Extended Abstracts of the 1995 International Conference on Solid State Devices and Materials, Osaka, 1995, pp. 836-838

X-Ray Reflectometry and Infrared Analysis of Native Oxides on Si(100) Formed in Chemical Treatment

Yoshihiro SUGITA, Naoki AWAJI, Satoshi OHKUBO, Satoru WATANABE, Satoshi KOMIYA, and Takashi ITO

Fujitsu Laboratories Ltd.
10-1 Morinosato-Wakamiya, Atsugi 243-01, Japan

We determined the absolute density of oxides on Si by glancing incidence X-ray reflectometry (GIXR) for the first time. The chemical structures were revealed by FT-IR analysis and compared with the physical structures. Low-density and inhomogeneity were found in some conventional chemical oxides. We show that dense and chemically-homogeneous oxides could be prepared by ozonized water, a candidate for a feature cleaning solution.

1. Introduction

For MOS devices with gate oxides thinner than 8 nm, the effect of native oxides formed during chemical cleaning before the gate oxidation is important. The structures of the native-oxide depend on the reagents used during cleaning treatment[1]. Chemical and physical non-homogeneity was observed in each native-oxide[2-4]. It is expected that the density and thickness are dependent on the native oxides. However, measurement is difficult for very thin films.

GIXR was used to the quantitative analysis of the native oxide, for the first time. The absolute values were obtained for the native oxides prepared by some cleaning reagents.

2. Experiment

The substrates were n-type (1Ohm·cm) CZ-Si(100) for GIXR and non-doped FZ-Si(100) polished on both sides for FT-IR analysis. The native oxides were formed by boiled H_2SO_4 solution (83%H_2SO_4-4%H_2O_2), boiled HNO_3 solution (61%), boiled HCl solution (7%HCl-5%H_2O_2), boiled NH_4OH solution (4%NH_4OH-8%H_2O_2), and about 10 ppm ozonized water (room temperature), following 5%HF solution dipping. GIXR measurements were performed using a synchrotron radiation (SR) source. A bright SR-beam provides more than seven decades of reflectivity, necessary for the accurate analysis of very thin films, at a wavelength of 0.13 nm. FT-IR transmission and attenuated total reflection (ATR) experiments were carried out to characterize oxide, hydroxide, and Si hydrides in these films.

3. X-Ray Reflectometory Analysis

Figure1 shows the dependence of the reflectivities of the hydrogen-terminated Si prepared by 5%HF solution and the native oxide-on-Si prepared by HCl solution on the incidence angle. The difference in the two reflectivities is also shown in Fig.1.

The reflectivity slope mainly depends on the surface roughness. The surface roughness of Si substrates was estimated as 0.2 ± 0.01 nm (root mean square height) and the surface roughnesses of native oxides was 0.35 ± 0.01 nm, independent of the cleaning solutions within the experimental accuracy.

The oscillation of the differential curve in Fig.1 results from the film interference, of which the amplitude and the frequency represent the density and the thickness, respectively. Figure2 shows the calculated differential curves assuming a 1-nm-thick SiO_2 and a changing oxide density. Apparently the amplitude decreases with the oxide density to 2.33 g·cm^{-3}, that of Si substrate.

Figure3 shows the differential curves from the reflectivities of chemically-treated Si surfaces. Comparing Fig.2 and Fig.3, it is clear that the film density depends on the chemical treatments. The observed film thicknesses and densities ranged between 1.04-1.23 ± 0.05 nm and 2.07-2.23 ± 0.02 g·cm^{-3}, respectively, while the density of thermal oxide is 2.2-2.3 g·cm^{-3}. The low-density films were prepared in HCl solution, NH_4OH solution or HNO_3 solution.The dense films were prepared by H_2SO_4 solution or Ozonized water.

The characters of native-oxides estimated by GIXR are listed in Table 1.

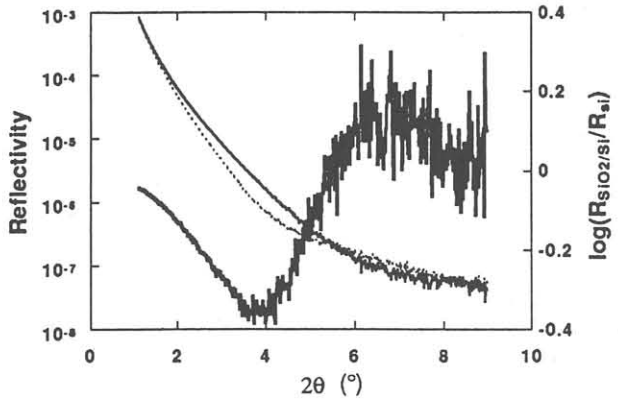

Fig.1 The experimental reflectivity data of the native oxide by HCl solution (thin dot line), its substrate (thin solid line) and the differences (thick lines). The left vertical axis represents reflectivity and the right vertical axis presents the difference (logarithmic scale). The horizontal axis represents the scattering angle 2θ.

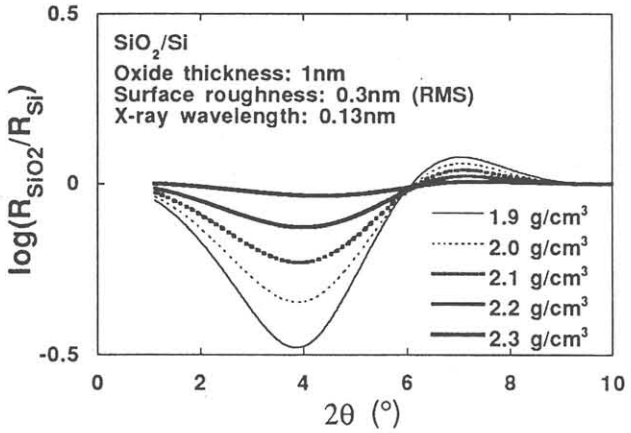

Fig.2 The simulated differential curves. The 1-nm-thick SiO_2 on Si is assumed and the density of SiO_2 varies from 1.9 to 2.3 $g \cdot cm^{-3}$. The surface roughness is 0.3 nm and the substrate roughness is 0.2 nm, typical experimental values respectively.

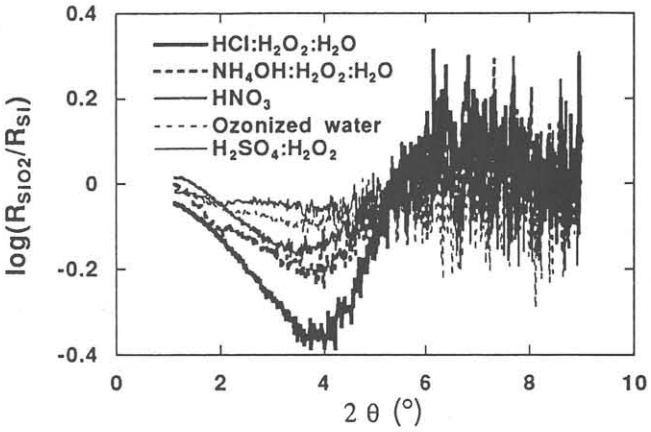

Fig.3 The experimental differential curves are obtained from the reflectivities of five types of native oxides and their substrates.

Table 1
Values of Native Oxides on Si Determined by GIXR

Chemicals	Density (g/cm^3)	Thickness (nm)	Roughness (nm)
HCl:H2O2:H2O	2.07	1.13	0.36
NH4OH:H2O2:H2O	2.11	1.07	0.35
HNO3	2.16	1.23	0.35
H2SO4:H2O2:H2O	2.23	1.04	0.35
Ozonized water	2.21	1.05	0.35
Error	±0.02	±0.05	±0.01

4. FT-IR Analysis

Figure4 shows the FT-IR transmission spectra with an incidence angle of 60°, choosing to surface-sensitize. The dip at 920 cm^{-1} is caused by Si-H scissors bending absorption originated from the reference Si(100) prepared by 5%HF solution. The peaks at 1050 cm^{-1} and at about 1200 cm^{-1} result from the TO and LO mode of Si-O-Si stretching, respectively[5]. The peak intensity depends on the quantity of SiO_2 on Si.

The same amounts of SiO_2 were observed on Si prepared by HCl solution and NH4OH solution. These are the half amounts observed on Si prepared by HNO3 solution, H2SO4 solution or ozonized water, suggesting an imperfection in the SiO_2 network.

The peak intensities and peak positions of the LO mode were different for each native oxide, suggesting that the chemical structures depend on the cleaning reagents[5-6].

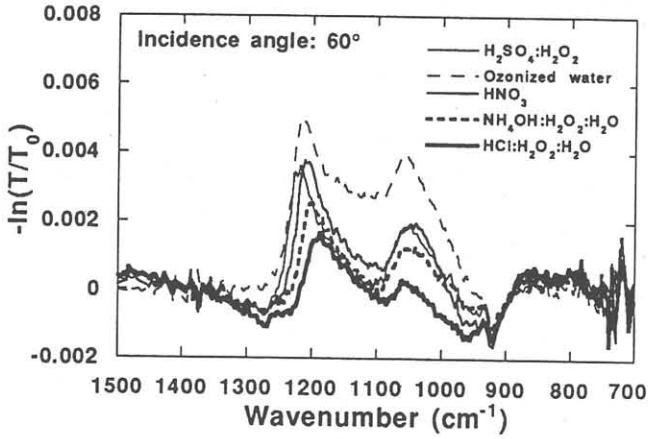

Fig.4 Measured FT-IR P-polarized transmission spectra. The incidence angle to the samples is 60°. The reference is hydrogen terminated Si(100) prepared in 5%HF solution.

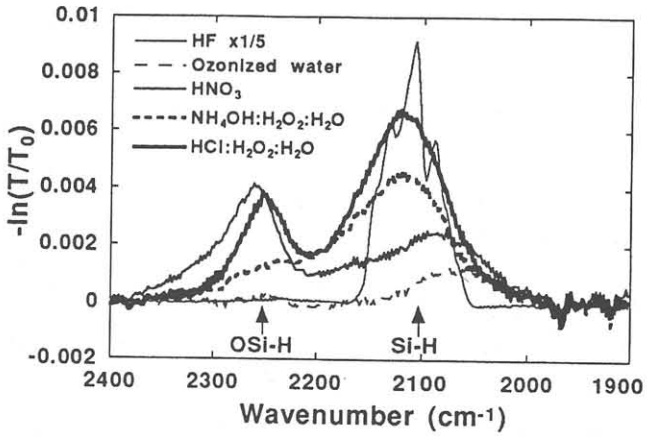

Fig.5 Measured FT-IR ATR spectra. The reference is Si(100) prepared by H2SO4 solution. The absorption spectrum prepared by HF solution is reduced to one-fifth.

Figure5 shows the FT-IR ATR spectra, presenting two types of Si-hydrides (OSi-H,Si-H) in the native oxides.

The OSi-H structure shows the existence of imperfect oxide (sub-oxide) and the Si-H structure reveals the existence of unoxidized part on the substrate surface[4]. The native oxides prepared by HCl solution or HNO3 solution have large amount of OSi-H and Si-H, whereas the native oxide formed by NH4OH solution has a little of OSi-H and a large amount of Si-H, the oxide prepared by ozonized water has very little of OSi-H and a little Si-H, similar to the oxide prepared by H2SO4 solution. The ATR spectrum of 5%HF-solution-treated-Si(100) shows a quantity of one mono-layer Si-H on Si(100).

5. Conclusion

The low-density oxides are prepared by boiled HCl solution, NH4OH solution or HNO3 solution. The dense oxide is prepared in room-temperature ozonized water, just as with boiled H2SO4 solution.

The chemical structures of these native oxides show a correlation with the physical characters. The native oxides having low-density contain many of suboxide and unoxidized areas at the substrate surface. The dense native oxides have homogeneous chemical structures.

Acknowledgment

We would like to thank S. Okamura and T. Hisatsugu for their interests and support.

References

1) M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami, and M. Ohwada, J. Appl. Phys. **68**. (1990) 1272.

2) R. Sugino, Y. Nara, H. Horie, and T. Ito, J. Appl. Phys. **76** (1994) 5498.

3) T. Aoyama, T. Yamazaki, and T. Ito, Appl. Phys. Lett. **61** (1992) 102.

4) H. Ogawa, and T. Hattori, IEICE Tras. Electron. **E75-C** (1992) 774.

5) G. Walrafen, Y. Cu, and M.Hokmabadi, J. Chem. Phys. **92** (1990) 6987.

6) G. Lucovsky, J. Fitch, E. Kobeda and E. Irene, "The Physics and Chemistry of SiO2 and Si-SiO2 interface", Plenum Press, New York (1988) 139.