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The Difference in Electronic States between the Surface and Bulk of Bi_2Se_3

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Core-level soft and hard X-ray photoemission (SXPES and HAXPES) measurements have been performed on Bi_2Se_3. The result indicated that, although surface region is oxidized, the bulk region detected by hard X-ray photoemission is not oxidized. Comparison of core-level binding energy between SXPES and HAXPES suggested that band bending occurs near the interface between the surface oxidized layer and the pristine Bi_2Se_3.

1. Introduction

In a topological insulator, valence bands and conduction bands are partially exchanged due to extremely strong spin-orbit interaction. Many researches have been performed seeking development of electric power-saving devices that uses the spin properties unique to topological insulators [1].

Bi_2Se_3 is one of the typical topological insulators and its space group is $D_{3d}^5(R\bar{3}m)$ [2]. The purpose of this study is to measure photoemission spectra of Bi_2Se_3 using Al Kα and Cr Kα and analyze the differences in the spectra to discuss the difference in electronic states between the surface and the bulk of the sample.

2. Experimental

Photoemission spectra were measured using two different X-ray sources, i.e., Al Kα (1486.7 eV) and Cr Kα (5414.7 eV) because photoemission using Cr Kα source can probe deeper part of sample than using Al Kα source. Measurements have been performed using scanning soft and hard X-ray photoemission apparatus at SA-1 in SR center of Ritsumeikan University.

The measured sample of Bi_2Se_3 is shown in Fig. 1. It was bought from Kojundo Chemical Laboratory Co., Ltd.. Photoemission spectra of the Bi $5d$ core level and the binding energy range of 153-169 eV including Bi $4f$ and Se $3p$ core levels were measured.

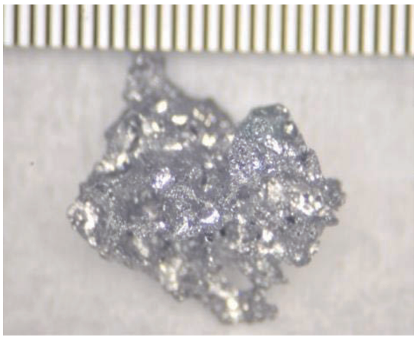

Fig. 1 The photograph of the measured sample.

3. Results and Discussion

The result of O $1s$ spectrum is shown Fig. 2, where the spectra plotted by the black and blue lines were measured by Al and Cr Kα sources, respectively. The spectrum for Cr Kα source was extended 20 times for visibility. Since the O $1s$ intensity is essentially absent in the spectrum measured by the Cr Kα source, we consider that the bulk of the sample is not oxidized.

The result of Bi $5d$ spectrum is shown Fig. 3. The vertical scale is adjusted by the peak height of Bi $5d_{5/2}$. In the spectrum measured by the Al Kα source, shoulders due to oxidized Bi is found besides the Bi $5d$ peaks due to Bi_2Se_3. It is considered that the sample is only oxidized in the outermost surface but is not oxidized in bulk.

Moreover, the peak location in spectrum measured by Al Kα is different from that for Cr Kα. In order to compare spectral shapes for Al Kα and Cr Kα, which have different full width at half maximum (FWHM), the spectrum measured by Al Kα was convolved by a Gaussian function with FWHM of 0.54 eV. The spectrum measured by Al Kα is further shifted -0.18 eV in Fig. 4.

Figure 4 suggests that the shape of the main peak shape is essentially same between two X-ray sources although binding energy is different by 0.18 eV.

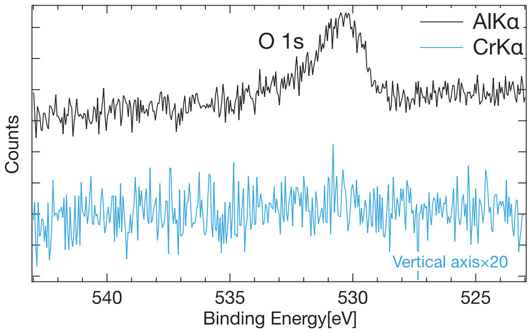

Fig. 2 The photoemission spectrum in the O $1s$ region. The spectrum for Cr Kα source was extended 20 times for visibility.

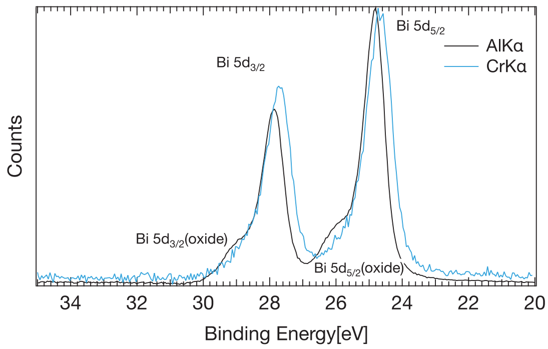

Fig. 3 The Bi 5***d*** photoemission spectrum of Bi_2Se_3 measured by Al Kα and Cr Kα sources.

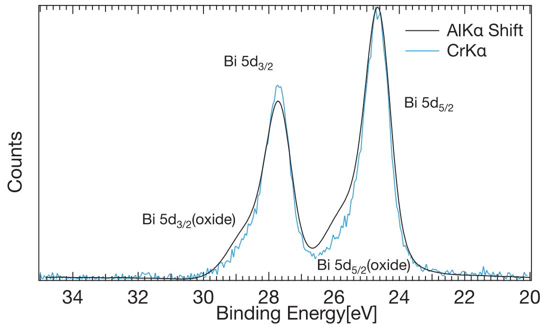

Fig. 4 The Bi 5***d*** photoemission spectrum of Bi_2Se_3, where the spectrum measured by Al Kα was convolved by a Gaussian function with FWHM of 0.54 eV and shifted by − 0.17 eV.

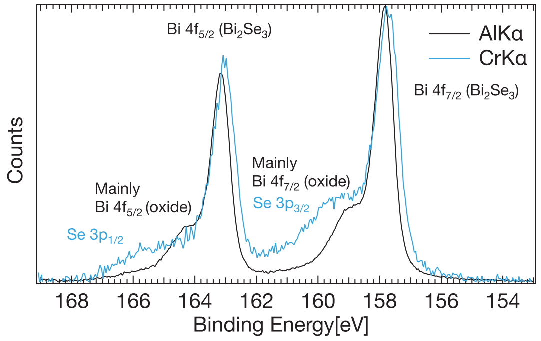

Fig. 5 The photoemission spectrum in the binding energy of 153 eV – 169 eV for Bi_2Se_3, including Bi 4*f* and Se 3*p* core levels.

Table 1 The binding energy of simple substance.

Electron Orbital	Binding Energy [eV]
Bi $4f_{7/2}$	157
Se $3p_{3/2}$	163
Bi $4f_{5/2}$	162
Se $3p_{1/2}$	169

Table 2 Sub shell photoionization cross section in kb **(10^{-21} cm^2)**.

Electron Orbital	1500 eV	5000 eV
Se $3p_{1/2}$	0.11561+2	0.8533+0
Se $3p_{3/2}$	0.3018+2	0.1574+1
Bi $4f_{5/2}$	0.9664+2	0.2030+1
Bi $4f_{7/2}$	0.1238+3	0.2516+1

The photoemission spectra in the binding energy range of 153 eV – 169 eV are shown Fig. 5. The vertical scales for Al Kα and Cr Kα are adjusted by the peak height of the rightmost peak.

We consider that there are peak of Bi $4f_{7/2}$ from Bi_2Se_3, Bi $4f_{7/2}$ from oxide, Se $3p_{3/2}$, Bi $4f_{5/2}$ from Bi_2Se_3, Bi $4f_{5/2}$ from oxide, and Se $3p_{1/2}$ in this binding energy range. The binding energies for elemental materials are shown Table 1.

Mainly four structures can be identified in each spectrum shown in Fig. 5. Two main peaks correspond to Bi 4*f* peaks for Bi_2Se_3. Although identification of other peaks is not necessarily straightforward, we tentatively assign the sub-peaks found in Al (Cr) Kα are Bi 4*f* from oxide (Se 3*p* from Bi_2Se_3) as discussed below.

Photoemission intensity can be accounted for by photoionization cross section. Table 2 shows photoionization cross section for photon energies 1500 eV and 5000 eV [3][4]. According to the cross sections, Bi $4f_{5/2}$ intensity ratio between the spin-orbit split Bi 4*f* subshells is

$$\frac{\mathrm{Bi}\ 4f_{\frac{5}{2}}}{\mathrm{Bi}\ 4f_{\frac{7}{2}}} = \frac{96.64}{123.8} = 0.76 \tag{1}$$

(1) in 1500 eV, and is

$$\frac{\mathrm{Bi}\ 4f_{\frac{5}{2}}}{\mathrm{Bi}\ 4f_{\frac{7}{2}}} = \frac{2.030}{2.516} = 0.81 \tag{2}$$

in 5000 eV.

In these values, the spectrum measured by Al Kα Bi $4f_{5/2}$ intensity is

$$\frac{1500\ \mathrm{eV}}{5000\ \mathrm{eV}} = \frac{0.7606}{0.8068} = 0.97 \tag{3}$$

times in comparison with the spectrum measured by Cr Kα, and it is consistent with results.

Next, the Se $3p_{3/2}$ intensity relative to Bi $4f_{7/2}$ is

$$\frac{\mathrm{Se}\ 3p_{\frac{3}{2}}}{\mathrm{Bi}\ 4f_{\frac{7}{2}}} = \frac{30.18}{123.8} = 0.24 \tag{4}$$

in 1500 eV, and is

$$\frac{\mathrm{Se}\ 3p_{\frac{3}{2}}}{\mathrm{Bi}\ 4f_{\frac{7}{2}}} = \frac{1.574}{2.516} = 0.63 \tag{5}$$

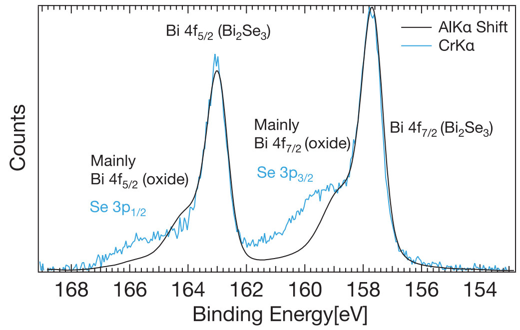

Fig. 6 The photoemission spectra of Bi_2Se_3 in the Bi 4*f* and Se 3*p* region, where the spectrum measured by Al K$\boldsymbol{\alpha}$ was convolved by a Gaussian function with FWHM of 0.47 eV and shifted by -0.17 eV.

in 5000 eV. The ratio for Al Kα is

$$\frac{0.2438}{0.6256} = 0.39 \tag{6}$$

time of that for Cr Kα. In addition, oxide peaks tend to appear in spectrum measured by Al Kα according to Fig. 2 and Fig. 3. Therefore, it is considered that sub-peak in about 160 eV is mainly Bi oxide in the spectrum measured by Al Kα but Se $3p_{3/2}$ in the spectrum measured by Cr Kα as indicated in Fig. 5. Further studies are needed as for the smallness of Se $3p$ intensity for Al Kα.

Besides, as in the case of the Bi $5d$ level, the peak position in spectrum measured by Al Kα is different from Cr Kα. By convolving the spectrum measured by Al Kα using a Gaussian function with FWHM of 0.47 eV and shifting by -0.17 eV in Fig. 6 the lineshapes of the main peaks coincide with that for Cr Kα.

The results for Bi 5*d* and 4*f* levels indicate that all core levels are shifted by about -0.17 eV in the surface region of the present sample. This suggests that band bending of about 0.17 eV occurs near the interface between the surface oxidized layer and the pristine Bi_2Se_3. For quantitative analysis, such detailed discussion as done in ref. [5] is needed.

4. Conclusions

To summarize, photoemission spectra of Bi_2Se_3 were measured using Al Kα and Cr Kα sources to investigate its electronic state. The peak intensity dependence on incident photon energy was discussed by calculating the photoionization cross section. Furthermore, it has been shown that the surface binding energy of Bi_2Se_3 is about 0.17 eV larger than the bulk binding energy, suggesting that band bending occurs near the interface between the surface oxidized layer and the pristine Bi_2Se_3.

Acknowledgement

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