# Si-$L_{2,3}$ soft X-ray emission spectra by quantitative analysis of silicides/Si system :simulation and experiment.

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Monte Carlo (MC) simulation was applied to a quantitative micro analysis of a thin-film/substrate system. In this simulation, we utilized characteristic Si-$L_{2,3}$ soft x-ray emission (SXE) band spectra for silicides/Si, because silicides and Si have their own spectral shapes in the Si-$L_{2,3}$ emission band, which is expected to be superior to the conventional method using x-ray intensity only. By combining MC simulation with Si-$L_{2,3}$ emission spectra, we tried to extract Si-$L_{2,3}$ spectra of the film materials from the mixed binary Si-$L_{2,3}$ spectra obtained from a NiSi(film)/Si(substrate) system by SXES measurement together with the thickness determination of the film.

## 1. Introduction

A quantitative analysis has been carried out by using either Si-$L_{2,3}$ soft x-ray emission spectroscopy (SXES) or Monte Carlo (MC) simulation for silicide(film)/Si(substrate) systems. MC electron trajectory simulation is an important tool for the study of electron beam-specimen interaction in solid targets to support quantitative analysis of x-ray microanalysis [1-4]. This simulation can deduce physical quantities such as depth distributions of generated x-ray and calculate x-ray intensities emitted from sample surface, where it is required to consider absorption and atomic number corrections. By using this simulation, it is possible to determine the thickness and the composition of films containing more than one element on the substrate. In this study, we applied this method to the analysis of silicides/Si system using Si-$L_{2,3}$ emission band spectrum for Si and several silicides. Typical Si-$L_{2,3}$ emission spectra for several materials are shown in Fig. 1. These soft x-ray emission spectra have their own spectral shapes in the Si-$L_{2,3}$ emission band. These shapes of spectra have very important information since we can extract the chemical bonding state by examining these spectral shapes.. A silicide film/Si system can be prepared by a solid phase reaction(SPR). In present study, we tried to extract a Si-$L_{2,3}$ spectrum of a film part from a NiSi(film)/ Si(substrate) system by using SXES measurement[5] and MC simulation.

## 2. Experimental and MC simulation Method

We had prepared samples for the spectrum extraction, and MC simulation program by ourselves. The sample preparation and the simulation model are shown below.

### 2. 1. Sample preparation

A NiSi(film)/Si(100) system was prepared as follows. A Ni(film)/Si(100) specimen was prepared by depositing Ni atoms on top of Si(100) in a vacuum chamber with a base pressure of $10^{-6}$ Pa. To make a NiSi/Si(100) system, the Ni/Si(100) specimen was heat

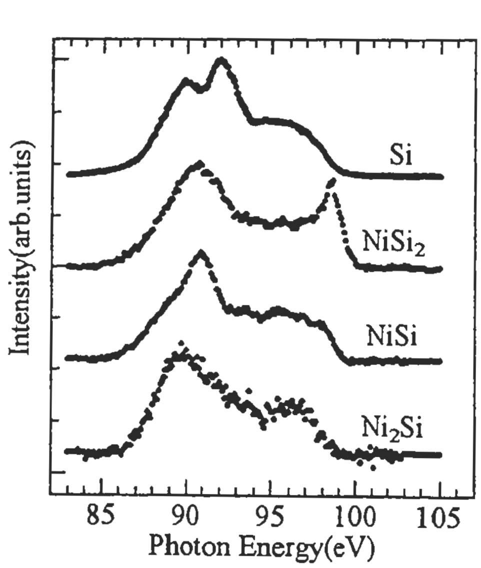


Fig. 1 Si-$L_{2,3}$ soft X-ray emission band spectra at $E_0$=5keV, incident energy, for Si, $NiSi_2$, NiSi and $Ni_2Si$ bulk.

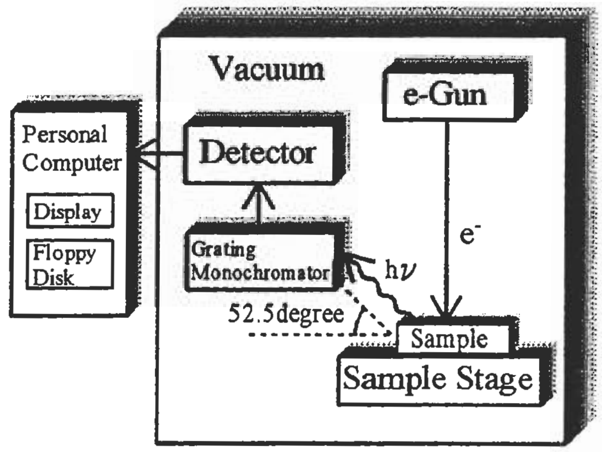


Fig. 2. A schematic illustration of the SXES system.

treated in an electric furnace under $N_2$+$H_2$ gas flow at 300°C for 30 min[6].

**2. 2. SXES Experiments**

The Si-$L_{2,3}$ spectra measurements were done with a SXES system equipped with an x-ray detector whose take-off angle were 52.5° (Fig. 2). The grating monochromator had 600 grooves/mm with a radius of 1 m and a coating of gold. An Si-$L_{2,3}$ soft x-ray emission spectrum was obtained at photon energies from 83 to 105 eV by a step of 0.1 eV for 3 sec per point. Incident electron energy ($E_p$) was varied between 4.0 and 7.5 keV. The x-ray intensity $I_{Exp}$ obtained in SXES measurement was an integrated one of each point intensity in region the photon energy of 85-100eV. Due to x-ray intensity in Si-$L_{2,3}$ range being very weak, we measured 50 times for each spectrum.

**2. 3. Simulation model.**

The present MC simulation has been mainly based on three equation described below for X-ray emission generated by incident electron scattering in a film/substrate system (Fig. 3) : the Mott cross section (2.1) for elastic scattering and mean free path [7], the Bethe equation for energy loss (2.2) [8], and the ionization cross section (2.3)[9].

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 + |g(\theta)|^2 \qquad (2.1)$$

$$-\frac{dE}{dS} = 7.85 \times 10^{10} \sum_i \frac{C_i \rho_i Z_i}{A_i E} \ln \frac{1.166E}{J_i'} \qquad (2.2)$$

$$Q(U_c) \cdot E_c^2 = a_Q \frac{\ln(U_c)}{U_c}. \qquad (2.3)$$

The functions f(θ) and g(θ) can be obtained by

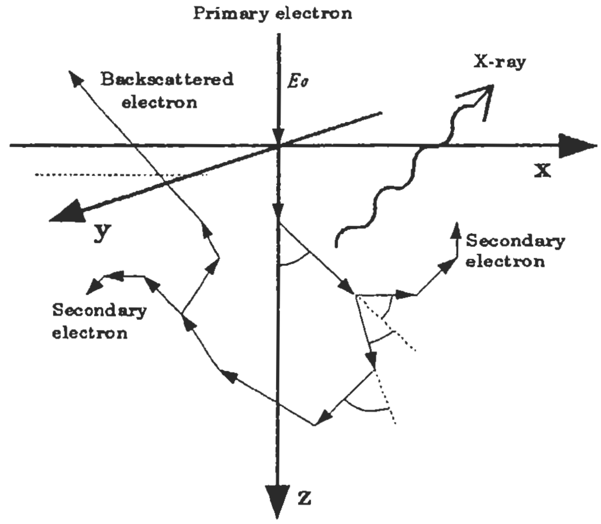


Fig. 3. Electron trajectory model.

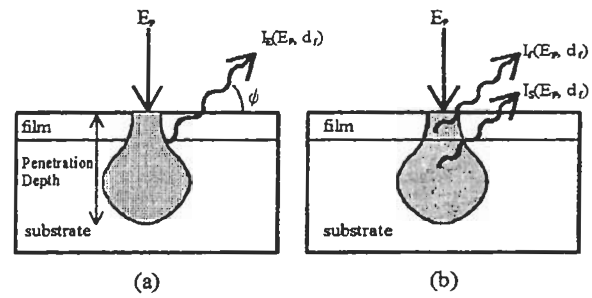


Fig. 4 Geometrical configurations of film/substrate system in (a) MC simulation and (b) SXES measurement.

solving the relativistic wave equation of Dirac through the use of the partial wave expansion method, where σ is the total elastic scattering cross section, θ is the scattered angle, E is the instantaneous energy of the electron (in eV), S is the path length along the trajectory (in cm), $C_i$ is the concentration of an *i*th element per unit volume, $A_i$ is the atomic weight, $N_A$ is the Avogadro's number, $Z_i$ is the atomic number, β is the screening parameter, and J' is the mean ionization potential suggested by Berger and Seltzer [10]. Q is the ionization cross section, $U_c$ is the overvoltage ratio $E/E_c$, and $a_Q$ a constant. Here $E_c$ is the critical excitation energy The x-ray generating calculation method with above three equations is called single scattering model. We have adopted hybrid model, where an inelastic scattering calculation is adopted to single scattering model in order to derive more accurate result [2].

10000 electron trajectories were traced in this study.

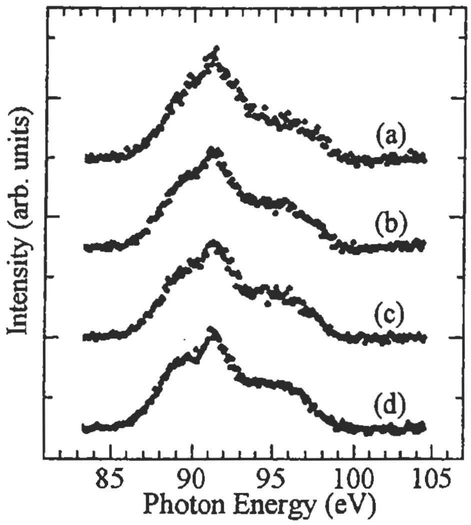


Fig. 5. Several Si-$L_{2,3}$ soft x-ray emission band spectra for a NiSi/Si system, annealed at 300℃ for 30 min, measured at different $E_p$'s: (a)Ep=4.0, (b) 5.0 (c) 6.0 and (d) 7.5 keV.

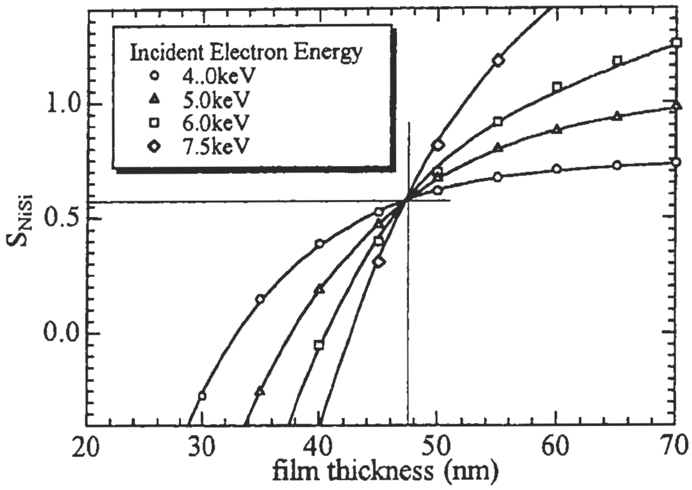


Fig. 6. Determination of film thickness $d_f$ and $S_{NiSi}$ from calibration curves of $S_{NiSi}$ versus $d_f$ at several incident electron energy Ep=4.0, 5.0, 6.0 and 7.5 keV.

### 3. Spectrum Extraction.

The spectra obtained in SXES measurement are mixed spectra emitted from silicide film and substrate Si, see Fig. 4. (a). Therefore, we have tried to calculate x-ray intensity separately from the film and substrate(Fig. 4. (b)) by MC simulation.

Due to the fact that the x-ray emitted per atom has different probability in each material, silicon and silisides, the term $S_{silicide}$ is defined as follows,

$$I_{silicide} = S_{silicide} \cdot I_{Si}, \tag{3.1}$$

where x-ray intensity $I_{Si}$ for Si is used as the standard. In MC simulation, x-ray intensity emitted from sample is expressed as

$$I_{Sim}(E_p, d_f) = S_{silicide} \cdot I_f(E_p, d_f) + I_S(E_p, d_f), \tag{3.2}$$

where $E_p$ is the incident electron energy, $d_f$ is the film thickness, $I_f$ and $I_S$ are intensities emitted from film and substrate, respectively. In SXES measurement, the x-ray intensity emitted is expressed by $I_{Exp}(E_p,d_f)$. Then we define a correction term $C_{Si}$ between $I_{Sim}$ and $I_{Exp}$ by

$$I_{Sim} = C_{Si} \cdot I_{Exp}, \tag{3.3}$$

where $I_{Sim}$ and $I_{Exp}$ is those obtained in SXES measurement and MC simulation, respectively. Si is used to derive $C_{Si}$. By using Eqs. (3.2) and (3.3),

$$C_{Si} \cdot I_{Exp}(E_p, d_f) = S_{silicide} \cdot I_f(E_p, d_f) + I_S(E_p, d_f) \tag{3.4}$$

is deduced. In these calculation, $S_{silicide}$ and $d_f$ are unknown parameters. If the calculation is carried out by Eq. (3.4) for several incident electron energies, we can determine $S_{silicide}$ and $d_f$. Then, we can obtain the x-ray intensity $I_f$ and $I_S$ emitted from film and substrate, respectively. Spectral ratio is decided by using $I_f$, $I_S$ and $S_{silicide}$. The spectral ratio R of film material to a measured spectrum is given by

$$R = \frac{S_{silicide} \cdot I_f}{S_{silicide} \cdot I_f + I_S}. \tag{3.5}$$

If R is obtained by Eq. (3.5), the Si-$L_{2,3}$ spectrum for the film material of a film/substrate system is estimated by subtracting Si-$L_{2,3}$ spectra for substrate material from measured one of the film/substrate system. Si-$L_{2,3}$ spectra are normalized by the intensity in the spectral region of Si-$L_{2,3}$ (83-100eV).

### 4. Experimental Results and Discussion

By using method described above, we have tried to extract Si-$L_{2,3}$ spectrum of NiSi from mixed spectra which are measured ones for NiSi/Si at several incident electron energies.

#### 4.1. SXES Spectra

Si-$L_{2,3}$ SXES spectra for a NiSi(film)/Si(100) for different $E_p$ are shown in Fig. 5. The Si-$L_{2,3}$ signal of Si increases with increasing $E_p$.

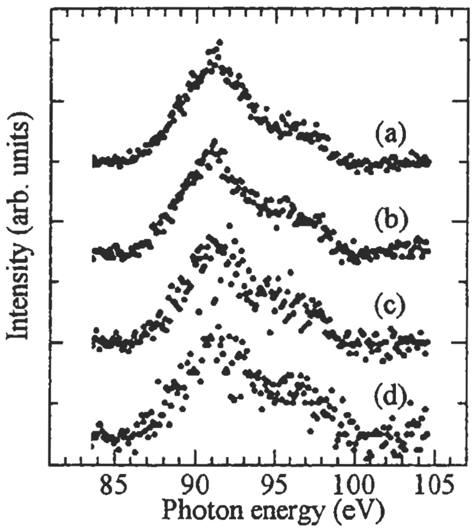


Fig. 7. Several Si-$L_{2,3}$ soft x-ray emission band spectra extracted from mixed spectra shown in Fig. 5 for NiSi/Si system measured at different $E_p$'s: (a) Ep = 4.0, (b) 5.0 (c) 6.0 and (d) 7.5 keV.

### 4.2 Spectrum Extraction

The x-ray intensity $I_f(E_p, d_f)$ and $I_S(E_p, d_f)$ in MC simulation are calculated at $E_p$ = 4.0, 5.0, 6.0 and 7.5 keV and $d_f$ = 5 - 100 nm by step of 5 nm.

Fig. 6 shows the calibration curves of $S_{NiSi}$ versus film thickness $d_f$ deduced by using Eq. (3.5) at incident electron energy $E_p$ = 4.0, 5.0 6.0 and 7.5 keV. Because these curves cross at one point ,*i. e.*, at $d_f$ = 47.2 nm and $S_{NiSi}$=0.54, in Fig.6, it can be said that NiSi film thickness for the NiSi/Si system prepared is 47.2nm and correction term $S_{NiSi}$ for NiSi is 0.54.

The next step is the determination of the ratio of Si-$L_{2,3}$ spectra of NiSi to that of Si for the NiSi/Si system by using Eq. (3.6). First, $I_f(E_p$, 47.2 nm) and $I_S(E_p$, 47.2 nm) are calculated at $E_p$ = 4.0, 5.0, 6.0 and 7.5 keV in MC simulation. The Si-$L_{2,3}$ spectral ratio R for NiSi(film) obtained are 71, 47, 32 and 20% at $E_p$ = 4.0, 5.0, 6.0 and 7.5 keV, respectively. Spectral ratio for Si(substrate) are, therefore, 29, 53, 68 and 80% at $E_p$ = 4.0, 5.0, 6.0 and 7.5 keV, respectively. The Si-$L_{2,3}$ spectra for NiSi is extracted by subtracting Si spectrum ratio times normalized intensity of Si-$L_{2,3}$ spectra for Si in Fig.1 from mixed spectrum shown in Fig. 5 at the same incident energy. The result is shown in Fig. 7. The spectra extracted at several $E_p$'s seem to be almost same, but the higher the incident electron energy, the more noisy in the spectrum since the x-ray intensity ratio emitted from NiSi(film) part of NiSi/Si system is decreasing.

In present study, we have succeeded to extract the original Si-$L_{2,3}$ spectrum of NiSi film part for the NiSi(film)/Si(substrate) system. When the ratio of the spectrum for NiSi film material is more than 50% in the mixed spectrum, the original Si-$L_{2,3}$ soft x-ray emission spectrum for NiSi for film material can be obtained.

### 5. Summary

In the present study, an extraction of Si-$L_{2,3}$ signal of the NiSi film for NiSi(film)/ Si(substrate) system has been performed through the use of MC simulation. The reasonable Si-$L_{2,3}$ spectrum for NiSi is deduced. Possible extensions are expected for the extraction of Si-$L_{2,3}$ spectrum for unknown silicides.

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