1. Introduction

Strong characteristic Kα X-ray lines are accompanied by weak lines due to the radiative Auger effect (RAE) [1, 2]. The characteristic Kα fluorescent X-rays (K-L\textsubscript{2,3} lines) are emitted by the 2p→1s electric dipole transition after one of the 1s electron photoionization. Though the probability is less than 0.01, one of the 2p electrons is excited into an unoccupied discrete or continuum level simultaneously with the Kα X-ray fluorescence, because of the perturbation of the sudden change of the atomic potential before and after the 2p→1s electric dipole transition. This many body effect is called the radiative Auger effect. Kawai et al. [3] pointed out that the profiles of the RAE X-ray fluorescence (XRF) spectra resembled those of the K X-ray absorption near edge structure (XANES). The energy resolution of the XANES spectra measured by the present method is as high as that measured by a synchrotron radiation facility. The time required to measure one XANES spectrum using the present method is as short as 25 minutes. The present method has a potential to be used as a new method of XANES spectroscopy, and has three remarkable characteristics: (1) high energy resolution, (2) short measuring time, and (3) a convenient alternative to the synchrotron radiation X-ray absorption spectroscopy.

2. Theory

The RAE X-rays associated with the Ka lines are emitted by the 2p→1s electric dipole transition. The second RAE electron cannot change the orbital...
angular momentum when it moves from 2p to an unoccupied orbital, as shown in Fig. 1. Thus the unoccupied orbital should have the same orbital angular momentum as that of the 2p orbital. This is the reason that the excitation of the 2p electron due to the RAE is said to be the electric monopole transition [2]. The probability of shaking an electron, i.e. the RAE spectral intensity, is crudely proportional to the p state density of the unoccupied orbital. This is similar to the 1s X-ray absorption fine structure (XAFS), because the K absorption spectra are the results of the 1s→εp or np electric dipole transition. Here, as shown in Fig. 1, εp indicates a continuum p state of which energy is ε, and np the n-th p orbital. The RAE spectra have information on the unoccupied p density of states.

Åberg et al. [13] pointed out that K-LL RAE 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 not satisfactory. The L_{2,3} absorption spectra represent the unoccupied s and d state density. We should rather compare the K-LL RAE spectra with the K edge spectra because of the monopole selection rule [2].

3. Experimental

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. But the range of interest could be measured within 25 minutes as is described in the discussion below. The samples measured were single crystals of Si and α-SiO_2, and powders of SiC and Si_3N_4. Powder samples were pressed into briquettes. The size of the four samples was 30 mm in diameter. X-ray energy was calibrated by the table of White and Johnson [14].

4. Results and Discussion

Representative measured X-ray fluorescence spectra of Si and SiC are shown in Fig. 2. We found the RAE energy loss structures. The structure below 1620 eV is the K-LL RAE, where one electron moved from the L to the K shell and another electron moved from the L shell to an unoccupied orbital. Theoretically, K-LM RAE is possible, where the second electron moves from M shell to an unoccupied orbital. It is ranging between 1630 and 1730 eV, which again ought to reproduce the K edge spectra. Small humps marked A, B, and C in Fig. 2 (the K-LL RAE spectral components) are shifted by 1 10 eV and marked D, E, and F. The shifted energy is approximately the difference between the total
energy of the $L^2$ and LM double hole states. The K-LL RAE component of C corresponds to F in the K-LM RAE. The humps are not found for D and E because these humps are hidden behind the strong K$\alpha_{1,2}$ main lines.

We must note other origins such as contamination for the small humps. The possible contamination lines are aluminum K$\beta$ and potassium K$\alpha$ as are indicated in Fig. 2, though these contamination lines are not found. The peak G in Fig. 2 is the internal X-ray Raman scattering [14], where a K$\alpha$ X-ray photon emitted by an atom in the solid was scattered by a 2p electron of other silicon atom in the solid, and lost the photon energy. The energy loss approximately equals to the 2p binding energy (100 eV).

Enlarged spectra of the measured Si compounds are shown in Fig. 3 together with genuine XANES spectra measured by Wong et al. [15] using an YB$_{66}$ crystal spectrometer at The Stanford Synchrotron Radiation Laboratory (SSRL). We have converted the synchrotron radiation (SR) XANES energy into $E_{0}$ - $E_{\text{XANFS}}$, where $E_{0}$ is a constant for all the four spectra in Fig. 3 and $E_{\text{XANES}}$ the synchrotron radiation X-ray energy. It is striking that these two sets of spectra (SR-XANES and EXEFS) resemble each other.

The XANES of oxide (Fig. 3d) has sharp peak (1852eV) and a shoulder. This is reproduced in the X-ray fluorescence spectrum (EXEFS) of SiO$_2$. In the spectra of (a) Si, (b) SiC, and (c) Si$_3$N$_4$, the fine structures in the SR-XANES spectra are again found in the XRF EXEFS spectra of the same compounds. It is found, however, that the energy intervals of the SR-XANES spectra are always larger than that of the EXEFS spectra. The difference is remarkable for

![Fig. 3: Measured K-LL RAE spectra of (a) Si, (b) SiC, (c) Si$_3$N$_4$, and (d) SiO$_2$ (EXEFS), compared with genuine XANES spectra measured using synchrotron radiation facility (SR-XANES) by Wong et al. [15].](image-url)
ionic solids, (C) Si$_3$N$_4$ and (d) SiO$_2$, though the overall line shapes are well reproduced. The XRF spectral energy is more contracted compared with the genuine XANES energy for Si$_3$N$_4$ and SiO$_2$. The localized unoccupied valence orbitals are more contracted by the attractive potential due to the L$^2$ holes. The effect of L$^2$ holes are negligibly small for delocalized unoccupied valence orbitals. The unoccupied orbitals of ionic compounds (Si$_3$N$_4$ and SiO$_2$) are more localized than those of covalent compounds (Si and SiC). The peak or hump at the edge (1 610-1615 eV in Fig. 3), the origin of which is unknown, is always found for these four silicon XRF spectra. The four EXEFS spectra in Fig. 3 are quite similar to the EPMA EXEFS spectra reported in Refs. [11, 12].

We have plotted Si and SiO$_2$ spectra in Fig. 4, which were the same data as those shown in Fig. 3, but one channel was 20s with 0.32° steps. One-eighth of the data in Fig. 3 were discarded when plotting Fig. 4. Other experimental conditions were same as those described above. The total measure time of one spectrum shown in Fig. 4 was 25 minutes. Genuine X-ray absorption spectra of Si and SiO$_2$ measured by Ohta et al. [16] using the 2.5GeV synchrotron radiation bending magnet beam line BL-11B at the Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Japan, are also plotted in Fig. 4. Though the EXEFS measurement was very quick, EXEFS well reproduces the fine structures in the SR-XANES spectra. This demonstrates that only 25 minutes are enough to obtain one XANES-like spectrum using a conventional X-ray fluorescence spectrometer.

The K-LL RAE intensity is atomic number dependent. It becomes weak when the atomic number larger [17, 18]. Thus the K-LL RAE is suitable for the measurement of elements whose atomic number is less than 20. We must use the K-MM RAE (called K$\eta$ line) to measure larger atomic number elements. 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 a 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.

5. Conclusions

Silicon K X-ray fluorescence spectra of Si, SiC, Si$_3$N$_4$, and SiO$_2$ are measured using a conventional wavelength-dispersive X-ray fluorescence spectrometer. It was shown that the fine structures in the line shape of the low energy tail of the Si K$\alpha_{1,2}$ characteristic X-ray fluorescence spectra resembled
those of the Si K XANES spectra for these four compounds. The present method becomes a convenient alternative to the X-ray absorption spectroscopy. The energy resolution of the present spectra was as high as that of the synchrotron radiation X-ray absorption spectra. The time required to obtain one spectrum by the present method was 25 minutes, which was short enough compared with the synchrotron radiation method. There are not any soft X-ray absorption spectroscopy beam lines for the routine chemical analysis. This is mainly because the absorption coefficient of such an X-ray energy is very large, and a windowless synchrotron radiation beam line, which directly connects from the electron storage ring to the measurement chamber is required.

In summary, the present method has the following five characteristics:

- High energy resolution.
- Short measuring time.
- Easy sample preparation which is identical to that required for XRF analysis.
- Convenient without using limited and distant synchrotron radiation facilities.
- Good at measuring soft X-ray absorption spectra which is usually difficult because windowless and ultrahigh vacuum beam line in a synchrotron radiation facility is required.

Papers reporting the present method applied to other elements and Japanese review articles will be published shortly [19-23].

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**References**
