Si X-Ray Absorption Near Edge Structure (XANES) in X-Ray Fluorescence Spectra

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Silicon *K* X-ray fluorescence spectra of Si and SiO_2 single crystals are measured using a wave dispersive X-ray fluorescence spectrometer. It is demonstrated that the fine structures in the line shape of the low energy tail of the *K*α characteristic X-ray fluorescence spectra resemble those of the *K* X-ray absorption near edge structure (XANES).

Strong characteristic *K*α X-ray lines are accompanied by weak lines due to the radiative Auger effect (RAE).[1,2] Kawai *et al.*[3] pointed out that the profiles of the RAE X-ray fluorescence (XRF) spectra resembled to that of the X-ray absorption edge, and Hayashi *et al.*[4] proved that the extended X-ray absorption fine structure (EXAFS) spectroscopy was able to be performed by the line shape analysis of RAE in XRF spectra.

The characteristic *K*α fluorescent X-rays are emitted by the $2p \rightarrow 1s$ electric dipole transition after one of the 1*s* electron's photoionization. One of the 2*p* electrons is excited into an unoccupied discrete (shake-up) or continuum level (shake-off) simultaneously with the *K*α X-ray emission, because of the sudden change of the atomic potential before and after the electric dipole transition, though this takes place with a very small probability. This many body effect is called the radiative Auger effect. The excitation of the 2*p* electron due to the RAE is the electric monopole transition,[2] and thus has information on the unoccupied *p* density of states similar to the 1*s* X-ray absorption fine structure (XAFS). The present authors recently reported that the radial distribution functions around the X-ray emitting atom in aluminum metal and aluminum oxides were obtainable by the Fourier transform of the RAE in the XRF spectra.[4,5] They proposed to call this EXEFS (abbreviation of extended X-ray emission fine structure).[6,7] In the present letter, we report that the Si *K*-edge X-ray absorption near edge structure (XANES) of Si and SiO_2 can be found in the XRF spectra. Usually the measurement of Si *K*-edge XANES is very difficult without using a soft X-ray synchrotron radiation beam line. However the measurement of the XRF spectrum of silicon is an easy routine work, and we demonstrate in the present work the XANES-like spectra are easily measurable using a conventional XRF spectrometer.

RIGAKU RIX2100 X-ray fluorescence spectrometer was used for spectral measurement. This spectrometer was designed for elemental analysis. The analyzing crystal used was PET (pentaerythritol) (002), $2d$=8.742 Å. The spectrometer chamber was evacuated by a rotary pump. The sample was excited by a Rh anode X-ray tube (40 kV and 70 mA). One channel was 10 seconds with the 0.02° (2θ) step from 105° to 148°. The total measure time for one spectrum was 6 hours. The samples measured were Si and α-SiO_2 single crystals.

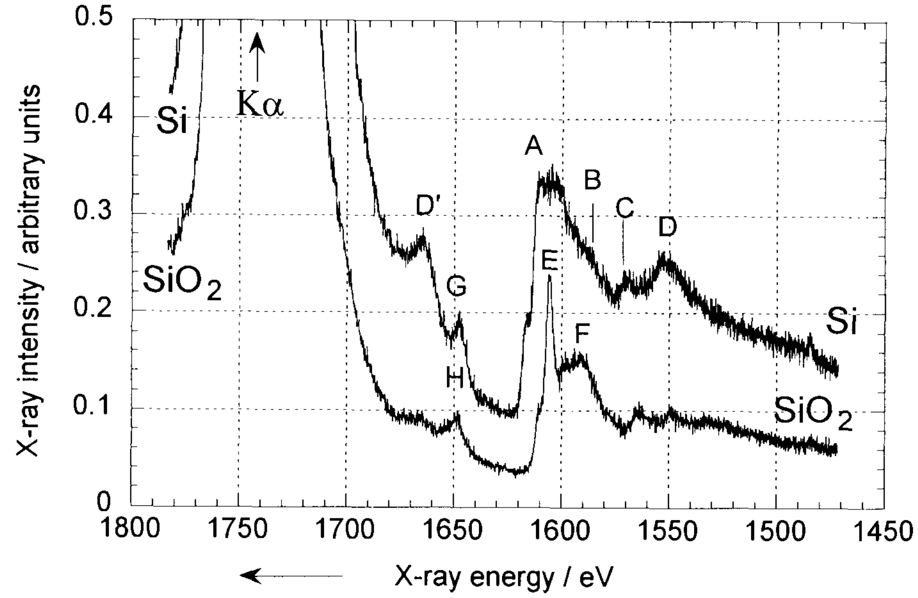

Figure 1. Measured Si *K* X-ray fluorescence spectra of Si and SiO_2. Peaks A-F correspond to those in Figure 2. Peaks D', G, and H, see text.

The measured X-ray fluorescence spectra of Si and SiO_2 are shown in Figure 1. The energy axis is inverted to compare with the genuine XANES spectra shown below. The overall spectral line shapes of both Si and SiO_2 reproduces the radiative Auger spectra measured by Åberg *et al.*[8] Figure 2 shows X-ray absorption spectra of Si and SiO_2 measured by Ohta *et al.*[9] These spectra were measured at the 2.5 GeV synchrotron radiation beam line BL-11B in the Photon Factory, National Laboratory for High Energy Physics.

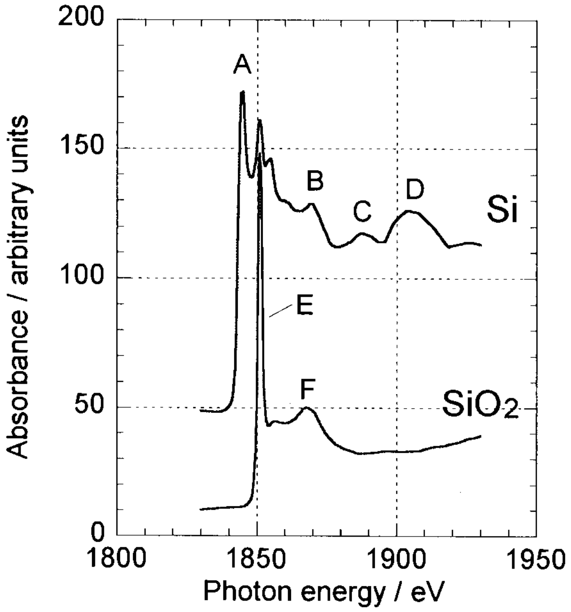

Figure 2. Si *K*-edge XANES of Si and SiO_2 taken and modified from Ohta *et al.*[9]

It is striking that these two sets of spectra resemble each other. The XANES of oxide has sharp peak (peak E, 1852 eV) and higher energy shoulder (peak F), but has no fine structure between 1880-1930 eV in Figure 2. These are reproduced in X-ray fluorescence spectrum of SiO_2 in Figure 1. The absorption edge of Si (peak A) is approximately 10 eV lower than the SiO_2 absorption peak (E), and a broad hump D at 1905 eV is found in Figure 2. These features are again reproduced in Figure 1. Other features, B and C, in Figure 1 are also reproduced in Figure 2. Therefore the fine structures in the low energy tail of characteristic X-ray lines are approximately identical to the X-ray absorption near edge structure.

Åberg *et al.*[8] pointed out that their radiative Auger X-ray fluorescence spectra of Si resembled the $L_{2,3}$ X-ray absorption spectra, but the agreement between the *K-LL* RAE and the $L_{2,3}$ X-ray absorption spectra was poor. We must rather compare the RAE with the *K* edge spectra, because of the monopole selection rule.[2]

It is theoretically valid that the *K-LM* RAE ranging between 1630 and 1730 eV in Figure 1 again reproduces the *K* edge spectra. The peak D' at 1670 eV corresponds to the peak D. However, since the *K-LM* RAE overlaps the strong *Kα* main peak, it is difficult to discriminate the weak *K-LM* RAE components from the strong background. Peaks G and H may be due to the internal Raman scattering. The origin of the high energy shoulders (1610 eV for SiO_2 and 1616 eV for Si in Figure 1) is not clear at the present stage. There are other several weak peaks, *e.g.* 1550 and 1565 eV for SiO_2 in Figure 1, the origins of which are again not yet clear.

The measurement of light element XANES is usually very difficult because ultra high vacuum soft X-ray beam line in a synchrotron radiation facility is required. However, we can measure the XANES-like spectra using conventional X-ray fluorescence spectrometer for elemental analysis. The present method does not require any variable wavelength X-ray sources, and thus has a potential to become a powerful tool to measure X-ray absorption spectra.

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