In-depth Chemical State Analysis of a Lanthanum Silicate Layer Formed by Thermal Oxidation of LaSi$_x$/Si(100)

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A lanthanum silicate surface layer was formed by thermal oxidation of LaSi$_x$/Si(100). Chemical states of the layered material were nondestructively analyzed from the Si Kβ spectra measured by an electron-induced x-ray emission spectroscopy in a grazing incidence setup. In-depth analysis was performed by changing the accelerating voltage of the electron beam. The Si Kβ spectrum was a sum of the spectral components of the surface silicate layer and the buried silicon substrate. The silicate component was decreased with increasing electron energies from 3.0 to 5.0 keV. For quantitative analysis, the Si Kβ spectra were decomposed into the components of surface silicate layer and buried silicon substrate by the least square method. The variation of the relative amount of the Si Kβ x-rays from the silicate layer is compared with that evaluated from the depth distribution of x-ray production calculated by a Monte Carlo simulation method. It was confirmed that they show similar energy dependences, and estimates of the silicate layer thickness were given as values from 200 to 400 Å.

Key words: La, silicate, Si Kβ, x-ray emission, grazing incidence

1. INTRODUCTION

X-ray emission spectroscopy (XES) with electron beam excitation is a powerful tool for chemical state analysis of thin films and interfaces [1-3]. The commercial instrument, electron probe microanalysis (EPMA), is widely used. Nondestructive depth profiling of chemical composition and chemical state of layered materials is obtained by changing the incident electron energy.

We have constructed a new XES apparatus, which is a wavelength-dispersive spectrometer (WDS) with an electron gun attached as the electron beam is injected into the sample at a grazing angle [4]. Electron induced XES at grazing incidence is a very surface sensitive technique though microanalysis is difficult in this setup [5]. We call the analysis method as grazing incidence electron-induced x-ray emission spectroscopy (GIEXES). The GIEXES setup is efficient for collecting weak-intensity x-rays emitted in a thin surface layer.

The apparatus was employed to the study of oxidation of a La silicide layer formed on silicon substrates. It was confirmed that the variations of the measured Si Kβ spectra with increasing incident electron energy demonstrates an extension of the probing depth. The results were discussed in connection with the depth distribution of x-ray production calculated by an empirical model, and estimations of the oxidized layer thickness were tentatively given as values of the order of a few tens of angstroms.

The aim of the present study is to quantitatively analyze GIEXES results on the basis of the depth distribution of x-ray production calculated by a Monte Carlo simulation method. In the case of estimation of depth distribution profiles of x-ray production, good agreement exists between calculated and experimental results [6, 7].

2. EXPERIMENTAL

The GIEXES apparatus is a wavelength-dispersive spectrometer with linear crystal motion. An electron gun is attached in such a way that the electron beam nearly perpendicularly impinges on the Rowland circle plane. A Johann-type Pentaerythritol (PET) crystal bent to the radius of 30 cm was used for measuring Si Kβ spectra. The x-ray dispersion on the detector slit (0.2 mm in width) was about 1.3 eV for the x-rays of 1835 eV. Some detailed description has been given in the previous paper [4].

The samples were newly prepared by the same process as used in the previous study. N-type Si(100) substrates were ultrasonically cleaned in acetone and semiconductor cleaning solution (Semico Clean 23). The clean silicon surface was obtained by flashing to 1200 °C in a vacuum. La was evaporated from a W filament while the film thickness was monitored by a quartz microbalance. The thicknesses of the deposited La layers were 130, 190 and 260 Å. Hence, the samples are denoted by sample1 (La130Å), sample2 (La190Å) and sample3 (La260Å) by following the deposited amounts of La. In the next step, in order to form La silicide, the samples were heated at 600 °C for 30 min. In the last step, the samples were thermally oxidized at 700 °C for 30 min in an oxygen atmosphere of 0.1 Torr. The atomic composition and chemical state of the constituent elements were analyzed by XPS at each step. In the previous study, it was concluded from the XPS

analysis that the oxidized layers were composed mainly of La silicate; Moreover, the mixed oxide was oxyorthosilicate (La$_2$[SiO$_4$]O) within the limit of the XPS semi-quantitative analysis. On the assumption that oxyorthosilicate layers were also formed in the present study, and all the La atoms were consumed in the silicate-forming reaction, the thicknesses of the silicate layers are calculated as 200, 300 and 400 Å for sample1 (La130Å), sample2 (La190Å) and sample3 (La260Å), respectively.

3. RESULTS AND DISCUSSION

Si Kβ x-ray emission spectra of sample3 (La260Å) at incident electron energies E_i of 3.0, 4.0 and 5.0 keV are shown in Fig.1. For comparison, the reference spectra of
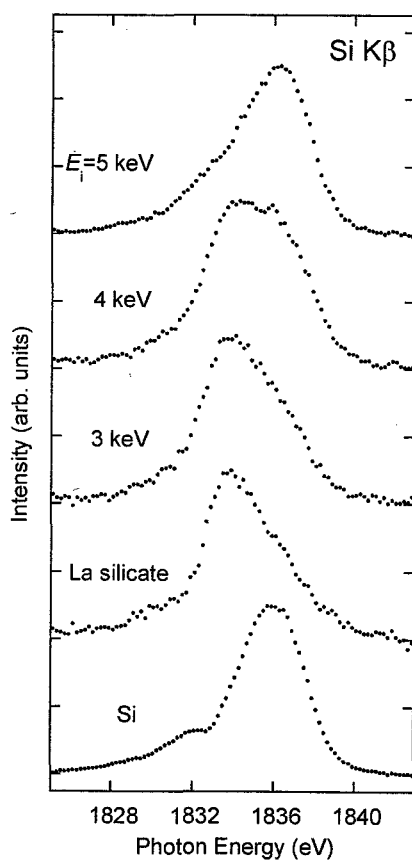

Fig. 1 Si Kβ x-ray emission spectra of sample3 (La260Å) at E_i=3.0, 4.0 and 5.0 keV. The reference spectra of silicate and silicon are also shown.

silicon and silicate are also shown. The spectrum of silicon was measured for a single crystal, and that of silicate was measured for a sample having a silicate layer the thickness of which is larger than the probing depth. All the spectra are normalized to a unit peak height. The spectrum of sample3 (La260Å) measured at E_i=3.0 keV shows a peak at a photon energy near 1833.6 eV, and the intensity gradually decreases on the higher energy side of the peak. These features of the spectrum are similar to those of silicate. At E_i=4.0 keV, the spectrum shows an almost symmetrical shape, and

its centroid is located at about 1834.4 eV. At E_i=5.0 keV, the spectrum shows a peak at a photon energy near 1835.8 eV, and features of the spectrum are similar to those of silicon.

Si Kβ x-rays are produced over a depth range from the surface down to the maximum depth reached by incident electrons before their energy falls below the critical energy of 1s core electron excitation. The measured x-ray spectrum is a sum of the spectral components of the material layers within the depth probed. As the incident electron energy increases, the injected electrons penetrate into the deeper regions of the sample, and the ratio of the spectral component of the silicon substrate increases. On the assumption that the silicide layer was fully oxidized, one can understand qualitatively the variation of the spectra as follows. At 3.0 keV, the Si Kβ spectrum is dominated by the spectral component of x-rays from the La silicate film. At 5.0 keV, the spectrum is dominated by the spectral component of x-rays from the silicon substrate though in this case the whole silicate layer and the upper regions of the silicon substrate were probed. At 4.0 keV, the spectrum corresponds to the medium case. The Si Kβ spectra measured for sample1 (La130Å) and sample2 (La190Å) show the same trend with increasing incident electron energy, so that they are omitted.

In order to quantitatively analyze the measured spectra, the sizes of the spectral components of silicate and silicon in the whole spectrum were evaluated by the least square method (curve fitting). Figure 2 shows Si Kβ spectrum of sample1 (La130Å) obtained at 3.0 keV (dots) and the fitted curve (sold line). The component spectra of La silicate (broken line) and silicon (dashed and dotted line) are also shown.
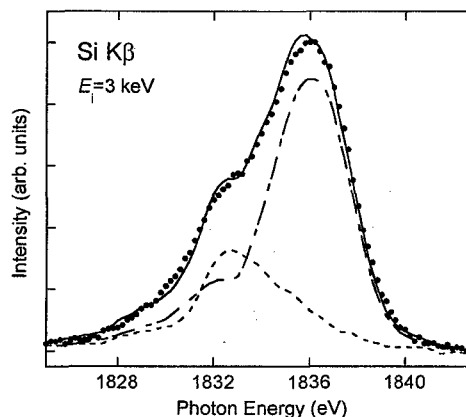

Fig. 2 Si Kβ x-ray emission spectrum of sample1 (La130Å) at E_i=3.0 keV (dots). The solid line is the weighted sum of the spectra of La silicate (broken line) and silicon (dashed and dotted line).

The ratio of the integrated intensity (over photon energy) of the silicate component to that of the whole spectrum is calculated as follows:

$$R_{film} = \frac{I_{film}}{I_{film} + I_{substrate}}. \qquad (1)$$

Here, I_{film} and $I_{substrate}$ are the integrated intensities of the spectral components of silicate and silicon, respectively. The calculated values of R_{film} for the spectra measured at $E_i=3.0$, 4.0 and 5.0 keV are presented in Table I. The results of spectrum analysis for sample2 (La190Å) and sample3 (La260Å) are also given in the table.

Table I Integrated Intensity Ratios of the Spectral Component of La Silicate to the Whole Spectrum (R_{film}).

	Incident electron energy (keV)		
	3.0	4.0	5.0
sample1 (La130Å)	0.31	0.19	0.17
sample2 (La190Å)	0.70	0.46	0.20
sample3 (La260Å)	0.92	0.64	0.25

The integrated spectral intensities (over photon energy) of each component are connected with the x-ray generation amounts in the corresponding material layers. The x-ray generation amounts in each material layer are calculated by integrating the depth distributions of x-ray production. As mentioned in §1, in the case of estimation of depth distribution profiles of x-ray production, good agreement exists between calculated (by a Monte Carlo simulation) and experimental results. Namely, calibration curves derived from a Monte Carlo simulation work as a guide for depth profiling of chemical state in material layers.

For this purpose, among various Monte Carlo simulation methods, we adopted a simple method based on the single scattering model described by Joy [8]. In order to simulate electron diffusion and x-ray production in layered materials, some modifications were made to the algorithm [9]. Figure 3 shows electron trajectories for primary energy of 3 keV at incident angle of 7°. The target was composed of a silicate overlayer (200 Å) and a silicon substrate. For the
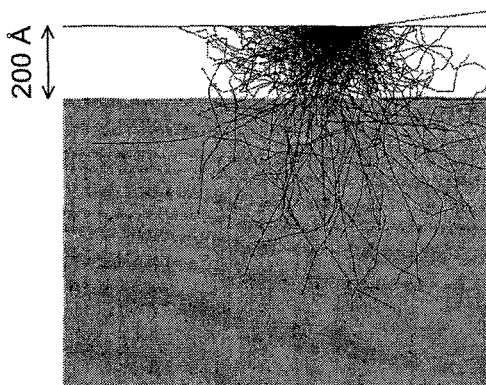

Fig. 3 Electron trajectories for primary energy of 3 keV at incident angle of 7°.

material parameters related to the silicate layer, the stoichiometry and density of oxyorthosilicate ($La_2[SiO_4]O$) were used. The first 1000 electron trajectories are shown in the figure. In the simulation, the electron diffusion region corresponds to the x-ray generation region because the cut-off energy for tracing electron trajectories is set to the critical energy for Si 1s core electron excitation.

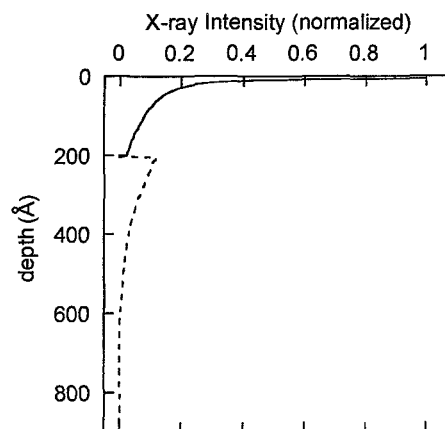The depth distribution of x-ray production is given in Fig. 4. The depth distribution functions of x-ray

Fig. 4 Depth distributions of x-ray production in the silicate layer (sold line) and in the silicon substrate (broken line).

production in the silicate layer and in the Si substrate are shown by solid line and dashed line, respectively. They have been corrected for self-absorption of x-rays and normalized to a unit peak height. The ratio of the x-ray generation amount in the silicate layer to the whole amount is calculated as follows:

$$R'_{film} = \frac{I'_{film}}{I'_{film} + I'_{substrate}}. \qquad (2)$$

Here, I'_{film} and $I'_{substrate}$ are x-ray generation amounts in silicate layer and in silicon substrate, respectively. The R'_{film} value is comparable directly to the R_{film} values calculated from the results of analysis of the measured spectra because constant factors (detection efficiency etc.) are canceled in the numerator and denominator.

A comparison of the incident electron energy dependence of R_{film} and that of R'_{film} is given in Fig. 5. The Monte Carlo simulations were performed for silicate layer thicknesses from 100 to 500 Å with 100 Å step (solid lines). In each calculation, 10000 electron trajectories were traced until the electron energy falls down to the cut-off energy for Si 1s electron excitation. R_{film}, obtained by curve fitting to the measured spectra (see Table I), is indicated by marker: solid circle for the sample1 (La130Å), solid triangle for the sample2 (La190Å), and solid square for the sample3 (La260Å). The broken lines are a guide to eye. It is clear that R_{film} decreases as the incident electron energy increases. This demonstrates the fact that the probed depth is extended
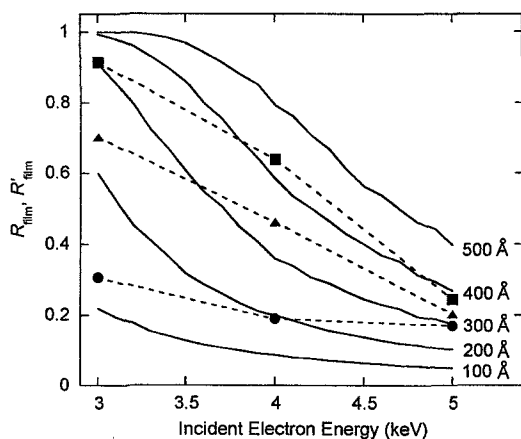
Fig. 5 Comparison of the incident electron energy dependences of R_{film} and R'_{film}. R_{film}, obtained by curve fitting to the measured spectra, is indicated by marker: solid circle for the sample1 (La130Å), solid triangle for the sample2 (La190Å), and solid square for the sample3 (La260Å). The curves of R'_{film} derived from the Monte Carlo simulations are shown by solid lines.

to the deeper region by increasing the incident electron energy. It is also seen that the broken lines of R_{film} overlap the curves of R'_{film} for the silicate layer thicknesses of 200, 300, and 400 Å, and they show the same trend in energy dependence. In Monte Carlo simulations in the present study, the reliability of the equations related to the electron-material interaction is degraded as the overvoltage, the ratio of traveling electron energy to the critical energy of core electron excitation, approaches 1 [8]. Thus, it is possible that the simulation results deviate from the experimental results as the incident electron energy decreases to 3.0 keV. Considering this, estimates of the thickness of the silicate layers are given as values ranging from 200 to 400 Å. As mentioned in §2, the thicknesses of the silicate layers are calculated as 200, 300, and 400 Å for sample1 (La130Å), sample2 (La190Å) and sample3 (La260Å) respectively, on the assumption that all the La atoms were consumed in the silicate-forming reaction. Thus, it is concluded that the above estimates of the silicate layer thickness agree roughly with values calculated from the deposition amounts.

4. CONCLUSION

The GIEXES results were quantitatively analyzed in connection with the depth distribution of x-ray production calculated by a Monte Carlo simulation method. The depth profile of chemical states in the depth range from surface to a depth of several hundreds of angstroms was obtained with a depth resolution in the order of a hundred angstroms. For further quantitative discussion, experiments for many layered materials with a defined thickness are required. Then, it is also possible to further improve the precision of Monte Carlo simulation in a gazing incidence setup.

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