The Increase of the Native Oxide Thickness of H-Terminated Si Surfaces by Gaseous Contamination in a Clean Room Atmosphere

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Gaseous impurities in a clean room atmosphere cause an increase in the native oxide thickness on Hterminated Si surfaces. Alkaline impurities generate OH⁻, which OH⁻ etches off H-terminated Si atoms. This destroys the effect of H-termination, so the native oxide thickness increases. Therefore, the control of gaseous contamination will become important in future ULSI fabrications.

1. Introduction

several techniques, Recently, including Htermination, have been reported to control the native oxide growth on Si surfaces 1-7), because native oxide degrades the electrical characteristics of thin gate SiO 2 films. Although it is well known that water vapor increases the native oxide growth rate, the influence of chemical gaseous contamination in the atmosphere has not yet been discussed. It has been reported that alkaline impurities in a clean room (CR), such as ammonia (NH₃), degrade the characteristics of chemically amplified resists 8). This fact indicates that even impurities having very small concentrations (on the ppb order), can have a chemical influence on a Si surface. Thus, there is a concern that chemical gaseous contamination could also affect a native oxide growth.

We investigated native oxide growth in a CR atmosphere with various contamination concentrations. We found that the native oxide thickness increased with concentration of chemical gaseous contaminants increase. We also investigated the effect of gaseous impurities for native oxide growth.

2. Experiment

The wafers used in the experiments were Boron doped p-type CZ (100) wafers with a resistivity of 9 to 12 Ohm cm. First, the wafers were dipped in 0.5% HF solution and rinsed in pure water for 5 min to remove the native oxide. Then, they were exposed in either a CR atmosphere or a purified atmosphere. The purified atmosphere was obtained using a chemical filter. The concentration of the chemical contaminants (F⁻, Cl⁻, SO_x and NH₃) in the purified atmosphere were less than one-tenth that in the CR atmosphere. We also investigated atmospheres with added impurities of HF, HCl, SO_x or NH₃. After the exposure, the native oxide thicknesses and the chemical bonds of the Si surfaces were evaluated with an attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectrometer. The ATR-FTIR spectra were measured using 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 a Ge prism were used.

3. Results and discussion

3.1 Native oxide growth in purified atmosphere

Figure 1 shows the ATR-FTIR spectra (700 cm⁻¹ to 1500 cm⁻¹) of surfaces exposed for 96 hours at the respective contamination levels. The Si-O LO phonon peak is seen at about 1150 to 1200 cm⁻¹. The intensity of the surface exposed to the purified atmosphere is found to be lower than that of the CR atmosphere.





Figure 2 shows the exposure time dependence of the Si-O LO phonon integrated peak intensities. We confirmed that these integrated peak intensities are directly related to oxide thickness by using thermal oxide films. These intensities increased with increasing exposure time. The intensity of the surface exposed to the purified atmosphere was lower than that exposed to the CR atmosphere for all exposure periods. These results indicate that the native oxide on the surface exposed to the CR atmosphere is thicker than that on the purified atmosphere. Thus, the chemical gaseous contamination appears to increase the native oxide thickness.



Fig. 2 Exposure time dependence of the integrated Si-O peak (1000-1250 cm⁻¹) intensities.

3.2 Increase in native oxide thickness by ammonia

To clarify the mechanism of the thickness increase, the native oxide thickness on surfaces exposed to an atmosphere containing various added impurities (F, Cl, SO_x or NH₃) were investigated. As shown in Figure 3, only in the case of the NH 3-added atmosphere did the native oxide thickness became greater as the impurity concentrations increased. This result shows ammonia have an increase effect of the native oxide thickness. Figure 4 shows the ATR-FTIR spectra (3000-4000 cm⁻¹) of the Si surfaces exposed for 3 h to the atmosphere with various NH₃ concentrations. The Si-OH peak is seen at about 3630 cm⁻¹. The peak intensity becomes higher as the NH ₃ concentration increases. Thus, we conclude that the OH⁻ generated by the reaction between NH $_3$ and H₂O affects native oxide growth.



Fig. 3 Exposure time dependence of the integrated Si-O peak intensities. The intensities are greater, as higher ammonia concentration.



Fig. 4 ATR-FTIR spectra of the Si surfaces exposed to a atmosphere with various ammonia concentrations. The Si-OH peak intensity is greater at higher ammonia concentrations.

3.3 Mechanism of increase in native oxide thickness by gaseous contamination

On the other hand, the ATR-FTIR results showed a change in the Si-H_x peaks as shown in Fig. 5. As the exposure time increased, the Si-Hx peaks attributed to O-Si-H₃ and O₂-Si-H₂ appeared. We measured and integrated the exposure time dependence of these Si-H_x (including the back bond oxidized Si-H_x) peak intensities. The results normalized by the integrated peak intensities of the unexposed surfaces are shown in Fig. 6. In the cases of the 170 and 20000 ppm NH ₃ concentrations, these normalized values increased during the initial stage of exposure and were greater than 1. This indicates that the number of Si-H_x bonds increased with increasing exposure time.



Fig. 5 ATR-FTIR spectra of the Si surfaces exposed to the atmosphere with different ammonia concentrations.



Fig. 6 Exposure time dependence of normalized integrated Si-Hx peak intensities with various ammonia concentrations.

If the total quantity of surface Si atoms remains constant, the normalized intensity should be 1 or less. The result suggests that there was an increase in the total quantity of Si atoms at the surface. This can be explained if we assume that the surface Si atoms are etched off by OH^- (Fig. 7(a)) and that the surface roughness increases which results in more Si atoms being exposed to the atmosphere. Then, Si-OH bonds form and the effect of the H-termination is lost (Fig. 7 (b)). As a result, the thickness of the native oxide increases.

4. Conclusion

We found that gaseous contamination in a CR atmosphere increases the thickness of the native oxide. The mechanism is assumed that alkaline impurities generate OH^- and the generated OH^- etch off H-terminated Si atoms.



(a) The surface Si atoms etched off by OH



(b) Formation of Si-OH bonds by OH⁻ or H₂O

Fig. 7 Mechanism of the increase in native oxide growth.

As a result, the effect of H-termination is lost and native oxide thicknesses increase. This demonstrates that gaseous contamination must be controlled to obtain highly reliable thin SiO $_2$ films.

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References

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1) T. Yasaka, K. Kanda, K. Sawara, S. Miyazaki and M. Hirose. : Extended Abstracts of the 1991 International Conference on SSDM, 487 2) M. Niwa, H. Iwasaki and S. Hasegawa, J. Vac. Sci. Technol., A8 (1990) 226 3) M. Niwano, Y. Takeda, K. Kuruta and N. Miyamoto, J. Appl. Phys., 72 (1992) 2488 4) Y. J. Chabel, G. S. Higashi, K. Raghavachari and V. A. Burrows, J. Vac. Sci. Technol., A7 (1989) 808 5) D. Graf, M. Grunder and R. Schlz, J. Vac. Sci. Technol., A7 (1989) 808 6) U. Jansson and K. J. Uram, J. Chem. Phys., 91 (1989) 7978 7) T. Takahagi, A. Ishitani, H. Kuroda and Y. Nagasawa, J. Appl. Phys., 69 (1991) 803 8) A. Saiki et al., Jan. J. Appl. Phys. Pt.1, 33