Extended Abstracts of the 1991 International Conference on Solid State Devices and Materials, Yokohama, 1991, pp. 574-576

Infrared Characterization of SiO_2 Ultra Thin Film by Grazing Internal Reflection

Masanori OKUYAMA, Yuichi MATSUI, Yasuo MIYAGAWA, Yoshihiro HAMAKAWA

Department of Electrical Engineering,
Faculty of Engineering Science, Osaka University
1-1, Machikaneyama-cho, Toyonaka, Osaka 560, Japan

Infrared absorption of SiO_2 ultra-thin film of 2-10nm thickness has been investigated by Grazing Internal Reflection(GIR) method. Measured sample is a Si block covered by SiO_2 and metal (MOS structure), and infrared light is reflected on the MOS face in large incident angles of about 70-80 degrees. The infrared light is confined in the SiO_2 layer and so the absorption is intensified very much. Very large absorption has been observed around $1240cm^{-1}$ corresponding to Si-O-Si bonding vertical to the Si surface. The measured data agree well with the calculated values. Moreover, slight absorptions of Si-H and Si-OH have been easily measured as strong signal change of about 1%.

1. INTRODUCTION

Recently, SiO_2 ultra thin film of nm-order thickness near MOS interface becomes important, as very large integration of semiconductor device has been developed very much and thickness of gate oxide has been reduced with decreasing the driving voltage. But, nondestructive characterization of inside and interface of the ultra thin film in the atmosphere is very difficult, although surface analyses in the vacuum such as XPS and AES are available. Infrared transmittance is very convenient to study atomic bondings in SiO_2 film of thickness of several thousands angstroms. However the infrared transmittance cannot be applied to measure ultra-thin SiO_2 film as optical density of the film along light path is very small. Attenuated Total Reflectance(ATR) of infrared light is useful to study adsorbates or bondings on the Si surfaces. Moreover infrared Grazing Internal Reflection (GIR) measurement can be done in the atmosphere, uses MOS structure as a sample, and is more sensitive than conventional ATR technique.[1] The high sensitivity is attributed to optical confinement in the SiO_2 film between semiconductor and metal. In this paper, we have investigated the GIR induced by infrared absorption in the SiO_2 ultra thin film and characterized the film in the form of a complete MOS structure.

2. THEORETICAL ANALYSIS OF GIR

Sample structure used for the GIR measurement is shown in Fig.1. Infrared light is introduced from a side of the Si trapezoid and is reflected by the bottom face of MOS structure. Reflectance on the bottom face is multiple-reflection of Si-SiO_2-Al structure and is expressed by

$$R = \left| \left[r_1 + r_2\exp(-2j\beta_1) + r_3\exp\{-2j(\beta_1+\beta_2)\} + r_1r_2r_3\exp(-2j\beta_2) \right] / \left[1 + r_1r_2\exp(-2j\beta_1) + r_2r_3\exp(-2j\beta_2) + r_3r_1\exp\{-2j(\beta_1+\beta_2)\} \right] \right|^2 \quad (1)$$

where r_i(i=1-3) is reflectance between ith and i-1th layers(0th layer: air, 1st layer: Si, 2nd layer: SiO_2, 3rd layer: Al), $\beta_i = 2n_i d_i \cos\theta_i / \lambda$, n_i: complex refractive index of ith layer, θ_i: incident angle in ith layer and λ wavelength. Reflectances of p and s polarization, R_P and R_S (reflectance of electric vector parallel and normal to the plane of incidence, respectively) are calculated using equation (1). Refractive indices of Si, SiO_2 and Al at λ =9.0 μm are 3.4180, 0.80-j2.6 and 21.1-j61.3, respectively. Reflectances of the structures having SiO_2 ultra-thin films

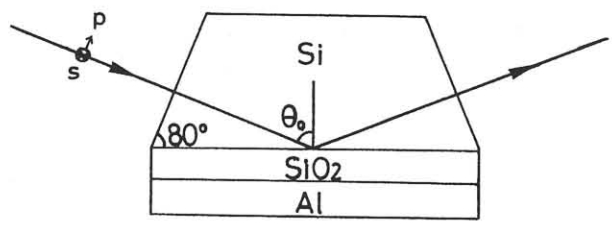

Fig.1 Sample structure for GIR measurement

with and without absorption (complex refractive indices are /0.80-j2.6 and 0.80, respectively), R & R_o, and their difference, δ R are calculated as a function of incident angle by using Eq.(1). Calculated R, R_o and δ R of the structure of SiO_2 film of 2nm are shown in Fig. 2. δ R increases with increasing the incident angle, approaches the maximum value, decreases again with increasing the incident angle and become zero. Moreover, δ R becomes larger again after having the maximum and another peak. δ R are calculated as a parameter of SiO_2 film thickness and are shown in Fig. 3. The maximum δ R are $\sim$0.25 - 0.5 at the SiO_2 thickness of 2 - 100nm. The maximum δ R and its incident angle are plotted in Fig. 4. The solid lines correspond to the maximum at low angle as shown in Fig. 2, and the broken lines to that at high angle. The maximum δ R at low angle increases abruptly with increasing the incident angle above about 2nm and almost saturates above about 10nm. The maximum δ R at high angle has a large peak at $\sim$1.2nm. The incident angle showing the maximum δ R decreases almost with increasing SiO_2 film thickness above about 2nm.

δ R was also calculated in the structure of the same thicknesses with that of Fig. 4 when extinction coefficient, k was changed from 0.02 to 2.4. The calculated values are plotted in Fig. 5 and 6. The maximum δ R much increases with increasing k, has the maximum near k=0.4 and decreases again. The largest value of the maximum δ R is about 0.5. This large absorption is enormous considering that the thickness of the SiO_2 film is 2nm.

3. GIR SPECTRA MEASUREMENT

SiO_2 ultra thin film was prepared by photo-CVD, thermal oxidation and chemical oxidation on Si trapezoidal element having an angle of 90 and 80°. Al metal film was also formed on the trapezoid as shown in Fig. 1. Infrared reflectance was measured by a fourier-transformation spectrometer (Japan Spectroscopic FT/IR-3) equipped with ATR

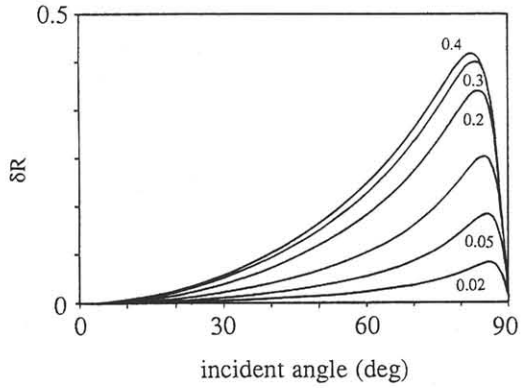

Fig. 5 Incident angle dependence of δ R.

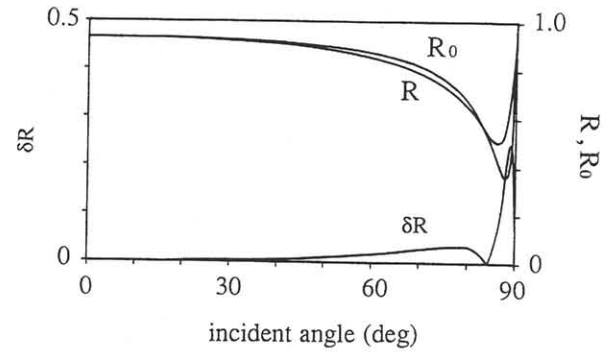

Fig. 2. Reflectances of the MOS structure having SiO_2 films(2nm thick) of k=2.6 and 0 (R and R_o), and δ R.

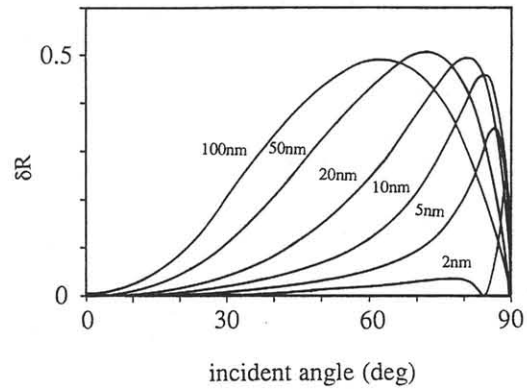

Fig. 3. δ R as a function of incident angle.

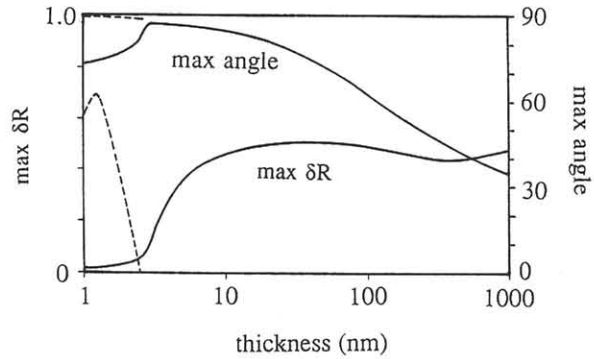

Fig. 4. Thickness dependence of maximum δ R and its incident angle

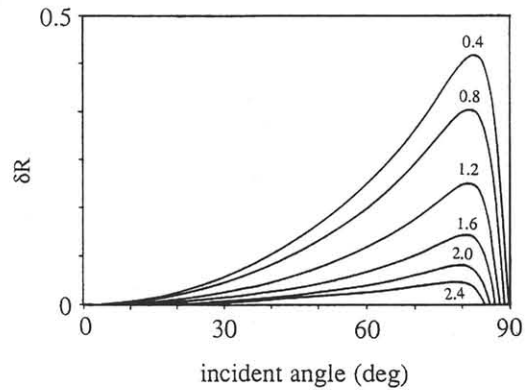

Fig.6 Incident angle dependence of δ R.

attachment. Infrared light beam was introduced from one side of the trapezoid and the reflected light was taken out from the other side. The absorption in the atmosphere and the Si trapezoid can be canceled by dividing R_P by R_S. R_P/R_S is corresponds to R/R_O as R_S is affected little by absorption in the SiO_2 film.

3. RESULTS

Infrared spectrum of R_P/R_S of the samples with and without SiO_2 film of thickness of about 2nm is shown in Fig. 7. Large peak appears near 1200cm^{-1} and small peaks are found near 2200 and 3700cm^{-1}. Magnified R_P/R_S near 1200cm^{-1} is also shown with transmittance of normal incidence in Fig. 8. The peaks are due to Si-O-Si stretching. The GIR spectrum yields a sensitivity almost 100 times larger than the conventional transmission. The large absorption near 1240cm^{-1} could be attributed to 180° Si-O-Si bond[2] which exists near the interface and is active to the p-polarization light.

The measured values of $1-R_P/R_S$ of the films of thickness of 2, 5, 10nm are plotted in Fig. 9. The calculated values of $1-R_P/R_S$ are drawn as a function of incident angle in Fig.9 by solid lines. Complex refractive index used for this calculation is 0.6+j0.6 which is considerably different from the reported value of SiO_2 bulk. The measured data agree well with the calculated values. Therefore, the refractive indices are considered to be different from the bulk value. The angle of the maximum $1-R_P/R_S$ shifts when the film thickness is changed. Moreover, by the GIR, weak Si-OH absorption peak could be measured easily as shown in Fig. 10.

REFERENCES

1) R. Brendel: Appl. Phys. A50 587 (1990).
2) J. E. Olsen and F. Shimura: J. Appl. Phys. 66 1353 (1989).

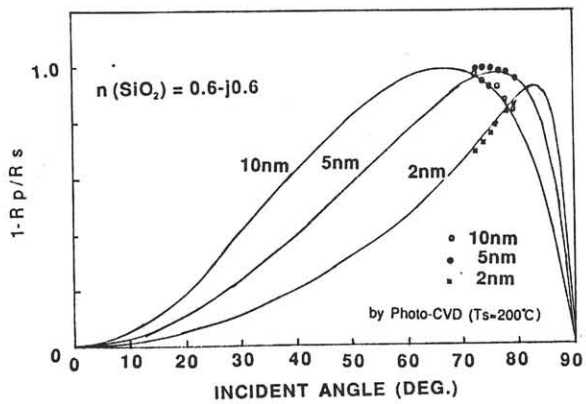

Fig. 9. GIR spectra, $1-R_P/R_S$ as a function of incident angle. Solid lines; calculated values.

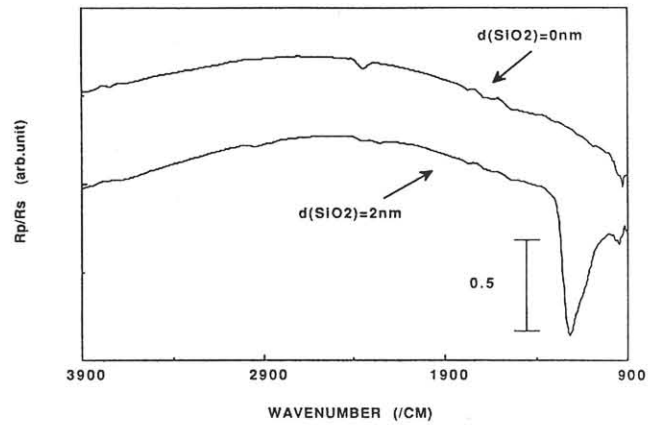

Fig. 7. GIR spectra, $1-R_P/R_S$ of the samples with and without SiO_2 film of thickness of 2nm.

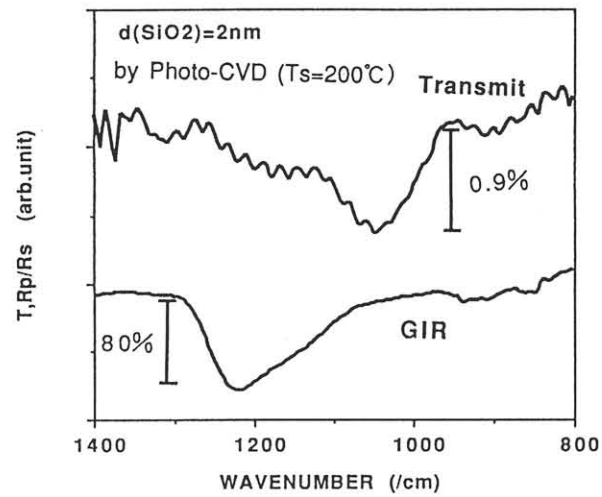

Fig. 8. Comparison of transmittance and GIR spectra near 1200cm^{-1}.

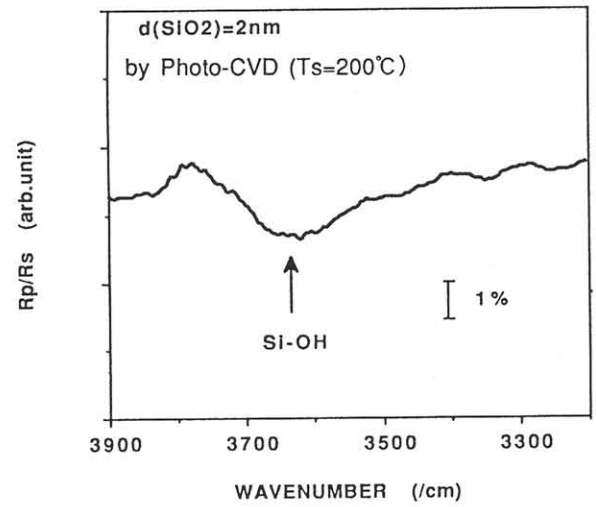

Fig. 10. GIR spectrum of Si-OH absorption.