Original Paper

Analysis of SiO_2 Films on Si Substrate by GD-OES Depth Profiling and GIXR Measurements

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The international standardization on analysis of oxide films formed on the solid surfaces by glow discharge optical emission spectrometry (GD-OES) is now active from the background of demand of the quantification of oxide films on solids. In the quantification of GD-OES depth profiles, an effective density of oxide films is needed to estimate the quantitative depth profiles from the relationship between emission intensities of elements and sputtering time. In this work GD-OES depth profile of SiO_2/Si films, which were formed on the surface of silicon by annealing in air, were quantitatively analyzed. Furthermore, the thickness of the oxide films estimated by GD-OES was compared with that by grazing incidence X-ray reflectivity (GIXR). The results showed that the results obtained by GD-OES were consistent with those GIXR.

1. Introduction

The international standardization on analysis of oxide films formed on the solid surfaces by glow discharge optical emission spectrometry (GD-OES) is now in progress. This is because the quantification of the composition and thickness of oxide films formed on the surfaces of metals and semiconductors is strongly required. In the quantification of GD-OES depth profiles, several parameters are necessary to calculate the composition and thickness of films from the relationship between the emission intensities from elements and the sputtering time in depth profiling [1,2]. In this work, GD-OES depth profiling of SiO_2/Si films, which were prepared by annealing silicon wafers in air, were carried out. The quantitative relationship between the composition and thickness of the oxide films were estimated from the GD-OES data.

The oxide films should be analyzed by another method in order to evaluate the thickness and density of the oxide film. The grazing incidence X-ray reflectivity (GIXR) method [3,4] was used for estimating the thickness and density of the oxide film on the silicon substrate in this work. The density estimated from the GIXR data was compared with the value used in the quantitative GD-OES depth profile analysis. Also, the thickness of an oxide film calculated form a GD-OES depth profile was compared with that estimated by GIXR analysis. On the basis of these different results, the validity of depth profiling by GD-OES is discussed.

2. Experimental

Silicon wafer oxidized in air (SiO_2/Si film), of which the oxide thickness were ca. 200 nm, 100nm, 50 nm, and 10nm, were prepared. They are referred to as Sample A, B, C and D hereafter.

GD-OES apparatus used was Horiba JY-5000RF. GD-OES depth profiles were obtained by measuring emission intensities for elements as a function of sputtering time under specific conditions [5]. The quantitative relationship between the composition and thickness were estimated according to a standard procedure [1,2].

GIXR measurements were performed with an X-ray diffractometer (PANalytical, X'Pert PRO MRD), in order to obtain the reflection curves of SiO_2/Si films. A mono-

chromatic X-ray beam of Cu $K\alpha_1$ obtained with Ge-220 double crystal monochromator coupled with a Göbel mirror was used as incident beam. The density and thickness of oxide films were estimated by comparing experimental reflection curves with theoretical curves.

3. Results and discussion

3.1 GD-OES depth profile analysis

The methods for calibration and quantitative evaluation of GD-OES depth profiles are described briefly here. They are based on the concept of emission yield, which is defined as the emitted light of a spectral line per unit sputtered mass of the element. As the emission yield is an element- and instrument-dependent quantity, it should be determined independently for each spectral line and instrument. The assumption in this quantification technique is that the integrated signal intensity from one element (or its spectral line) is proportional to the sputtered mass of that element. This means that the emission yield is independent of the sample matrix. This has been investigated by several work [2,5], and is up to now widely accepted to be valid, or it is at least to a first approximation. The relationship mentioned above can be mathematically expressed as follows:

$$R_{i\lambda} = I_{i\lambda} \times \partial t / \partial m_i \qquad (1)$$

where m_i is the sputtered mass of element i during time increment; $I_{i\lambda}$ is the emission intensity of spectral line λ of element i; $R_{i\lambda}$ is the emission yield of spectral line λ of element i. Equation (1) is equivalent to:

$$I_{i\lambda} = c_{iM} \times q_M \times R_{i\lambda} \qquad (2)$$

where c_{iM} is the mass fraction of element i in sample M; q_M is the mass loss rate or the sputtering rate of sample M.

Calibration is performed by determining calibration functions based on the emission yield concept, by means of calibration samples. These samples are generally of bulk with known concentrations, in which it is necessary to determine the sputtering rate of calibration sample. Samples with coatings of known composition and thickness may be used. Due to the matrix-independence of emission yields, the calibration samples do not have to be of similar composition to the unknown samples that are to be measured.

There is a basic form of the equations for the calibration functions used in commercially available spectrometer systems:

$$c_{iM} = k_{i\lambda} \times I_{i\lambda} / q_M - B'_\lambda \qquad (3)$$

where $k_{i\lambda}$ equals $1/R_{i\lambda}$; and B_λ' is a spectral background term at wavelength λ. These parameters are the actual calibration constants, obtained by regression analysis of the calibration data according to a standard least squares fit algorithm.

A quantitative GD-OES depth profile of Sample A (ca 200 nm SiO_2/Si film), which was obtained by the above procedure, is shown in **Fig.1**. In the quantification, the effective density of oxygen was assumed to be about 2.2 g/cm^3, which is the density of SiO_2 glass. Although there is some fluctuation in the mass fraction of the oxide film, the depth profile reveals the characteristic features of the oxide film. The fluctuation of the mass fraction may be attributed to changes of emission intensity during sputtering.

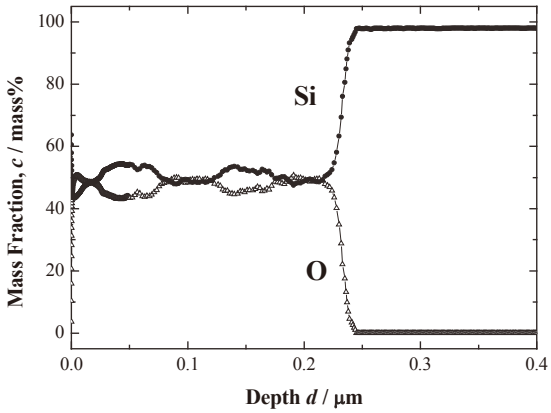


Fig.1 GD-OES depth profile of Sample A (ca.200nm SiO_2/Si).

3.2 GIXR analysis

The thickness and density of oxide films can be estimated from analysis of GIXR data using the following method. In GIXR, the refractive index, n, for X-rays of energy E is given by the following equation [3].

$$n = 1 - \delta + i\beta \qquad (4)$$

$$\delta = \frac{\lambda^2 r_e}{2\pi v_c}\sum_j \left(Z_j + f_j'(E)\right) \quad (5)$$

$$\beta = \frac{\lambda^2 r_e}{2\pi v_c}\sum_j \left(-f_j''(E)\right) \quad (6)$$

where λ is the X-ray wavelength; r_e the classical electron radius; v_c the volume of unit cell; Z_j, $f'_j(E)$ and $f''_j(E)$ are the atomic number, the real and imaginary parts of the anomalous dispersion term of j-th element, respectively. As δ is positive in all cases, n is less than unity. Therefore, the total external reflection may occur for angles of incidence α lower than the critical angle α_c. If the absorption for X-rays is considerably small, the critical angle is simply expressed by,

$$\alpha_c = \sqrt{2\delta} = \lambda\sqrt{\frac{r_e}{\pi v_c}\sum_j \left(Z_j + f_j'(E)\right)} \quad . \quad (7)$$

As $\{Z_j+f'_j(E)\}/M_j$ (M_j : an atomic weight of j-th atom) is approximately equal to 1/2, the critical angle is related with the density α as follows,

$$\alpha_c = \lambda\sqrt{\frac{r_e N_A}{2\pi}\rho} \quad , \quad (8)$$

where N_A is Avogadro's number.

Under a condition of the angle of incidence less than α_c, the characteristic depth denoted by $D(\alpha)$ at which the electric field fallen by a factor e^{-1} is described by,

$$D(\alpha) = \frac{\lambda}{4\pi q} \quad (9)$$

$$q = \frac{1}{\sqrt{2}}\sqrt{\sqrt{(\alpha^2-\alpha_c^2)^2+4\beta^2}+\alpha_c^2-\alpha^2} \quad .(10)$$

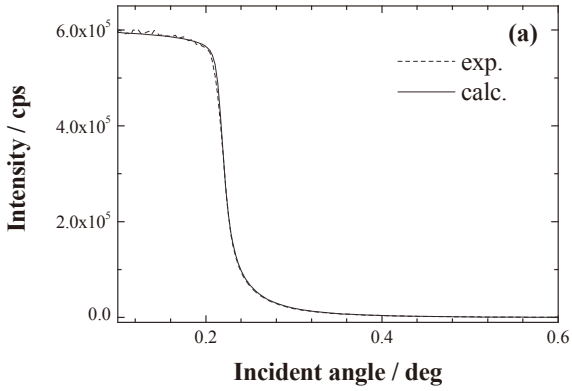
On the other hand, the reflectivity of X-rays, $R(\alpha)$, which is defined by the ratio of the incident to the reflected intensities is expressed by,

$$R(\alpha) = \frac{(\alpha-p)^2+q^2}{(\alpha+p)^2+q^2} \quad (11)$$

$$p = \frac{1}{\sqrt{2}}\sqrt{\sqrt{(\alpha^2-\alpha_c^2)^2+4\beta^2}-\alpha_c^2+\alpha^2} \quad (12)$$

where q is given by Eq.(9).

Thus, theoretical GIXR profiles are estimated on the basis of the model layered structure. **Figure 2** shows experimental and calculated reflection curves of Sample A (ca 200 nm SiO_2/Si) in linear and logarithm scale. The oscillating intensity observed in the logarithm plot was focused to fit calculated results with experimental data, as shown in Fig.2(b). The thickness and density of the oxide films can be estimated based on from this fitting.



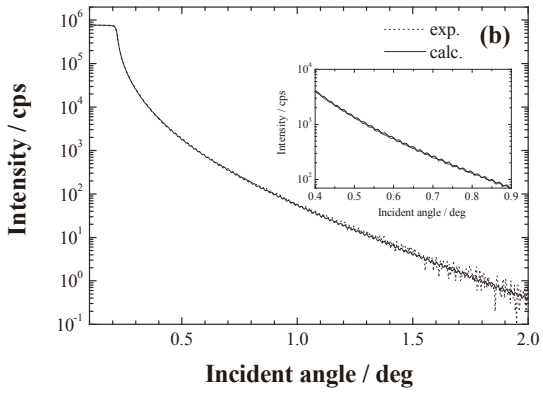


Fig.2 Experimental and calculated reflection curves of Sample A (ca.200nm SiO_2/Si) in (a) linear scale and in (b) logarithm scale.

In a similar manner, experimental and calculated reflection curves of Sample B (ca. 100 nm SiO_2/Si), C (ca. 50 nm SiO_2/Si) and Sample D (ca. 10 nm SiO_2/Si) are shown in **Fig.3**. It is noted that the periodicity in oscillation of the intensity increases with decreasing the thickness of the oxide films. The oxide thickness and density obtained by these fitting are summarized in **Table 1**. The density estimated from the GIXR is approximately 2.2 g cm^{-1}, which is consistent with the value used in GD-OES analysis. The thickness of the oxide film on Sample A estimated from GD-OES depth profiles was fairly consistent with the value estimated by the GIXR method, although further systematic investigations by GD-OES should be carried out.

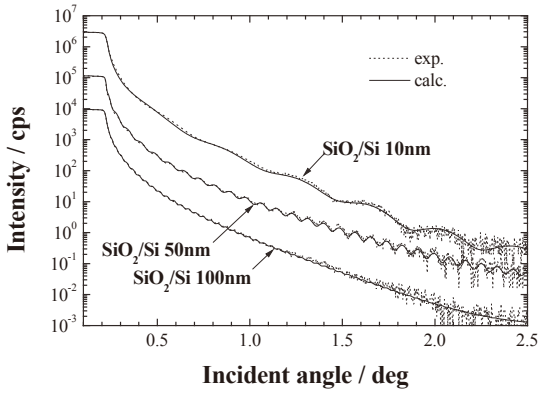


Fig.3 Experimental and calculated reflection curves of Sample C (ca.50nm SiO_2/Si) and Sample D (ca.10nm SiO_2/Si).

Table 1 Thickness and density of Sample A and Sample B estimated from GIXR analysis

	Thickness (nm)	Density (g/cm^3)
Sample A	231	2.22
Sample B	105	2.24
Sample C	51	2.26
Sample D	11	2.24

4. Conclusions

GD-OES depth profiling was performed for SiO_2/Si films, which were prepared by annealing silicon wafers in air. The quantitative relationship between the composition and thickness of the oxide films were estimated from the GD-OES data.

The oxide films were characterized by the grazing incidence X-ray reflectivity (GIXR) method, in order to evaluate the thickness and density of the oxide film. The density was estimated to be approximately 2.2 g cm^{-1} from the GIXR data, irrespectively of the oxide film thickness. The density was almost consistent with the value used in the quantitative GD-OES depth profile analysis. The oxide thickness obtained by GD-OES analysis was also in agreement with that estimated by GIXR analysis. These results indicate that the GIXR method is a potential method for checking depth profiles obtained by GD-OES.

Acknowledgements

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