with various crystal orientations. It would be difficult to obtain atomically flat surfaces with these surfaces during the actual fabrication process.

Therefore, we investigated the native oxide growth rate of hydrogen-terminated Si surfaces with various degrees of flatness to clarify the effects of surface flatness. We used HF aqua solution treatment of various concentrations to obtain various degrees of flatness and to clarify the effects of the fluorine atoms remaining in the surfaces on the native oxide growth. After the HF treatment, the Si wafers were not rinsed in the water to avoid native oxide growth as well as the removal of surface fluorine.

2. Experiment

B-doped p-type CZ-Si (100) and (111) wafers (9~12 Ω -cm) were first dipped in 5 % HF solution to remove the originally existing native oxide and were rinsed in ultra-pure water for 10 min. Then, they were dipped in HF solutions of various concentrations (0.05~5%) for 10 min and were dried by N₂ gas blow. These samples were evaluated just after the HF treatment and after exposure in a clean room atmosphere (40% relative humidity).

The surface flatness and native oxide growth rate were estimated by the number of Si-H_x bonds and Si-O bonds at the surfaces obtained by ATR-FTIR (attenuated total reflection-Fourier transform infrared spectroscopy) measurement. The ATR-FTIR spectra were measured by a Nicolet model 730 FTIR spectrometer with a resolution of 4 cm⁻¹ by accumulating 1000 scans in N₂ ambient. The p-polarized light (incident angle: 60°) and Ge prism were used for the measurement. The concentrations of fluorine atoms remaining on the Si surfaces as well as native oxide thicknesses were measured using XPS (X-ray photoelectron spectroscopy).

3. Results and discussion

3.1 Surface flatness

Figure 1 shows the ATR-FTIR spectra (between 2000 cm⁻¹ and 2200 cm⁻¹) of the Si (100) and (111) surfaces just after the HF solution dip (0.05~5%). The peaks originated by Si-H, Si-H₂ and Si-H₃ bonds are observed. The ratio of the Si-H₂ peak intensity for Si (100) and Si-H peak intensity for Si (111) surfaces to each total Si-H_x peak intensity are summarized and shown as a function of HF concentration in Figure 2. Since the surface flatness becomes higher as these values increase³⁾, the result

indicates that the surface becomes atomically flat as the HF concentration decreases. At the same time, it can be seen that the flatness of the Si (111) surface becomes easily higher compared with Si (100).

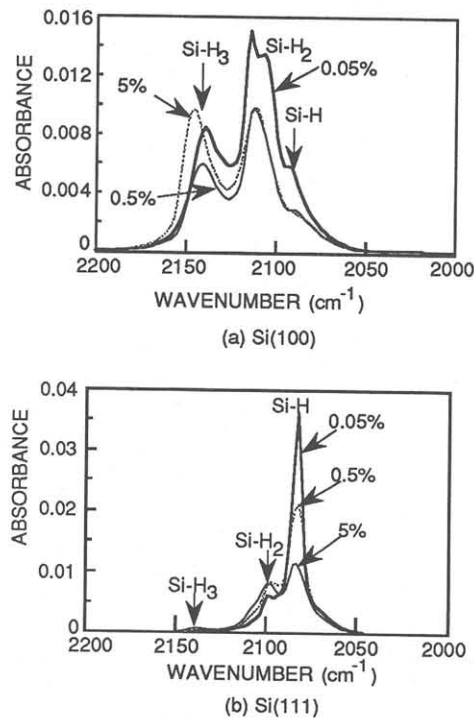


Fig. 1 HF concentration dependence of Si-H_x peaks on the Si surface after dipping in HF solution.

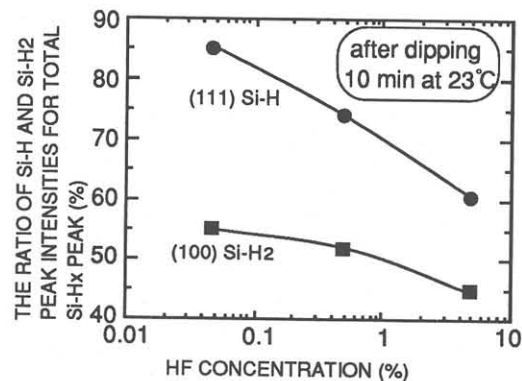


Fig. 2 The HF concentration dependence of surface atomic flatness.

3.2 Native oxide growth rate

Figure 3 shows the change of the ATR-FTIR spectra of the HF aqua solution treated Si (100) surface during clean room atmosphere exposure. One spectrum is obtained from the Si surface just after the 5% HF solution dip and the others are obtained after native oxide growth in a clean room atmosphere. The peaks originated by Si-O LO phonon ($\approx 1170\text{ cm}^{-1}$) and interstitial oxygen⁴⁾ ($\approx 1100\text{ cm}^{-1}$) are observed. The Si-O LO phonon peak intensities increase as exposure time increases. On the

other hand, it can be seen that the peak intensities of interstitial oxygen were saturated as exposure time increases.

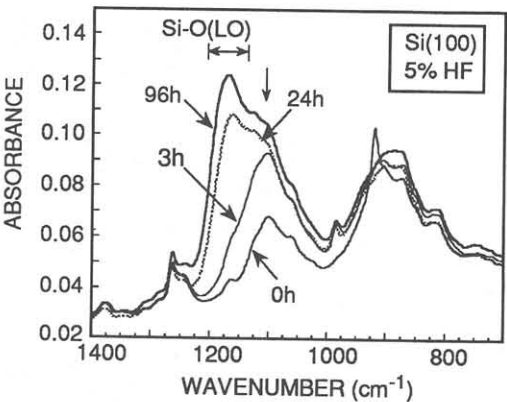


Fig. 3 ATR-FTIR spectrum of the surface after dipping in HF 5% solution and oxidized by clean room atmosphere exposure (exposure time : 0~96h).

Figure 4 shows exposure time dependence of the integrated intensities of these peaks. The integrated intensities increase as exposure time increases. We confirmed that the integrated intensities are directly related to oxide thickness by using thermal oxide films (thickness: 10~30Å). Thus, we speculate that the increase of the integrated intensity indicates the growth of native oxide. The increase rate of the integrated intensities, which is obtained from the 0.05 % HF solution treated sample, is higher than that of 5 % HF solution treated sample, regardless of surface orientation. The result contradicts the prediction that the sample with hydrogen-terminated flat surface dose not tend to be easily oxidized. The native oxide growth rate is found to be higher with higher flatness surfaces in this case.

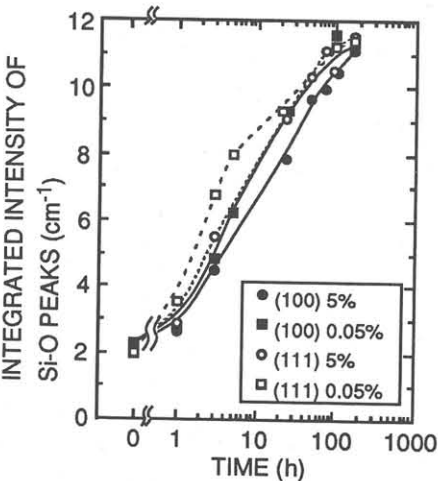


Fig. 4 Exposure time dependence of the integrated Si-O intensity from 1000 cm^{-1} to 1350 cm^{-1} .

3.3 The effects of surface fluorine

To further clarify the cause of native oxide growth on higher flatness surfaces, behavior of the fluorine concentration remaining on the surface is investigated. Figure 5 shows an example of F_{1s} photoelectron spectrum measured using XPS just after the HF treatment of the surface. The deconvoluted spectra are also shown in this figure. Two F_{1s} peaks corresponding to a $C-F_x$ compound and a Si-F bond were obtained. It is expected that the fluorine atoms that correspond to the $C-F_x$ compound do not affect the native oxide growth. Thus, we discuss the results based on only the peak intensities of the fluorine atoms that formed the Si-F bonds.

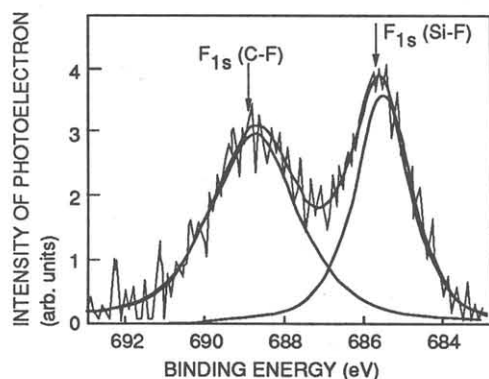


Fig. 5 Example of F_{1s} photoelectron spectrum measured using XPS.

Figure 6 shows the HF concentration dependence of F_{1s} peak intensities just after the HF treatment. The F_{1s} peak intensity increases as the HF concentration increases. The intensity of the 5% HF solution treated sample is 5 times greater than that of the 0.05% HF solution treated sample. Figure 7 shows the exposure time dependence of the surface fluorine concentration and native oxide thickness of the 5% HF solution treated measured using XPS. It can be seen that the native oxide thickness increases at the period when the fluorine concentration rapidly decreases. From these results, we could speculate that the terminated fluorine atoms play a

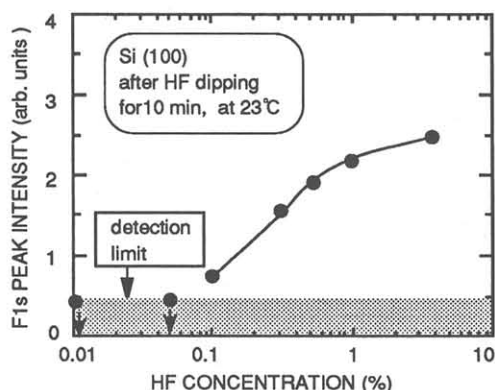


Fig. 6 The HF concentration dependence of F_{1s} peak intensity.

big role to suppress the native oxide growth on HF treated surfaces. The native oxide growth rate becomes higher for less fluorine termination and higher flatness surfaces.

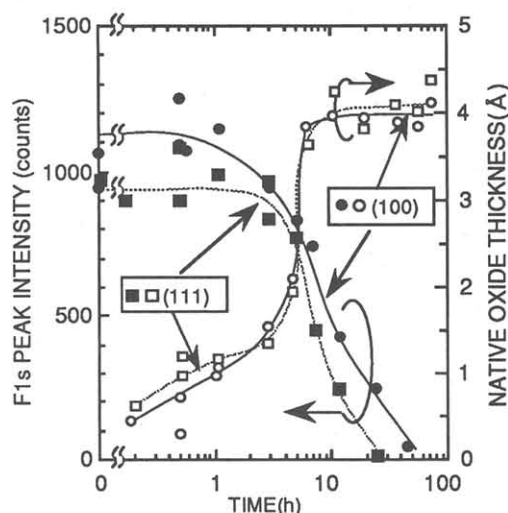


Fig. 7 Time dependence of surface F_{1s} peak intensities and native oxide thicknesses measured using XPS.

4. Conclusion

In conclusion, the native oxide growth rates of HF treated Si (100) and (111) surfaces are not found to be sensitive to the atomic flatness of the surface. These results indicate that the native oxide growth rate on the defective surface would be difficult to control using only hydrogen termination, and other means such as F termination should be investigated.

Reference

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