

## Analysis of SiO<sub>2</sub> Thin Film on Si Wafer

IR spectroscopic analysis has been used for a long time as an analysis method for silicon wafers to analyze the interstitial oxygen atom concentration in silicon, substitutional carbon atoms in silicon crystals, nitride films on a silicon wafer surface, and the oxygen content of nitride films.

While relatively thick films of SiO<sub>2</sub> used for insulation could be analyzed, good results were not achieved for

sub-nanometer thin films, mainly due to sensitivity problems.

In this Application News SiO<sub>2</sub> thin films between one and several nanometers thick formed on silicon wafers are analyzed with the Shimadzu IRPrestige-21, using the transmission and ATR (single-reflection, Ge prism) methods.

### ■ Vibrational Peaks of SiO<sub>2</sub>

Transmission measurements were conducted at three different angles of incidence on a 4.2nm SiO<sub>2</sub> thin film formed on a silicon wafer. The angles of incidence used were 0°, 30° and 45° with respect to a line normal to the silicon wafer surface. A silicon wafer with no SiO<sub>2</sub> film was used as the reference to eliminate the effects of oxygen on the silicon wafer (Si interstitial oxygen: near 1110cm<sup>-1</sup>). Fig. 1 shows the results of the measurements.

Distinct peaks are apparent near 1250cm<sup>-1</sup> and 1065cm<sup>-1</sup> in the transmission spectrum for 45° angle of incidence. However, the 1250cm<sup>-1</sup> peak is smaller at 30° angle of incidence and almost disappears at 0°. Conversely, the intensity of the peak near 1065cm<sup>-1</sup> changes little.

As the transmission measurements observe the vibration of molecules in the direction perpendicular to the light propagation, it seems that the 1250cm<sup>-1</sup> peak results from vibrations in the direction normal to the silicon wafer surface.

Fig. 2 shows the results of single-reflection ATR (Ge prism) measurements of the same sample superimposed over the spectra shown in Fig. 1. This diagram shows that the peak intensity from the ATR measurements is almost 20 times greater than the intensity in the transmission spectrum at 45° angle of incidence, but the peak is shifted to near 1244cm<sup>-1</sup>.

This phenomenon is thought of as the peak intensity in the normal direction of the vibration peak was increased by the standing waves created between the prism and silicon wafer, as in high-sensitivity reflection.

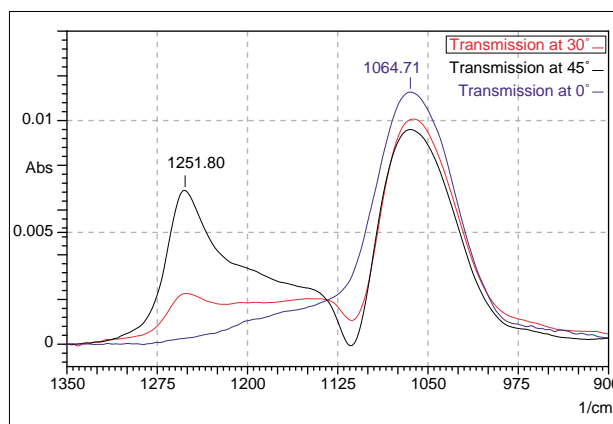


Fig.1 Transmission Spectra of SiO<sub>2</sub> on Si Wafer  
Angles of incidence: 0° (blue), 30° (red), and 45° (black)

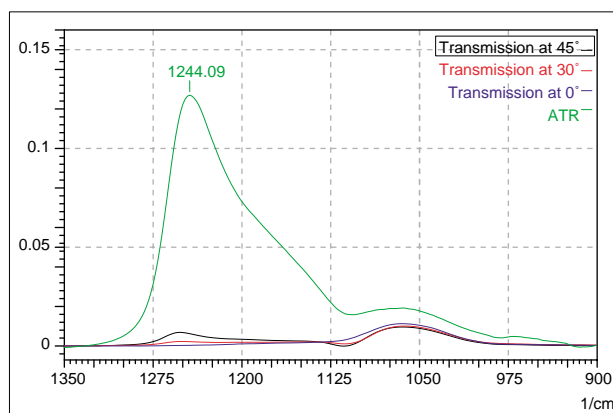


Fig.2 Transmission Spectra & ATR Spectrum

### ■ Measurement of SiO<sub>2</sub> Sub-nanometer Thin Films

Four silicon wafers with different SiO<sub>2</sub> thin films were measured using the transmission method at 45° angle of incidence and using the single-reflection ATR (Ge prism) method. The film thicknesses of the SiO<sub>2</sub> films were 4.2, 1.3, 0.8, and 0.4nm (\*Note). Fig. 3 shows the results for 45° transmission measurements and Fig. 4 the results for ATR measurements. It is apparent that even the thinnest (0.4nm) SiO<sub>2</sub> film was detected. The thinner the oxide layer was, the peaks near 1250cm<sup>-1</sup> and 1065cm<sup>-1</sup> shift toward the lower wavelength end.

To determine the correlation between the peak intensity in the 45° transmission spectra and the film thickness, the peak height was plotted up the vertical axis and the film thickness along the horizontal axis. Fig. 5 shows the results for the high-wavelength peak and Fig. 6 the results for the low-wavelength peak. These results indicate that a good correlation was achieved between peak intensity and film thickness.

#### \*Note

SiO<sub>2</sub> films can be removed from silicon wafers by washing with hydrofluoric acid. However, due to the effects of oxygen and water, a natural silicon oxide film forms readily if the silicon wafer is stored in the atmosphere. The rate of film growth is largely dependent on the film thickness. In air, a monomolecular (0.2nm) film forms within one hour after washing with hydrofluoric acid. However, it takes some time to form a film 1nm thick; up to one month has been reported.

In these measurements, a reference sample that had been left several days after washing with hydrofluoric acid was used. A natural silicon oxide film (film thickness (0 +  $\alpha$ ) nm) formed on the reference sample surface. Similarly, on a measured sample with a 0.4nm film thickness, the actual film thickness may change to (0.4 +  $\beta$ ) nm. This change in film thickness is normally larger in regions of lower thickness ( $\alpha > \beta$ ), such that the actual difference in film thickness should not exceed 0.4nm.

#### Acknowledgement

The information on the thin film samples in this analysis was obtained with the cooperation of Dr. K. Nakamura, major researcher at the Ultra-fine Profiling Technology Research Laboratory, National Institute of Advanced Science and Technology (AIST).

Table 1 Analytical Conditions

Resolution	: 4cm <sup>-1</sup>
Accumulation	: 200(Trans), 100(ATR)
Detector	: DLATGS

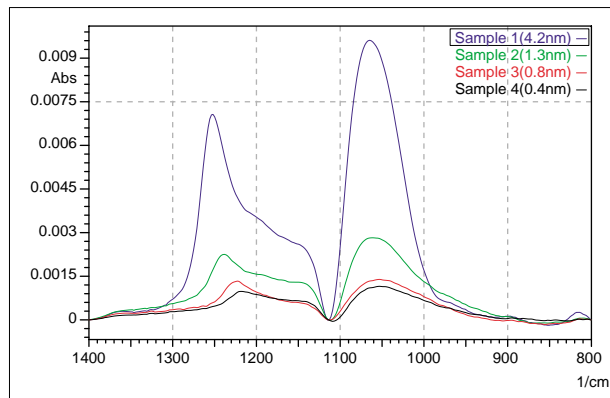


Fig.3 Transmission Spectra of SiO<sub>2</sub> Thin Film (45°)  
Film thicknesses: 4.2nm (blue), 1.3nm (green), 0.8nm (red), 0.4nm (black)

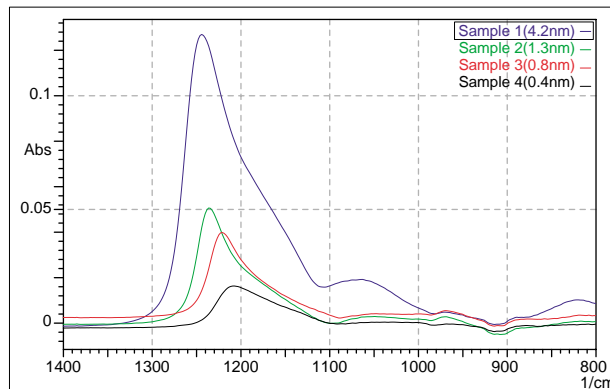


Fig.4 ATR Spectra of SiO<sub>2</sub> Thin Film  
Film thicknesses: 4.2nm (blue), 1.3nm (green), 0.8nm (red), 0.4nm (black)

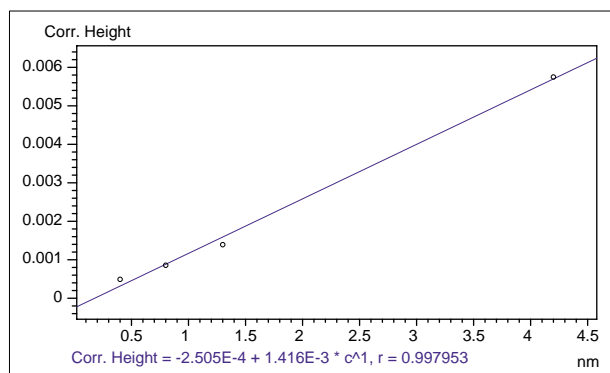


Fig.5 Calibration Curve (High-wavelength Peak)

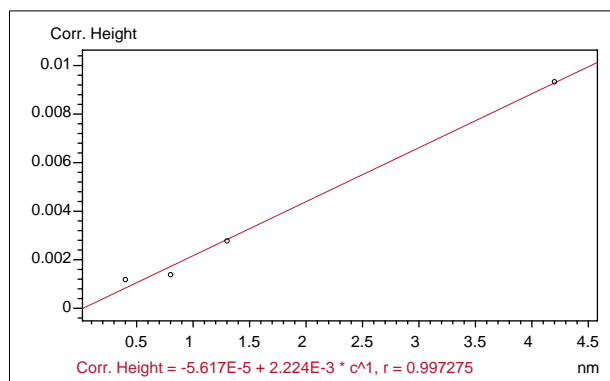


Fig.6 Calibration Curve (Low-wavelength Peak)

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