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# Studies of multilayer structure in depth direction

## by soft X-ray spectroscopy

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**Abstract** It is demonstrated that two kinds of soft X-ray spectroscopy are useful as nondestructive methods to investigate multilayer structures modified by interdiffusion or by chemical reaction of adjoining layers in depth direction. One is the total electron yield (TEY) spectroscopy involving angular dependence measurement. Using this method, it was found that in LiF/Si/LiF trilayers, the Si layers exhibited a characteristic similar to porous Si, and in CaF<sub>2</sub>/Si/CaF<sub>2</sub> trilayers, it was found that CaF<sub>2</sub> segregated through the Si layer. Moreover, it has been shown that the thickness of the top layer of a Mo/Si X-ray multilayer can be determined by analyzing TEY signals generated by the standing wave. The other is the soft X-ray emission spectroscopy involving spectral shape analysis. Using this method, it was found that in Mo/Si X-ray multilayers, the interdiffusion or chemical reaction giving rise to deterioration of reflectance character occurs in as-deposited samples as well as in heated samples. In antiferromagnetic Fe/Si multilayers, it was confirmed that there was no existence of pure Si layers, but insulating FeSi<sub>2</sub> layers were present. This result suggests that the source of antiferromagnetic coupling is not conduction electrons but quantum wave interference.

**Key words** Multilayer structure, Depth direction, Total electron yield, Soft X-ray emission, Standing wave, Silicon compound

CLC numbers TH744.15, TM203

## 1 Introduction

Over the recent several decades, artificial layered structures have been extensively developed as useful functional structures for semiconductor devices <sup>[1]</sup>, magnetic devices <sup>[2]</sup>, X-ray high-reflectance mirrors <sup>[3]</sup>, and so on. They are initially designed as multilayers consisting of uniform layers with the same properties as those of bulk materials and having clear-cut interfaces (boundaries). However, in real cases, some layers have structures different from those of bulk materials, and some adjoining layers mix by interdiffusion or react chemically, so that the interfaces are not

clear-cut. These factors often affect the characteristics of real multilayers, and therefore these real multilayers sometimes exhibit novel features. Accordingly, investigation of the multilayer structures in depth direction is important to control these factors.

Cross sections of multilayers have been usually investigated using transmission microscopy (TEM). Recently, cross-sections of some semiconductor junctions have also been investigated by scanning photoelectron microscopy using Schwarzschild objectives <sup>[4]</sup>. In these cases, the samples have to be sliced vertical to the layers and polished using ion-beam etching, so that

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these methods are destructive against the samples. However in many cases, nondestructive methods such as *in-situ* investigation are required. X-ray diffraction is the nondestructive method that is widely used to measure apparent thicknesses of single layers and period distances of multilayers, and lattice distances of layer materials. However, it is not easy to specify the kinds of materials in boundaries and main layers, in which interdiffusion/chemical reaction or modification of structure occurs. Photoelectron spectroscopy is an excellent method to investigate clean surfaces and thin overlayers (<1 nm), provided the kinds of materials are specified <sup>[5]</sup>. However it is not appropriate to investigate deep layers.

Soft X-ray spectroscopy is a powerful tool to obtain information on the chemical states of materials. One such soft X-ray spectroscopy is the total photoelectron yield (TEY) spectroscopy in which photoelectrons, secondary electrons, and Auger electrons are measured totally. The TEY measurements give spectra similar to the absorption spectra of uniform bulk materials, without the need to prepare their thin samples <sup>[6]</sup>, under conditions that the product of the absorption coefficient and the escape depth of the electrons from the surface are small <sup>[7,8]</sup>. The other is the soft X-ray emission (SXE) spectroscopy in which SXE emitted by the transitions of electrons from valence bands to shallow core-hole levels is measured. Binding energies of the core levels are element-specific, so that the elements in the regions of interest of multilayers can be assigned by choosing photon energies of excitation or by measuring photon energies of emission. In addition, positions and shapes of spectral structures in the absorption and emission spectra reflect the chemical state of each compound, so that TEY and SXE measurements can be used for assigning the kind of the compound. Furthermore, they can be applied to the analysis of multilayers in depth direction. The reason is as follows. The TEY measurement can give information of a few to several nanometer-thick layers/multilayers due to the short escape depth of the electrons. (The probe depth of a few to several nanometer is larger than that in the photoelectron spectroscopy, ~1 nm.) Therefore, it is widely used for the study on adsorbed/overlayered surfaces <sup>[9]</sup>. Furthermore, incident-angle dependence

of TEY can give information in depth direction, because the probe depth can be changed and interference effects if any can be observed. To the best of our knowledge, there is no angle-dependence measurement on multilayers. On the other hand, the escape depth of the SXE is of the order of 10 nm-100 nm, so that the SXE measurements give information not only of thin overlayers <sup>[10]</sup> but also of the materials covered with other materials and buried interfaces. They have been applied to investigate the chemical reaction between overlayers and substrates caused by heating, and more attention is paid to the change of spectral profile [11]. The SXE studies are still in the developing stage. The structural analysis in depth direction using TEY and SXE spectra is carried out with the aid of simulations. Standing waves are generated in the periodic multilayers when wavelengths are appropriately chosen (Bragg reflection), as in the crystals. Periodic multilayers act as standing wave generators. By exciting standing waves, the multilayer structures have been also investigated in depth direction by detecting TEY <sup>[12]</sup> or SXE <sup>[13]</sup>, or by analyzing photoelectrons<sup>[14]</sup>.

In this report, it will be shown that TEY and SXE are useful nondestructive methods to investigate the structure of multilayers composed of a few layers as well as periodic multilayers in depth direction. Samples studied are semiconductor-insulator layered structures, soft X-ray high-reflectance multilayers, and magnetic multilayers. The heating effects on soft X-ray multilayers will also be dealt with in this article.

## 2 Soft X-ray spectroscopy

#### 2.1 TEY spectroscopy

The simplest TEY method is to measure drain current due to electrons emitted from a sample in a vacuum chamber. The electrons are collected by the sample chamber, where the sample is insulated from the chamber, but connected to an electrometer. The dependence of TEY on the angle of incidence of light is measured by rotating the samples. The TEY spectra are simulated by the usual formulae extended for multilayers <sup>[8]</sup>. Fig. 1 shows a schematic of multilayers, where the layers are numbered upward from the substrate. Optical constant of each layer is expressed in

dielectric constant  $\varepsilon$ . Optical constants are compound-specific and dependent on its structure or phase. Therefore, the optical constants are important parameters to specify compounds, and are available from the database for ordinary materials <sup>[15]</sup>. Light passes through the vacuum and is incident on the multilayer. A part of it is reflected at the surface. The other part enters the multilayer and is refracted or reflected at interfaces, and is absorbed by each layer generating photoelectrons. Generation rate of the photoelectron is proportional to the absorption coefficient. These photoelectrons migrate into the multilayer generating secondary electrons. And then, a part of the photoelectrons that leave the surface is detected. The TEY is proportional to the sum of electrons that leave the surface of each layer, as illustrated by e<sup>-</sup> in Fig. 1. Transmission rate p for an electron to pass through each interface includes the effects of potential barrier at the interface and the generation rate of secondary electrons in the layer below the interface, which are treated as fitting parameters. Experimental values of the escape depth were obtained. As the generation rate of photoelectrons is proportional to the squared absolute value of the electric field, enhancement of the TEY occurs at the site of intense electric field (antinode) of the standing wave in the multilayer. Therefore, a part of the layers can be selectively excited by the standing wave, and this excitation can be used to obtain the required data in depth direction.



Fig. 1 Schematic of optical processes in multilayer.

#### 2.2 SXE spectroscopy

Core electrons in the sample are excited by electron beams or synchrotron radiation. The latter excitation has advantages such as low heat load, polarization, high intensity, and so on, in comparison with the former excitation. Undulatory radiation is recently available as a brilliant light of high intensity. The SXE spectra are recorded on spectrometers using spherical gratings equipped with the position-sensitive detectors <sup>[16]</sup>. The SXE spectra give the valence band structure as photoelectron spectra, and provide element-specific, compound-specific, and symmetry-specific information. In multilayers, the SXE from each layer is detected (see Fig. 1 with regard to  $e^{-}$  as SXE and p=1). The SXE spectrum is a superposition of the spectrum of each layer. The structural analysis of multilayers with specification of compounds can be carried out by analyzing the spectral shape with curve-fitting analysis using the spectra of reference materials, which are model compounds of the layers. That is, the measured spectrum is decomposed by the reference spectra, their thicknesses being the fitting parameters. As the escape depth of SXE is usually larger than the period distances of multilayers, the analysis can be carried out without taking into account the self-absorption effect. For the periodic multilayer, the peak of the squared absolute value of the electric field in standing waves can selectively excite some layers, so that the standing wave method detecting SXE can also give information in depth direction. The analysis is similar to that of TEY.

## 3 Semiconductor-insulator layered structures

Semiconductor-insulator layered structures are potential candidates as materials used in electronic devices <sup>[1]</sup>. Therefore, it is important to investigate their properties to achieve high performance.

### 3.1 LiF/Si/LiF trilayers

Here an investigation of LiF/Si/LiF trilayers on Si(100) substrates using TEY spectroscopy is described <sup>[8]</sup>. The trilayers were fabricated by the use of a molecular beam epitaxy (MBE) instrument equipped with electron-beam evaporators. First, a Si substrate was cleaned by Shiraki method <sup>[17]</sup>, in which the substrate was rinsed with HF solution to remove oxide layer. It was mounted on a sample holder in high vacuum and was heated to purge the remaining oxygen from the surface. Second, LiF was deposited such that its thickness is 5 nm. Third, Si was deposited on the deposited LiF. The thickness of Si was chosen as 2 nm, 3.5 nm, and 5 nm, respectively. Finally, 2 nm thick LiF was deposited as a top layer.

The TEY spectra measured for Si(100)/LiF/Si/LiF trilayers of three different Si thicknesses around Si L edge ( $\lambda \sim 12$  nm) for various angles of incidence are shown in Fig. 2. The TEY spectra were obtained for linearly polarized light, of which electric vector lies on the plane of incidence (p-polarized light, see Fig. 1). At an angle of incidence of 0°, the TEY spectra for three samples have the same broad spectral shape lying on the background, which increases with increasing photon energy. They are different from those of both crystalline and amorphous Si <sup>[18]</sup>, but similar to one of the spectra of porous Si <sup>[19]</sup>, which shows gradual rise around the edge (100 eV-

104 eV). In the case of 2-nm thick Si sample, when the angle of incidence exceeds 65°, the spectral structures seem to correspond to those of crystalline Si as seen in Fig. 2(a). In the cases of 3.5 nm and 5 nm thick Si samples, the spectral shapes drastically change at angles of incidence of 65°-70°, showing a dip with several structures between 99.5 eV and 102 eV as seen in Figs. 2(b) and (c). At an angle of incidence of 75°, the dip disappears and the intensity increases again. The gross spectral feature is not similar to that of crystalline Si, but the small structures correspond to those of crystalline Si. Accordingly, it is suggested that the structure of the Si layer in the direction parallel to the sample surface is similar to that of porous Si, and that in the perpendicular direction, to crystalline Si. Therefore, simulations were carried out assuming that the optical constants perpendicular to the surface are the same as those of crystalline Si, whereas those parallel to the surface are the same as those of porous Si. The latter were trial ones derived from the TEY spectra of porous Si using Kramers-Kronig analysis under certain assumptions.



Fig. 2 Measured TEY spectra of Si(100)/LiF/Si/LiF trilayers around Si L edge using p-polarized light.

Fig. 3 shows the simulated TEY spectra of Si(100)/LiF 5 nm/Si 5 nm/LiF 2 nm trilayer for an angle of incidence of 75° with various transmission rates p. The transmission rate  $p_1$  at LiF/Si interface and  $p_3$  at LiF/vacuum interface are assumed to be 1, whereas the rate  $p_0=p_2$  at Si/LiF interface is a fitting parameter. When  $p_0=p_2$  is larger than 0.8, the structure

between 100 eV and 102 eV is a peak, whereas when  $p_0=p_2$  is smaller than 0.5, the entire structure transforms into a dip. The dip is caused by the interference effect of the light in the trilayer. The most appropriate value to reproduce well the present results is  $p_0=p_2=0.3$ . By inclusion of the background, which linearly increases with photon energy, the simulation

results reproduce well the spectral feature at 75°, as shown in Fig. 2(c). The other simulations also reproduce well the features, wherein no dip appears in the case of 2 nm thick Si as shown in Fig. 2(a) and small dips appear in the case of 3.5 nm thick Si as shown in Fig. 2(b). The result that  $p_1$  (transmission rate at LiF/Si interface) is larger than  $p_0$  (transmission rate at Si/LiF interface) is consistent with the fact that the band gap of LiF (~12 eV) is larger than that of Si (~ 1 eV).

The TEY measurements specified the structure of Si in Si/LiF trilayers, which was different from the structure of ordinary Si. Furthermore, it was shown that the angle-dependence measurement of TEY is a useful method to elucidate the multilayer structures.



**Fig. 3** Calculated TEY spectra of bulk-Si/LiF/Si/LiF trilayer around Si *L* edge for p-polarized light.

#### 3.2 Si/CaF<sub>2</sub> dilayers and CaF<sub>2</sub>/Si/CaF<sub>2</sub> trilayers

A study on Si/CaF<sub>2</sub> dilayers and CaF<sub>2</sub>/Si/CaF<sub>2</sub> trilayers is presented as a second example <sup>[20]</sup>. CaF<sub>2</sub> can be epitaxially grown on a Si(111) substrate due to a small lattice mismatch between the two. Once it was considered that this character had an advantage in forming semiconductor–insulator junctions, and there were several reports on Si growth on the CaF<sub>2</sub> layer aiming at the fabrication of devices <sup>[21, 22]</sup>. The present samples were grown on the clean surfaces of Si(111) also using the MBE instrument. The reflection-high-energy-electron-diffraction (RHEED) measurement ensured that the surface before the deposition was of  $7 \times 7$  pattern and it changed to  $1 \times 1$  pattern after the CaF<sub>2</sub> deposition.

Figs. 4(a), (b) and (c) show, respectively, the TEY

spectra of Si substrate, dilayers of Si(111)/CaF<sub>2</sub> 7 nm/ Si 3 nm, and Si(111)/CaF<sub>2</sub> 7 nm/Si 12.5 nm between 98 eV and 110 eV for angles of incidence ranging from 0° to 80°. Dotted curves represent the experimental results and broken curves represent the simulation. The TEY spectral shapes of Si substrate hardly changed with the angle of incidence. The spectra of the dilayers are similar to those of crystalline Si, when the angle of incidence is between 0° and 60°. This feature is different from that of Si(100)/LiF/Si/LiF trilayers, where the TEY spectra resemble those of porous Si in normal incidence. At angles of incidence above 60°, dip structures appear around 99 eV. Around 80°, the dip structure becomes large. Small structures correspond well to those observed in crystalline Si around Si L edge. Figs. 5(a), (b), and (c) show TEY spectra of monolayer of Si(111)/CaF2 1.5 nm, and trilayers of Si(111)/CaF<sub>2</sub> 7 nm/Si 3 nm/CaF<sub>2</sub> 1.5 nm and Si(111)/CaF<sub>2</sub> 7 nm/Si 12.5 nm/CaF<sub>2</sub> 1.5 nm, respectively. These spectra are similar to those of dilayers shown in Figs. 4(b) and (c). These similarities that the spectra of Si(111)/CaF<sub>2</sub>/Si dilayers are similar not only to those of Si(111)/CaF<sub>2</sub> monolayer but also to those of Si(111)/CaF<sub>2</sub>/Si/CaF<sub>2</sub> trilayers suggest that the Si layer is covered with a top CaF<sub>2</sub> layer. It means that the CaF<sub>2</sub> diffuses into the Si layer from the bottom CaF<sub>2</sub> layer and segregates to the surface. The simulation was made, segregation effect being taken into account. The simulation reproduces well the experimental results by the use of the layers with thickness differing from nominal ones to a certain extent.

In addition, a measurement of *in-site* ellipsometry using He-Ne laser ( $\lambda = 633$  nm) was made to investigate the growth processes of a CaF<sub>2</sub> layer on Si(111) substrate and a Si layer on a grown CaF<sub>2</sub> layer. The results suggested that the Si layer on the CaF<sub>2</sub> layer seemed to be a uniform mixture of Si and CaF<sub>2</sub>.

The optical measurements give average information within the lateral extent x and the divergence of the light x'. These quantities satisfy the relation expressing diffraction effect,  $xx' > \lambda/4\pi$ , where  $\lambda$ represents the wavelength of the light. From the TEY and ellipsometry results with a reasonable assumption of x', it was suggested that the mixture layer of Si and CaF<sub>2</sub> was composed of Si platelets or islands with diameter of 20 nm—100 nm, covered and surrounded by CaF<sub>2</sub>.

The present results are consistent with the results obtained so far and give more detailed information. The conclusion drawn from this experiment is that the epitaxial growth is not appropriate for Si-CaF<sub>2</sub> system. A practical fabrication method suppressing segregation has been proposed. <sup>[22]</sup>.



Fig. 4 TEY spectra of Si wafer and Si(111)/CaF2/Si dilayers around Si L edge using p-polarized light.



Fig. 5 TEY spectra of Si(111)/CaF<sub>2</sub> monolayer and Si(111)/CaF<sub>2</sub>/Si/CaF<sub>2</sub> trilayers around Si L edge using p-polarized light.

## 4 X-ray multilayers

X-ray multilayers are usually composed of two materials periodically or quasi-periodically by the use of magnetron sputtering or ion-beam sputtering instruments. When Bragg equation  $n\lambda = 2d \sin \hat{\theta}$  $(\hat{\theta} = 90^\circ - \theta)$  is satisfied, positive interference occurs and the reflectance is enhanced, so that multilayers are used as high-reflectance coating materials in soft- and hard X-ray regions <sup>[3]</sup>. They can also be used as polar-izers in the soft X-ray region.

#### 4.1 Top layer of Mo/Si multilayers

Thicknesses of top layers can be precisely estimated by analyzing TEY spectra of multilayers, taking into account the standing wave effect. The TEY spectra calculated for [Mo/Si]40 multilayers are represented by solid curves in Figs. 6(a), (b), and (c), which are covered with 2.6 nm, 1.8 nm, and 1 nm thick Mo top layers, respectively <sup>[23]</sup>. A reflectance spectrum is represented by the broken curve in Fig. 6(a), but not shown in Figs. 6(b) and (c), because they are almost the same as the broken curve in Fig. 6(a). The thin curves in Figs. 6(b) and (c) represent the same TEY spectrum as that in Fig. 6(a). On the one hand, the TEY spectrum shows a bell shape when the Mo top-layer thickness is equal to that of the regular Mo layers as seen in Fig. 6(a). On the other hand, the TEY spectra become asymmetric when the top-layer thickness decreases as seen in Figs. 6(b) and (c). This change in the TEY spectral shape originates from the standing wave effect in the multilayer as explained below. Figs. 6(d), (e), and (f) show absorbed energy per unit volume plotted against depth of the multilayer for the samples of 2.6 nm, 1.8 nm, and 1 nm thick Mo top layers, respectively. The vertical lines represent the boundaries of Mo and Si, and the hutched area represents the top Mo layer. The excitation photon energies correspond to those at A (.....), B (-----), and C (-----) in Fig. 6(a). Contribution of the top layers to TEY is dominant because of the small escape depth. Standing wave is generated by the light at B and when thickness of the top layer is the same as the regular one, absorbed energy in the top layer at B is larger than that at A and C, so that the TEY spectrum has a bell-shaped peak at B. However when the top-layer thickness decreases, the absorbed energies at A and B decrease in comparison with that at C, so that the TEY spectra show no more bell shape. Accordingly, the TEY spectral shape is very sensitive to the top-layer thickness, and the standing wave can be used for the analysis of the top-layer thickness. Using this aspect, the top-layer structures of Mo/SiC/Si/SiC/Mo+SiO<sub>2</sub> multilayers were analyzed <sup>[23]</sup>. Decrease in reflectance caused by surface roughness is expressed by Debye-Waller-type factor <sup>[3]</sup>. By an analysis of their reflectance spectra using this factor, surface roughness of the multilayers was estimated.



Fig. 6 (a), (b), (c) - simulated TEY and reflectance spectra and (d), (e), (f), depth dependence of absorbed energy for  $[Mo/Si]_{40}+Mo$  multilayer around Si *L* edge. See details in text.

#### 4.2 Buried interfaces of Mo/Si multilayers

First, specification of materials at the interface of as-deposited Mo/Si multilayers using SXE spectroscopy is described <sup>[24]</sup>. In this case, the thickness of Mo layers was fixed as 3.4 nm and that of Si layers was chosen as 0.5 nm, 1.2 nm, 2.8 nm, 5.9 nm, and 13.3 nm. When the thickness of Si layer was greater than 5.9 nm, the spectrum was similar to that of amorphous Si (see the top portion of Fig. 8). On the other hand, when the thickness of Si layer was 0.5 nm, the spectrum was similar to that of Mo<sub>3</sub>Si <sup>[25]</sup>. The spectra of

the samples of 1.2 nm and 2.8 nm thick Si layers seemed to be a superposition of the spectra of both amorphous Si and Mo<sub>3</sub>Si. This means that a thin Mo<sub>3</sub>Si layer exists between Mo and Si layers by interdiffusion even in the as-deposited multilayers, and the interface is not clear-cut. Such interdiffusion affects performance of the high-reflectance multilayers. Recently, Mo/Si multilayers with high reflectance (71% at 13 nm for normal incidence) have been fabricated by suppressing the interdiffusion with insertion of B<sub>4</sub>C barrier between Mo and Si layers <sup>[26]</sup>.

Second, heating effect on reflectance of multilayers and observation of structural change after heating are described. Fig. 7 shows reflectance spectra of a Mo/Si multilayer before and after heating (annealing at 400°C for 5 hours) for an angle of incidence of 45°. Electric vector of the incident light is perpendicular to the plane of incidence (s-polarized light). Before heating, the reflectance was 47% and the peak position was located around 85 eV, whereas after heating, the reflectance decreased by 10% and the peak shifted by 7 eV to high-energy side. This means that the physical and chemical structure changed, and the period distance of 11.08 nm before heating became 10.21 nm after heating. Fig. 8 shows Si L emission spectra of amorphous Si, MoSi<sub>2</sub> and the Mo/Si multilayer after heating <sup>[27]</sup>. In this case, the sample of the Mo/Si multilayer (Mo 2.7 nm/Si 8.3 nm) and the condition of heating (annealing at 400°C for 10 hours) were different from those of the above experiment. The Si L emission spectrum of Mo/Si multilayer before heating (as-deposited) resembles that of amorphous Si. After heating, the spectrum changed and seemed to be a superposition of the spectra of amorphous Si and MoSi<sub>2</sub> (see the bottom portion of Fig. 8). By decomposing the spectrum after heating with those of amorphous Si and MoSi<sub>2</sub>, it was suggested that the thicknesses of amorphous Si and MoSi<sub>2</sub> after heating were 2.3 nm and 3.0 nm, respectively. This structural change might be the reason for the decrease in reflectance and the decrease in period distance. A diffusion coefficient was estimated. Recently, a detailed study has been made using Si  $K_{\rm B}$  emission, and activation energy of the diffusion process was deduced <sup>[28]</sup>. Mo/Si multilayers bearing high heat load have been developed with the incorporation of SiO<sub>2</sub> or SiC diffusion barrier

between the two layers <sup>[29]</sup>.



**Fig. 7** Reflectance of Mo/Si multilayer before and after heating for s-polarized light. Angle of incidence: 45°.



**Fig. 8** Si L emission spectra of amorphous Si, Mo/Si<sub>2</sub> and Mo/Si multilayer after heating.

#### 5 Fe/Si magnetic multilayers

Several kinds of magnetic multilayers have been developed, which have advantages of large hysteresis loop, perpendicular magnetic anisotropy, and so on <sup>[2]</sup>. One of them is the giant magnetic resistance. The multilayers are composed of ferromagnetic layers and nonmagnetic layers. Without an applied magnetic field, the ferromagnetic layers show antiferromagnetic coupling, whereas with the field, they show ferromagnetic coupling. For transfer of conduction electrons across the multilayer, the electric resistance is larger without magnetic field than with it due to the difference in scattering feature between the electrons with spins of

opposite directions.

The Fe/Si multilayer is one such antiferromagnetic coupling multilayers <sup>[30]</sup>. In the multilayer, the origin of the antiferromagnetic coupling was an open question. It was not clear whether the coupling originated from conduction electrons (RKKY (Ruderman, Kittel, Kasuya and Yoshida) theory) or from the interference effect of quantum wave <sup>[31]</sup>. That is, it was not clear whether the materials including Si are conductive or insulating.

Fig. 9 shows cross-sectional TEM image of Fe 4 nm/ Si 6.6 nm multilayer of nonmagnetic coupling <sup>[32]</sup>. The dark layer is Fe layer and the bright layer is Si layer. The gradation layer is found at every Fe–Si interface, which originates from interdiffusion effect. The multilayers showing antiferromagnetic coupling have shorter period distance compared with the multilayer shown in this figure. In them, clear Si layers could not be found in the TEM images, whereas only the gradation layers were found. In the following text, investigation of the chemical states of the gradation layers including Si by SXE spectroscopy is described.



Fig. 9 Cross-sectional TEM image of the Fe 4 nm/Si 6.6 nm multilayer.

Fig. 10 shows Si *L* emission spectra of Fe/Si multilayers and amorphous Si. The top layers of Fe/Si multilayers were Fe. Thickness of Fe was fixed as 3 nm and that of Si (*t*) was changed from 0.5 nm to 3 nm, nominally. When t=0.5 nm, the coupling was ferromagnetic (F); when t=1 nm, 1.3 nm, and 1.5 nm, anti-ferromagnetic (AF); when t=1.7 nm, ferromagnetic; (F) and when t>2 nm, noncoupling (NC). The strongest antiferromagnetic coupling occurs at t=1.3 nm. As *t* changed, the magnetic property changed and the Si L emission spectrum changed.

For analysis of the emission spectra, it is necessary to decompose the spectra with those of reference compounds, which are stoichiometrically stable. In this case, these compounds are Fe<sub>3</sub>Si, FeSi, and FeSi<sub>2</sub> as suggested from the phase diagram of Fe and Si. First, fitting analysis was made using SXE of crystal-line compounds measured so far <sup>[33]</sup>; however, it was not successful. It suggested that the structures of these compounds are not crystalline but amorphous in the present samples. Therefore, to obtain the spectra of amorphous samples, Si *L* emission spectra of Fe<sub>1-x</sub>Si<sub>x</sub> alloys were measured, and spectra of reference materials were obtained by interpolation. Fig. 11 shows the interpolated Si *L* emission spectra of Fe<sub>3</sub>Si, FeSi, and FeSi<sub>2</sub> from the spectra of Fe<sub>1-x</sub>Si<sub>x</sub> alloys.



**Fig.10** Si *L* emission spectra of Fe/Si multilayers. F, AF, and NC represent ferromagnetic, antiferromagnetic, and nonmagnetic couplings, respectively.



**Fig.11** Interpolated Si L emission spectra of Fe<sub>3</sub>Si, FeSi, and FeSi<sub>2</sub>.

The spectra of the multilayers obtained using the reference spectra were analyzed (shown in Fig. 10). As a typical example, analysis of the spectrum of Fe/Si 1.3 nm is described as follows. The model is shown in Fig. 12. The left column represents the nominal structure. The middle column represents the fitting model. In the fitting model, interdiffusion layers are situated in the order of Fe<sub>3</sub>Si, FeSi, and FeSi<sub>2</sub> from Fe to Si layers. It was assumed that SiO<sub>2</sub> was located in Si and Fe silicides. The fitting result is shown in the right column. Thickness of Fe<sub>3</sub>Si, which is metallic, was 0.5 nm. In the middle layer, amorphous Si was not found, but FeSi<sub>2</sub>, which is insulator and nonmagnetic, was found. Therefore, it is concluded that the conduction electrons do not contribute to the antiferromagnetic coupling, but the quantum wave interference model is appropriate to explain the present case. The fact that Fe<sub>3</sub>Si is metallic and FeSi<sub>2</sub> is insulating was confirmed by the TEY measurements. In Fe<sub>3</sub>Si, a steep rise of TEY around Si L absorption edge corresponding to the Fermi edge was observed, whereas in FeSi<sub>2</sub>, the rise was not steep, which suggested the existence of band gap.

Nominal	Fitting model	Result
Fe (3.0 nm)	Fe	Fe (1.4 nm)
	Fe <sub>3</sub> Si	Fe <sub>3</sub> Si
Si (1.3 nm)	FeSi FeSi₂ Si FeSi₂ FeSi₂	(0.5 nm)) FeSi <sub>2</sub> (0.7 nm) Fe <sub>2</sub> Si
	∭Fe₃Si	(0.5 nm)
Fe (3.0 nm)	Fe	Fe (1.4 nm)
(0.0 mm)		

Fig. 12 Model of structure of Fe/Si multilayer.

In the above analysis, thicknesses of a certain kind of interdiffused layers above and below the Si layer are implicitly assumed to be equal (symmetric), but recently a possibility that the thicknesses are different (asymmetric) has been pointed out by an SXE standing wave experiment <sup>[34]</sup>. A small contribution from SiO<sub>2</sub> was recognized in the sample. SXE measurements with excitation by the light of grazing incidence (total reflection) were performed, and it was suggested that the SiO<sub>2</sub> top layer was generated by oxidization of the Fe<sub>3</sub>Si layer nearest to the Fe topmost layer <sup>[35]</sup>.

#### 6 Summary

It has been pointed out that interdiffusion or chemical reaction of adjoining layers often occurs in multilayers, affecting their characteristics and sometimes showing novel features, and the investigation of the multilayer structure in depth direction is important. It has been demonstrated that TEY and SXE spectroscopic measurements are useful as nondestructive methods to investigate chemically the multilayer structure in depth direction. Using the angular-dependence measurement of TEY with electric vector parallel to the layers, it was found in the trilayer of Si/LiF that Si layers had a characteristic similar to porous Si, and in trilayers of CaF2/Si/CaF2, it was found that CaF<sub>2</sub> segregated through Si layer. It has been shown that the top-layer thickness of Mo/Si X-ray multilayer can be determined by measuring the standing wave effect on TEY spectra. By spectral shape analyses of SXE spectrum compared with those of reference materials, it was found in Mo/Si X-ray multilayer that heating caused interdiffusion or chemical reaction, giving rise to deterioration of reflectance character. Furthermore, in antiferromagnetic Fe/Si multilayers, it was confirmed that there was no existence of pure Si layers, but insulating FeSi2 layers were present. This suggested that the antiferromagnetic coupling did not originate from conduction electrons, but from quantum wave interference. Further investigation by the standing wave method used in the detection of SXE pointed out the possibility that the structure of the multilayer is not symmetric in depth direction.

In this article, special physical structures such as magnetic structure are not concerned. The use of soft X-ray scattering using circularly polarized light for analysis of magnetic structure in depth direction has been demonstrated elsewhere <sup>[36,37]</sup>.

#### References

- Seeger K. Semiconductor physics (6th ed.). Heiderberg (Germany): Springer-Verlag, 1997
- 2 Fujimori H, Shinjo T, Yamamoto R, *et al.* (eds.) Metal superlattices. Tokyo (Japan): Agne Gijutsu Center, 1995 (in Japanese)
- 3 Yanagihara M, Yamashita K. in X-ray spectrometry: Recent technological advances, ed. by Tsuji K, Injuk J, Van Grieken R. Chichster (UK) : John Wiley & Sons, 2004 : 63
- Barbo F, Bertolo M, Bianco A, *et al.* Rev Sci Instr, 2000, 71: 5
- 5 Ibach H (ed.). Electron spectroscopy for surface analysis. Topics in Current Phys 4. New York (USA): Springer-Verlag, 1977
- 6 Gudat W, Kunz C. Phys Rev Lett, 1972, **29**: 169
- 7 Nakajima R, Stohr J, Idzerda Y U. Phys Rev, 1999, B 59:
   6421
- 8 Ejima T. Jpn J Appl Phys, 2003, 42: 6459
- 9 Konigsberger D C, Prins R (eds.). X-ray absorption: Principles, applications, techniques of EXAFS, SEXAFS and XANES. Chem Anal **92.** New York (USA): Wiley, 1988
- 10 Wassdahl N, Nilsson A, Wiell T, et al. Phys Rev Lett, 1992, 69: 812
- 11 Iwami M, Appl Surf Sci, 1997, 113/114 : 377
- 12 Kawamura T, Takenaka H. J Appl Phys, 1994, 75 : 3806
- 13 Gose S K, Dev B N. Phys Rev, 2001, B 63: 245409
- 14 Yang S -H, Mun B S, Kay A W, et al. J Elect Spectr Rel Phenom, 2001, 114-116: 1089
- 15 Henke B I, Gullikson E M, Davis J C. At. Data and Nucl Data Tables, 1993, 54: 181. See also http://www-crxo.lbl.gov/optical constants/
- 16 Samson J A, Edeler D L (eds.). Vacuum ultraviolet spectroscopy II, San Diego (USA): Academic Press, 1998
- 17 Ishizaka A, Shiraki Y. J Electrochem Soc, 1986, 133: 666
- Brown F C, Bachrach R Z, Skibowski M. Phys Rev, 1977, B 15: 4781

- 19 Inoue K, Maehashi K, Nakashima H. Jpn J Appl Phys, 1993, 32: L361
- 20 Ejima T, Ohuchi K, Watanabe M. Jpn J Appl Phys, 2005, 44: 5171
- 21 Smith III T P, Phillips J M, Augustyniak W M, et al. Appl Phys Lett, 1984, 45: 907
- 22 Muratake S, Watanabe M, Suemasu T, *et al.* Electronics Lett, 1992, **28**: 1002
- 23 Ejima T, Muramatsu Y, Takenaka H, *et al*. AIP Conf Proc (American Institute of Physics), 2004, **705**: 1126
- 24 Miyata N, Ishikawa S, Yanagihara M, et al. Jpn J Appl Phys, 1999, 38: 6476
- 25 Nemoshkalenko V V, Shpaqk A P, Krivitsky V P, et al. Phys Lett, 1973, A 45: 369
- 26 Bajt S, Alameda J B, Barbee Jr T W, *et al.* Opt Eng, 2002,
  41: 1797
- 27 Miyata N, Imazono T, Ishikawa S, *et al.* Surf Rev Lett, 2002, 9: 663
- 28 Jonnard P, Jarrige I, Benbalagh R, et al. Surf Sci, 2005, 589: 164
- 29 Ishino M, Yoda O. J Appl Phys, 2002, 92: 4952
- 30 Endo Y, Kitakami O, Shimada Y. Phys Rev B 1999, 59: 4279
- 31 Bruno P. Phys Rev, 1995, B 52: 411
- 32 Imazono T, Hirayama Y, Ishikawa S, et al. Jpn J Appl Phys, 2004, 43: 4327
- Jia J J, Callcott T A, O'Brien W L, *et al.* Phys Rev, 1992,
   B 46: 9446
- 34 Hamamoto R, Sugawara M, Ichikura S, *et al.* KEK proceedings of the workshop on 'buried' interface science with X-rays and neutrons, 2006 (to be published)
- 35 Imazono T, Hirayama Y, Ichikura S, *et al.* Jpn J Appl Phys 2004, **43**: 4334
- 36 Sacchi M, Mirone A, Hague C F, *et al.* Phys Rev, 2001,
   B63: 32
- 37 Kortright J B. Synch Rad News 2004, 17, (6): 16