

Transient Oxide Layer at a Thermally Grown SiO₂/Si Interface, Interpreted Based on Local Vibration and X-Ray Reflectivity

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The macroscopic density of thermally grown SiO₂ on Si under various growth conditions such as change of temperature and the atmosphere and, the related vibrational properties were analyzed using X-ray reflectivity analysis and IR absorption spectroscopy. With an assumed stoichiometry of the oxide layer, we revealed the existence of a denser layer (1 nm-thick, 2.35-2.4 g/cm³) at the SiO₂/Si interface, while the layer density of the remaining region was constant within each oxide.

Introduction

It is known that the macroscopic density of a silicon dioxide grown on Si depends on the oxidation conditions, such as temperature and atmosphere.¹⁾ It is expected that microscopic structure of amorphous-SiO₂ (a-SiO₂) depends on the growth conditions and is related to the reliability of metal-oxide-semiconductor devices.

The infrared absorption spectroscopy used for proving vibration of the Si-O stretching is a sensitive technique for revealing the structure of a-SiO₂. Although the dependence of IR absorption on the growth conditions and thickness of an examined layer have been reported,²⁾ obtained results have often been analyzed without any reference to optical effect.³⁾ It was pointed out again recently that observed absorption spectrum is strongly affected by the oxide layer thickness due to the well-known anomalous dispersion and multiple reflections.⁴⁻⁶⁾

We measured X-ray reflectivity of a-SiO₂/Si using a powerful and highly parallel synchrotron radiation (SR) beam. It enable us to determined accurate the density and the morphology of a thin film without disturbance due to chemical structure.^{7,8)} By comparing microscopic observations with macroscopic observations, we were able to deduce the structures of a thermally grown oxide on Si.

Experiments

The substrates used were 4-inch n-type (1 ohm-cm) CZ-Si(100) wafers for X-ray reflectivity measurement and no-doped both side polished FZ-Si(100) prism shaped wafers for IR analysis. The wafers were pre-cleaned with modified RCA procedure and then oxidized using a quartz furnace. The oxidation temperatures were 850°C, 900°C and 1000°C. Both the dry (pure O₂) and the wet (85°C H₂O bubbled with pure O₂) oxidizing atmospheres were used.

Polarized FT-IR transmission experiments were carried out with an incidence angle of 70°. With this incidence angle, both the longitudinal optic (LO) mode and the transverse optic (TO) mode absorption are detectable, as predicted by the Berreman effect.⁹⁾ It allowed us to analyzed the local structure of a-SiO₂ precisely.

X-ray reflectivity was measured by varying the glancing incidence angle (ψ) using a 2ψ - ψ scanning apparatus

diffractometer. The employed X-ray wavelength was 0.13 nm. We used an SR-beam line equipped with an Si(111) double crystal monochromator at the National Laboratory of High Energy Physics (KEK) for the measurement.⁸⁾ The measured reflectivity versus incidence-angle data was analyzed using an optimizing program based on the Marquardt non-linear minimization fitting technique.

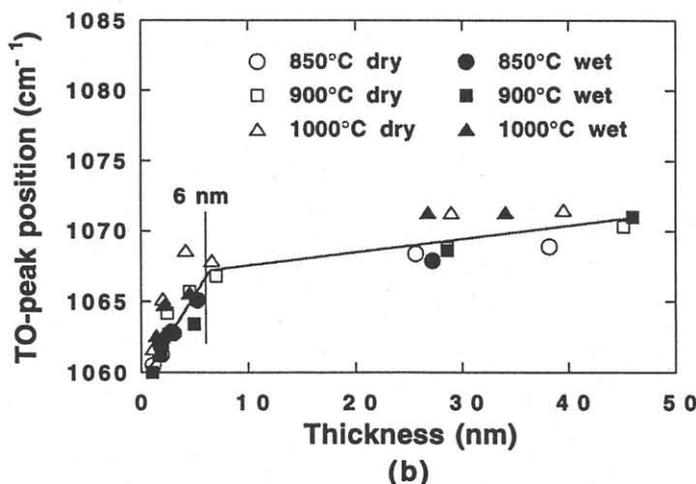
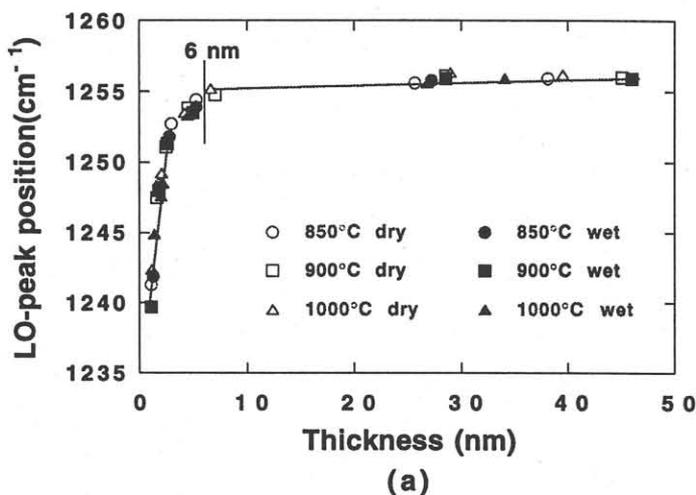
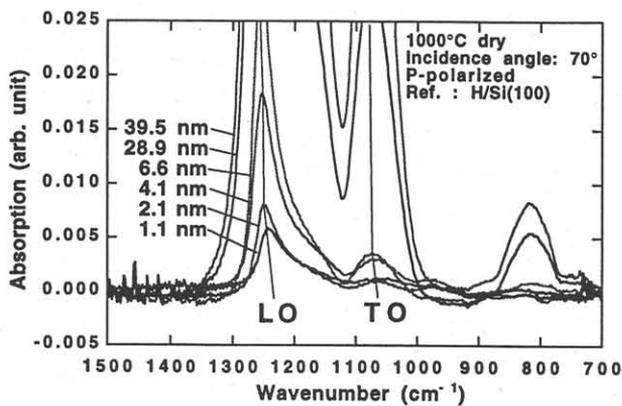
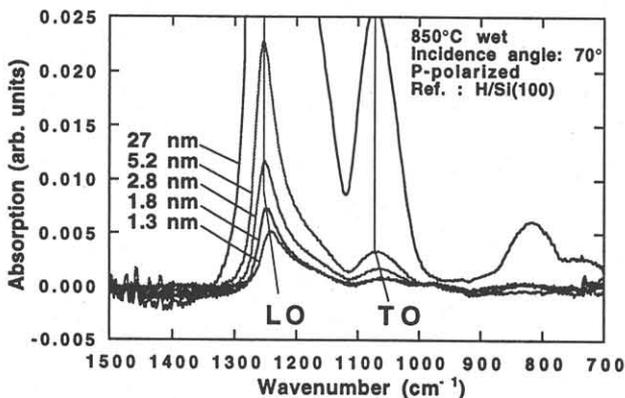


Fig. 1 Peak frequency vs. thickness for Si-O stretching in oxides etched back using a 0.5% HF solution. LO peak was measured with p-polarization and TO peak were measured with s-polarization. Measurements resolution was 4 cm⁻¹.



(a)



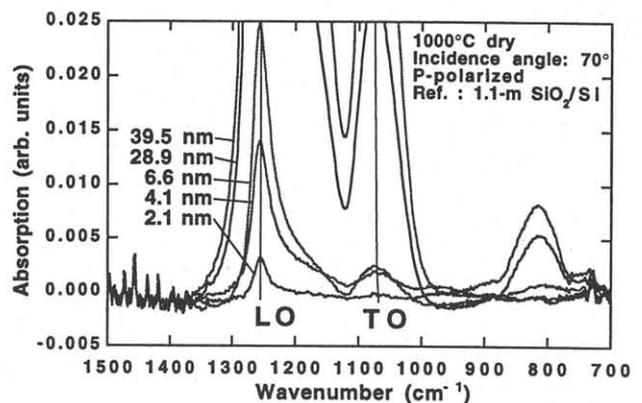
(b)

Fig. 2 IR absorption spectra of thermally grown silicon oxide observed with using an incidence angle of 70° and the p-polarization condition. Film thickness was reduced using 0.5% HF solution. The reference spectrum was measured with hydrogen terminated Si(100) prepared using HF solution. The spectra in (a) were obtained from oxides prepared by 1000°C dry O_2 oxidation. The spectra in (b) were obtained from oxides prepared by 850°C wet oxidation.

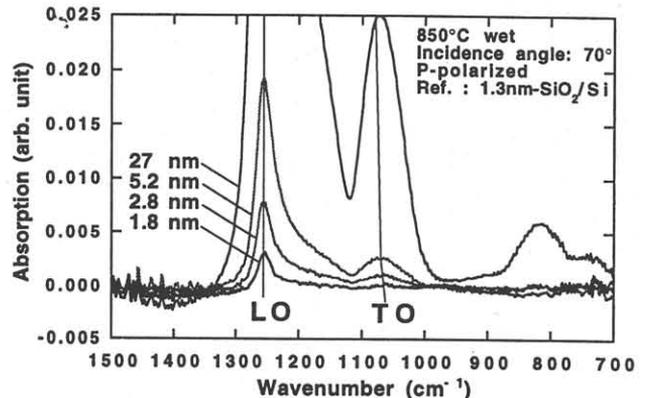
Results and discussion

We etched the oxides using an HF solution to reduce film thickness, and analyzed the IR properties as a function of thickness. Figure 1 shows the relationship between Si-O asymmetric stretching frequency and thickness. For films thicker than 6 nm, the observed TO peak position varies with film thickness, while the LO peak position remains relatively constant. A previous Raman scattering study on densified SiO_2 glass revealed that both the TO mode and the LO mode Si-O stretching shifts toward the red direction with density.¹⁰ The almost constant LO mode frequency obtained when the layers are thicker than 6 nm indicated the uniformity of oxide density in the thickness direction. This rules out the idea of gradual density change with growth thickness.²⁾

When the thickness was reduced to below 6 nm, simultaneous red shift of both TO mode and LO mode peaks were observed. This feature is observed for all oxides formed with various conditions in this experiments. A large red shift is a direct indication of the existence of a thin modified layer. To verify its thickness from our IR experiment, we plotted data points in two different ways.



(a)



(b)

Fig. 3 Observed IR absorption spectra for thermally grown silicon oxide prepared by the same conditions used for Fig. 2. Note that the reference spectrum was obtained with an about 1 nm thick oxide on Si(100) prepared by HF solution. The red shift seen in Fig. 2 is completely canceled for LO and mostly canceled for TO.

Figure 2 shows an example of p-polarized IR spectra with a reference H/Si spectrum and figure 3 shows the same IR spectra with another reference spectrum obtained with an 1-nm-oxide/Si. The red shift shown in figure 2 was canceled in figure 3 by changing the reference. The thickness of modified layer at the interface was estimated to be less than 1 nm.

We also noted, in figure 3, a small red shift of TO. The significant absorption by Si-O stretching causes distortion of IR spectra between the TO and LO regions and the positions of the observed TO absorption peak depends on the oxide layer thickness. The red shifts of TO observed in figure 3 was mostly due to optical effect. We mentioned, however, the relationship between TO peak and layer thickness cannot be fully explained using such anomalous dispersion and reflections.¹¹⁾

We utilized X-ray reflectivity to verify our IR data. The results suggested the existence of a thin dense interfacial layer in SiO_2 . X-ray reflectivity analysis is advantageous for studying macro-structure. The thin film on a substrate causes variation of reflectivity curve. The parameters involved in curve fitting calculation for a reflectivity curve

are film density, film thickness, surface roughness, and interface roughness.⁸⁾

Single oxide layer analysis produces reasonable results for thick oxide layers. However, for films that are thinner than 10-nm, curve fitting of the oscillating curve is unsatisfactory as shown in figure 4 (a), since the conditions of the single layer model do not apply in this case. Therefore, we add a dense oxide layer at the interface and applied the double layer analysis instead. This curve fitting method produces successful results for the oscillating curve, as demonstrated in figure 4 (b). The modified layer was about 5% denser than the upper layer. The thickness of the transient layer was about 1 nm for all samples in combination with various film thicknesses, and was almost independent of the SiO₂ layer growth condition.

The X-ray reflectivity analysis supported our interfacial model. We showed experimentally that there was a dense transient layer at the interface, and its macroscopic density was found constant throughout its thickness, except for a thin transient region.

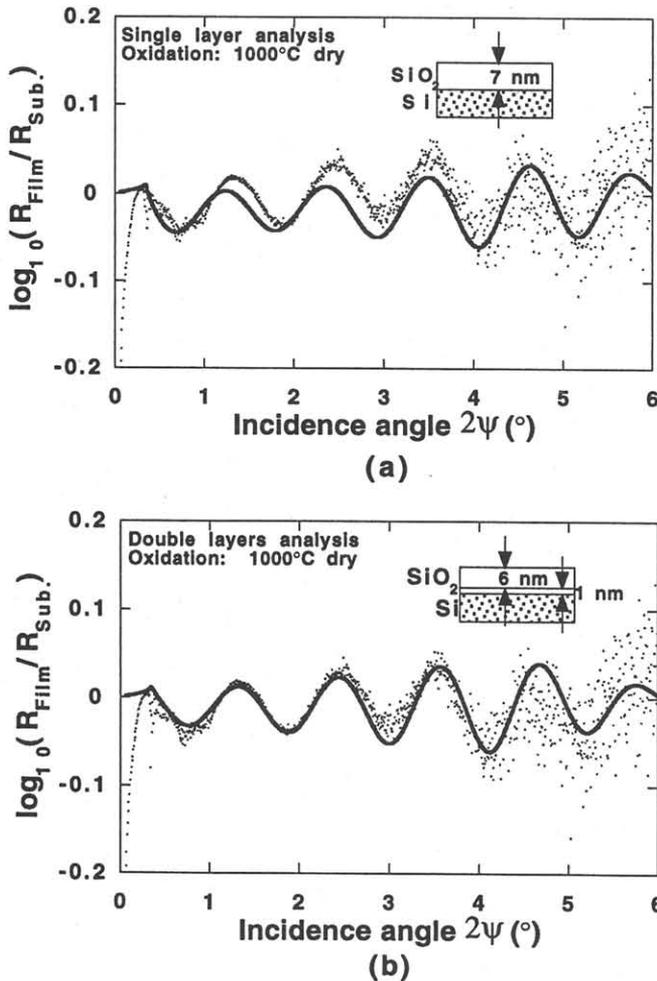


Fig. 4 Curve fitting based on a single-layer oxide on Si model (a) and a double-layer oxide on Si model (b), for data obtained by X-ray reflectivity analysis. Dots in the figure indicate the thin film oscillation data extracted from a measured X-ray reflectivity-incidence-angle curve. The thin line is the calculated fitting result.

Conclusion

The macroscopic density of SiO₂ on Si(100) and its local vibration were examined. IR transmission analysis revealed a thickness dependence of both the TO and LO mode of Si-O asymmetric stretching.

Simultaneous red shift of TO and LO originate from a modified layer of 1-nm thick at the interface. It strongly suggested that the a-SiO₂ network in that region had been densified due to compressive stress. The observed frequency shifts in TO toward the red direction decreased with the oxide film thickness. This red shift observed over a wide range relative to the film thick, however, was mainly optical effect oriented. There was no relation between the red shift and oxide density, contrasting to previous report. By X-ray reflectivity analysis, the density and the thickness of the modified layer were estimated to be 2.35-2.4 g/cm³ and about 1 nm, respectively. The macroscopic density of the film is considered constant in the thickness direction for oxides without an transient layer.

We think that the densification of the transient layer is caused by the volume expansion of SiO₂ during thermal oxidation or SiO₂/Si hetero-junction formation.

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