BL-27A/2019G032

Multi-atom resonant photoemission in silicon compounds

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1 Introduction

XAFS (EXAFS, XANES) is a powerful method to determine electronic and geometrical structure of materials. Owing to the element specific feature of core-level excitation, structures around a specific atom can be determined by XAFS even for a multi-component solid. However, in the case of complex materials composed of three or more elements, XAFS has a limitation that the atomic species adjacent to the analyzing atom cannot be specified. Taking semiconductor materials like silicon compounds as an example, structures around silicon atom in binary solid such as SiO_x [1] and SiN_x [2] has been extensively investigated by Si *K*-edge XAFS. However, for ternary compounds like silicon oxynitride (SiO_xN_y), the structural analysis by XAFS has a limitation because atomic species adjacent to silicon atom cannot be specified.

In the present study, multi-atom resonance (MAR) [3] in photoemission spectroscopy was applied to the silicon compounds in order to investigate whether species of the neighboring atom can be specified or not by MAR.

2 Experiment

Two kinds of pellet samples were prepared. One was SiO_2 and the other was Si_3N_4. The powder sample was mixed with matrix material at a weight ratio of 1:1. As matrix material, boron nitride (BN) power was used for SiO_2, and cellulose powder was used for Si_3N_4. The mixed powder was pulverized by motor, and then pressed into a pellet at a pressure of 3 ton/cm^2.

The experiments were performed at the BL-27A soft X-ray station, Photon Factory. X-ray photoelectron spectra (XPS) were taken with hemispherical electron energy analyser (VSW. CLASS-100). The photon beam was irradiated at 55 deg. from the surface normal, and the electron take-off direction was the surface normal. An electron flood gun was used during the measurements. XAFS spectra were measured by plotting a sample drain current as a function of photon energy. The sample current was normalized by the photon intensity measured by the drain current of aluminium mesh located in front of the sample.

3 Results and Discussion

Fig. 1 shows the Si *K*-edge XAFS spectra for SiO_2 and Si_3N_4. The most intense peaks indicated as arrows originate from the resonant excitation corresponding to the dipole-allowed Si $1s \rightarrow 3p^*$ transition.

Fig. 2 shows the wide-scan XPS spectrum for SiO_2 excited by 2000 eV photons. In addition to the O 1*s* peak originating from SiO_2, the N 1*s* and B 1*s* peaks due to the matrix BN powder were observed at almost equal intensity. Similar spectrum was obtained for Si_3N_4.

Next, the intensity of these peaks were measured by scanning X-ray energy around the Si *K*-edge. Fig. 3 shows the intensity of B 1*s*, N 1*s* and O 1*s* peaks for SiO_2 as a function of photon energy. The XAFS spectrum is also shown in the lower part. The intensity of the O 1*s* peak was reduced around the Si $1s \rightarrow 3p^*$ resonance, which is due to the MAR. But the intensities of the B 1*s* and N 1*s* peaks were

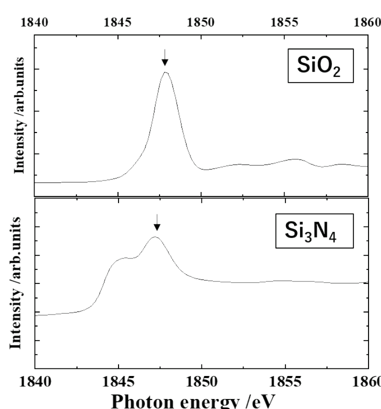

Fig. 1: Si *K*-edge XAFS spectra for SiO_2 and Si_3N_4.

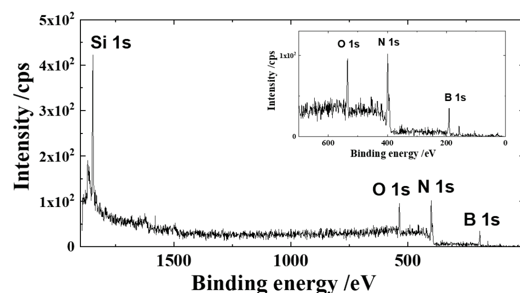

Fig. 2: XPS wide scan spectrum for SiO_2.

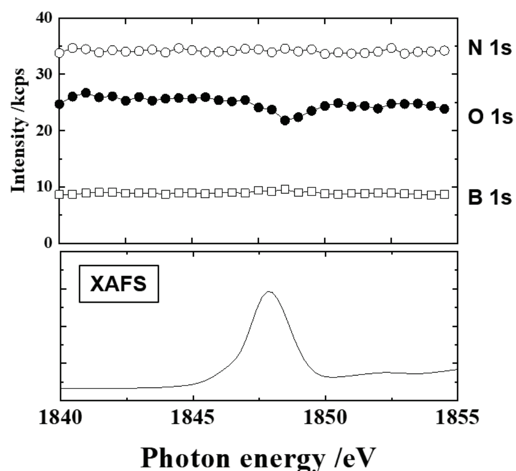

Fig. 3: Intensity of B1*s*, N 1*s* and O 1*s* peaks in XPS spectrum for SiO_2 as a function of photon energy around the Si *K*-edge. XAFS spectrum is also shown in the lower part in the same energy scale.

almost constant regardless of the photon energy. This is simply explained that neither boron nor nitrogen atoms are bonded to silicon because boron nitride was used as a matrix material.

Fig. 4 shows the intensity of N 1*s* and O 1*s* peaks for Si_3N_4 as a function of photon energy. Similar to the SiO_2 result, the intensity of the N 1*s* peak was reduced around the Si 1$s \rightarrow 3p^*$ resonance, which is due to the MAR, because nitrogen is directly bonded to silicon. On the other hand, the intensity of the O 1*s* peak was almost constant regardless of the photon energy. This is also explained that oxygen atoms are not bonded to silicon because O1*s* originates from oxygen in cellulose that was used as a matrix material.

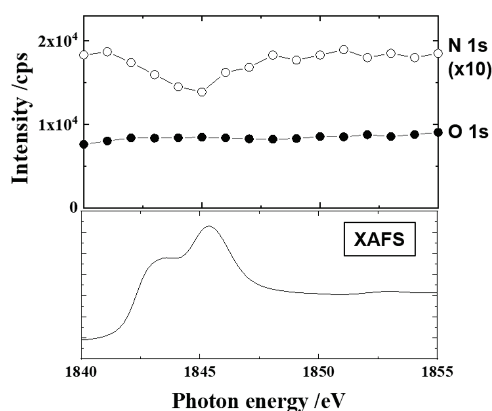

Fig. 4: Intensity of N 1*s* and O 1*s* peaks in XPS spectrum for Si_3N_4 as a function of photon energy around the Si *K*-edge. XAFS spectrum is also shown in the lower part in the same energy scale.

Although the precise mechanism of the observed changes in photoelectron intensity is not clear, we tentatively consider the mechanism as follows. Generally, a photoionization cross section of an atom "A" (σ_A) by X-ray irradiation is independently defined for the atom even for a molecule "A-B". Therefore, the changes in photoelectron intensity of the atom "A" around the resonance at the neighboring atom "B" cannot be interpreted by the extension of the theory on single atom resonance to binary molecule. However, at the energy of the core-to-valence resonance of the atom "B", σ_B drastically increases, which coherently induces the reduction of σ_A. This means that we have to newly consider the photoionization cross section of a molecule σ_{A-B}, at the resonance energy of one of the atoms.

Although further theoretical study is needed to clarify the precise mechanism of the present phenomenon, it was experimentally demonstrated that the intensity of O 1*s* (or N 1*s*) photoelectrons is reduced around the Si 1$s \rightarrow 3p^*$ resonance only when the oxygen (nitrogen) atom is directly bonded to silicon. Considering that the observed intensity changes give information about the atomic species neighboring an atom, the phenomena will be applied to a method for structural analysis of multi-component compounds such as silicon oxynitride (SiO_xN_y).

References

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