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Effect of Surface Contamination on Thickness Evaluation of SiO_2/Si by X-ray Reflectometry

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In order to evaluate the thickness of SiO_2 films on Si substrates accurately for the development of a thickness standard material, we suggested the application of a heat cleaning method in atmosphere to remove surface contamination. We observed the changes in the X-ray reflectivity profiles before and after heating in order to estimate the influence of the surface contamination on the thickness evaluation. The reflectivity increased, especially in the higher angle region, by the heat cleaning of the samples in atmosphere. The change in the reflectivity was attributed to the decrease in the surface roughness caused by the contaminant desorption. The thicknesses estimated by the fitting analysis of the sample after heating also decreased by the order of 0.1–0.2 nm. The surfaces of the heated sample were recontaminated in atmosphere; this recontamination was observed as the increase in the evaluated thickness at a rate of approximately 0.01 nm/h.

Key words: standard material, X-ray reflectivity, XRR, film thickness, SiO_2/Si, surface contamination

1. INTRODUCTION

Nanoscale fine structures used in electronic devices and other composites are continuously shrinking in size, and it is expected that the technologies for the fabrication and evaluation of these structures will become more sophisticated in the future [1].

X-ray reflectometry (XRR) is a powerful technique for the characterization of structural properties such as thickness, roughness, and density of thin and multilayer films with nanometric layers. One of the most significant features of XRR is that it can be used to determine the absolute thickness of such films nondestructively and without the need for a reference material. However, the metrology of thickness evaluation in these films has not been fully established thus far. Recent our several experiences of international comparisons and round robin tests conducted for thickness evaluation [2, 3] suggested that much attention had to be paid to the procedures of XRR measurement and sample handling to realize accurate thickness evaluation.

One of our goals is to develop thin and multilayer film standard materials in order to increase the accuracy of thickness evaluation and depth analysis. Standard materials for film thickness determination, in which an ultrathin SiO_2 film is placed on a Si substrate, are currently under development. The target thickness of the SiO_2 layers is less than 10 nm with an uncertainty less than the thickness of 1 monolayer. The contamination of the SiO_2 surface is one aspect that significantly influences the uncertainty. One method to achieve a small uncertainty is to remove the surface contaminants and prevent the surfaces from readsorbing them during the measurement process. Recently, we focused on establishing an effective surface cleaning method. In a previous study [4], we employed a heat cleaning method that involved the use of a hot plate in atmosphere to remove the adsorbates from the SiO_2 surface. We observed that in the case of the samples subjected to the heat cleaning treatment, the reproducibility of the thicknesses evaluated by ellipsometry was significantly high. In addition, investigations using X-ray photoelectron spectroscopy (XPS) indicated that the carbon-derived contaminants on the surface decreased markedly by the heating.

In the present study, XRR measurements were performed for SiO_2/Si samples before and after the heat cleaning treatment to study the influence of the surface contaminants on the XRR profile and the estimated SiO_2 thickness. In addition, the effect of the contaminant readsorption after heating was confirmed by repeated measurements conducted in atmosphere.

2. EXPERIMENTS

The XRR measurements were performed using a high-resolution X-ray diffractometer (Rigaku ATX-G2) with a rotating anode Cu Kα source (18 kW). In this system, a parabolic multilayer mirror collected the X-ray beam to form a parallel beam. This beam was compressed and monochromated with an asymmetric channel-cut-type Ge(111) monochromator. The incident and reflected beams were collimated with 0.05 mm slits and the

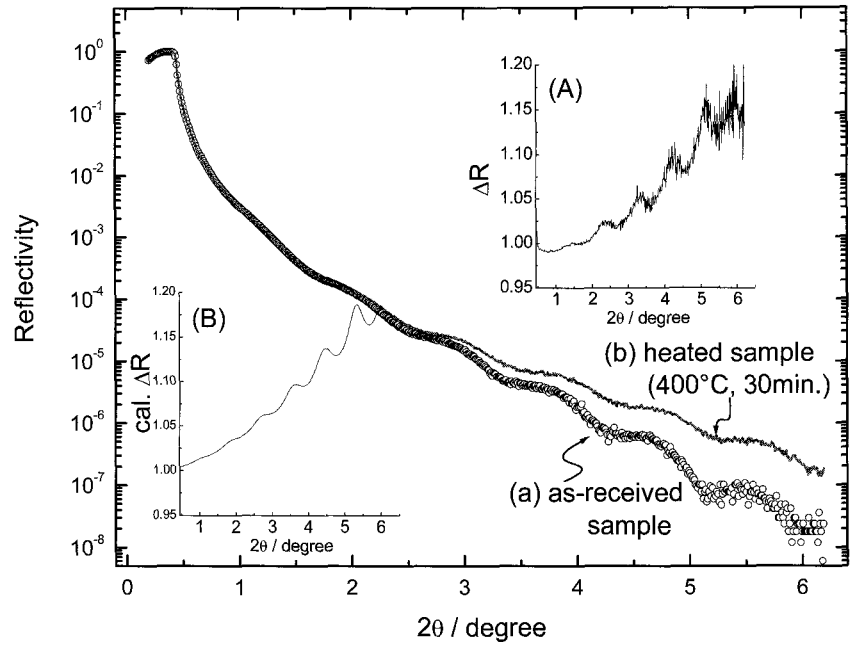

Fig. 1 XRR profiles for the SiO_2/Si sample (a) before and (b) after heating at 400 °C for 30 min. $\Delta R = \log(R_{as-sample}) / \log(R_{heated-sample})$ in inset (A) shows the change in the XRR profile by the heating; $R_{as-sample}$ and $R_{heated-sample}$ are the reflectivities for profiles (a) and (b), respectively. Inset (B) shows the calculated ΔR for an SiO_2 (10 nm)/Si structure with surface roughnesses of 0.3 nm and 0.5 nm ($cal.\Delta R = \log(R_{rough\_0.5}) / \log(R_{rough\_0.3})$).

reflectivity was measured using a scintillation counter. The specular reflectivity profiles were recorded by θ–2θ scans.

The samples—thermally oxidized Si(100) surfaces—were obtained from a semiconductor manufacturer. The layers were grown on 8-inch wafers, and they were cut into 15-mm square chips. Each chip was enclosed in a plastic case and then sealed in a laminated packet with N_2 gas. The XRR measurements were performed for the samples that had been just removed from the package (termed as-received) and for those that had been subjected to heat cleaning at 400 °C for 30 min (termed heated sample).

3. RESULTS AND DISCUSSION

The XRR profiles for the SiO_2/Si sample before and after heating are shown in Fig. 1. The nominal thickness of the sample was 10 nm. In this figure, profile (a) is the XRR profile for the as-received sample (open circle) and profile (b) is the one for the heated sample (solid line). These measurements were carried out by using the same sample and the heating treatment was performed after the measurement of profile (a). The reflectivity in profile (b) is markedly higher than that in profile (a) (above 2θ = 2°). Since the surface roughness caused a decrease in the reflectivity, especially in the higher 2θ region, the difference between the two profiles in the figure can be attributed to a change in the surface roughness. The results indicate that the surface roughness of the heated sample decreased by the contaminant desorption. In order to emphasize the change in the XRR profiles by the heating, $\Delta R = \log(R_{as-sample}) / \log(R_{heated-sample})$ is superimposed on Fig. 1 (shown in inset (A)). Here, $R_{as-sample}$ and $R_{heated-sample}$ are the reflectivities of the as-received (profile (a)) and heated samples (profile (b)), respectively. ΔR in inset (A) signifies that not only the increase in the intensity corresponding to the difference between the reflectivity decays in profiles (a) and (b) but also the oscillation amplitude changes before and after heating. A simulation study was performed to explain the characteristics of ΔR. The ΔR values for the SiO_2 (10 nm)/Si structure with surface roughnesses of 0.3 nm and 0.5 nm, i.e., $cal.\Delta R = \log(R_{rough\_0.5}) / \log(R_{rough\_0.3})$ were theoretically calculated and are shown in inset (B). The calculations were performed using equal

Table I The thickness and roughness estimated from the XRR profiles for the as-received and the heated sample calculated using a single-layer model with a uniform SiO_2 layer on a Si substrate

	Thickness	Roughness
(a) as-received sample	10.30 nm	0.50 nm
(b) heated sample	10.13 nm	0.33 nm

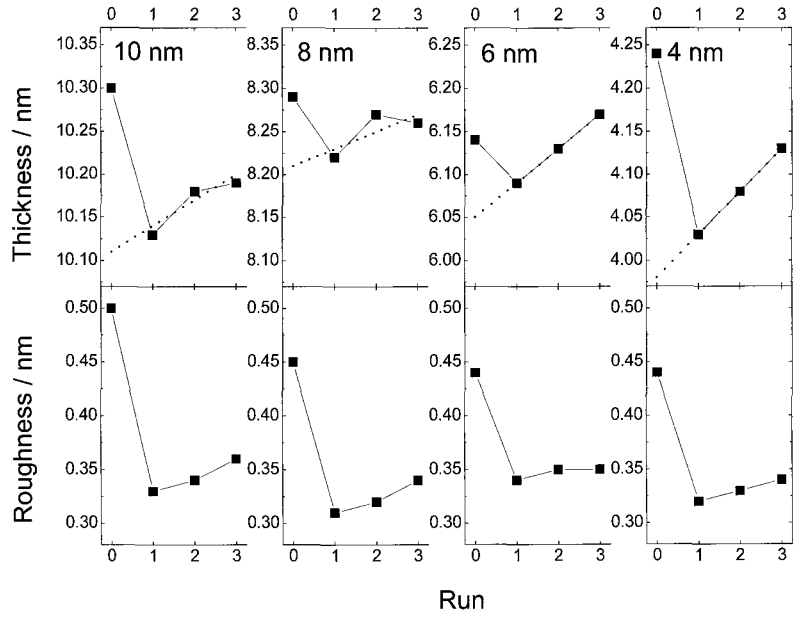

Fig. 2 Thicknesses and roughnesses evaluated from repeated XRR measurements for SiO_2/Si samples. Run 0 is the measurement performed for the as-received sample. Run 1 is the measurement for the heated sample, and Runs 2 and 3 are the measurements after Run 1. The dotted line was obtained by the least-squares fitting using the thicknesses estimated in Runs 1 and 3.

structural parameters, except for the surface roughness. The behavior of $cal.\Delta R$ is similar to that of the experimental result, as shown in inset (A), with respect to the changes in the intensity and amplitude of oscillation with 2θ. The results indicate that the oscillation amplitude in the XRR profile of the sample with a rough surface can be greater than that in the case of a smooth sample. We concluded that the decrease in the surface roughness with the removal of the contaminants could be confirmed by (i) the change in the reflectivity decay and (ii) the decrease in the oscillation amplitude after heating.

The oscillation period in the XRR profile differs slightly before and after heating, as shown in Fig. 1. The overall thickness of SiO_2 and the contaminants on the Si substrate reduced after the heating since the period of profile (b) became longer than that of profile (a). We have already reported that the thickness of a SiO_2 film on a Si substrate does not change by heating at 400°C, which was confirmed by the XPS experiments [4]. Therefore, this change in the period can be attributed to the desorption of the contaminants from the surface. The thicknesses and roughnesses estimated from profile (a) and (b) are shown in Table I; these values were calculated by using a single-layer model with a uniform SiO_2 layer on a Si substrate. The fitting result indicates that the thickness and roughness decrease by approximately 0.2 nm by heating; this reduction corresponds with the removal of the contaminants.

Figure 2 shows the thicknesses and roughnesses obtained from repeated measurements conducted for SiO_2/Si samples of several thicknesses in order to confirm the stability of the evaluations by XRR after heating. All the experiments were performed in atmosphere. The nominal thicknesses of the samples were 10, 8, 6, and 4 nm. The changes in the estimated thicknesses and roughnesses are plotted against the number of measurement runs. On the horizontal axis, Run 0 indicates the XRR experiment performed for the as-received samples. Run 1 is the measurement for the heated sample, and Runs 2 and 3 are measurements performed continuously after Run 1. Each XRR measurement took approximately 2.5 h to complete.

The decrease in the estimated thicknesses caused by the removal of the surface contaminants ranged from 0.1 to 0.2 nm for all the samples. The variations of these values could be attributed to the differences in the amount of contaminants on the surfaces. In the subsequent measurements of each sample after Run 1, the estimated thicknesses gradually increased with the number of measurements. The change in the estimated thicknesses between runs was approximately 0.05 nm, indicating that XRR is capable of detecting small changes that are influenced by surface contamination.

Because each measurement took around 2.5 h to complete, the thicknesses calculated from Run 1 were influenced by the surface contamination that occurred due to the adsorption during the measurement. The thickness just after the heat cleaning could be estimated by the least-square fitting of the change in the thickness with time. In

Fig. 2, the dotted lines were obtained by the fitting. The estimated thicknesses for each sample just after heating were 10.11 nm, 8.21 nm, 6.05 nm, and 3.98 nm with a maximum error of 0.04 nm. The rates of thickness increase in the samples were 0.008, 0.005, 0.008, and 0.013 nm/h, respectively. The proposed technique is effective to reliably obtain the thickness of SiO_2 statistically with the error of reproducibility and repeatability. The estimated roughnesses exhibited tendencies similar to those of the thicknesses after heating, and the value was decreased in the order of 0.1 to 0.2 nm. By exposing the samples to air after the heat treatment, the roughness increased at the rate of approximately 0.03 nm/h by contaminant readsorption.

The amount of contaminant readsorbed on the surface depends on the measurement environment. Recently, we attempted to control the measurement environment and conduct the measurements under N_2 gas flow and in vacuum. We found that the thickness increase caused by readsorption for 24 h after cleaning was less than 0.03 nm in the case of the sample maintained under a vacuum of 0.5 Pa [5].

4. SUMMARY

In order to study the influence of the surface contaminants on the XRR profile and the estimated SiO_2 thickness, XRR measurements were performed for SiO_2/Si samples before and after heat cleaning at 400°C for 30 min.

We observed that the reflectivity increased markedly in the higher angle region when the samples were heated in atmosphere. In addition, the oscillation amplitude of the profile decreased after heating. These changes in the profiles were attributed to the decrease in the surface roughness caused by the contaminant removal.

The influence of surface contaminants on the thickness evaluation was estimated. The estimated thicknesses decreased by approximately 0.1–0.2 nm after heating due to the removal of the surface contaminants. The difference between the thickness before and after heating cannot be ignored in order to evaluate the SiO_2 thickness with an uncertainty less than the thickness of 1 monolayer. By conducting XRR measurements after the heating, the thickness increase caused by the contaminant readsorption was observed and its rate of increase was found to be of the order of 0.01 nm/h in atmosphere.

Because the heat cleaning method in atmosphere is extremely simple and does not require any special equipment and chemicals, it has the potential to become an effective method for cleaning SiO_2 surfaces and can be used to establish the metrology of thickness evaluation.

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