Core-Level and Valence Band Photoemission of Pure Bismuth

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Results of soft and hard X-ray photoemission (SXPES and HAXPES) of pure bismuth is presented. In the core level spectra, intrinsic plasmon loss satellites are observed, where the plasmon energy is found to be 15 eV. In the valence band photoemission, characteristic difference is found between SXPES and HAXPES, which suggests that 6s, $6p_{1/2}$, and $6p_{3/2}$ bands are located at binding energy regions of 7.5-14, 2.5-6, and 0-2.5 eV.

1. Introduction

Bismuth shows various interesting phenomena such as the Seebeck, Nernst [1], Shubnikov–de Haas, and de Haas–van Alphen (dHvA) effects [2], and has been studied for a long time because of its anomalous electronic properties. Recently, its Rashba effect on surface state and/or topological behavior in bismuth compounds are focused on. Understanding of the electronic structure is important in order to reveal the origin of these phenomena. We planned soft and hard x-ray photoemission measurement (SXPES and HAXPES) with the cleaved single-crystalline bismuth, since the difference between SXPES and HAXPES spectra reflect the detailed surface and bulk electronic structure, because of the electronic mean-free path and photoionization cross-section.

2. Experimental

Polycrystalline bismuth was melted and cooled in Ar atmosphere to obtain a single-crystalline sample. The sample was cleaved in the preparation chamber and photoemission spectra have been measured at SA-1 of Ritsumeikan SR Center using a scanning soft and hard X-ray photoemission spectroscopy apparatus (ULVAC-PHI Quantes). Both soft X-ray photoemission measurements by Al K α emission (1486.6 eV) and hard X-ray photoemission by Cr K α emission (5414.7 eV) have been performed.

3. **Results and Discussion**

Figure 1 shows the Bi 4d core-level photoemission spectra measured by SXPES and HAXPES. The Bi $4d_{5/2}$ and $4d_{3/2}$ peaks are located at binding energy of ~440 eV and ~464 eV, respectively. The plasmon satellite peaks due to the inelastic energy-loss are seen as shoulder structures at binding energy of ~455 eV and ~479 eV, which indicate that the intrinsic plasmon energy is 15 eV.

Figure 2 shows the Bi 5d core-level photoemission spectra measured by SXPES and HAXPES. There are spin-orbit-split two sharp peaks (Bi $5d_{5/2}$ at ~ 24 eV and $5d_{3/2}$ at ~ 27 eV), and broad plasmon satellites due to the inelastic energy-loss from both Bi $5d_{5/2}$ and $5d_{3/2}$ are seen around 35-46 eV.



Fig. 1 Bi 4d core-level photoemission spectra of pure bismuth measured by SXPES and HAXPES.



Fig. 2 Bi 5d core-level photoemission spectra of pure bismuth measured by SXPES and HAXPES.



Fig. 3 Valence band photoemission spectra of pure bismuth measured by SXPES and HAXPES.

Figure 3 shows the valence band photoemission spectra of pure bismuth measured by SXPES and HAXPES. There are characteristic differences in the peak structures between SXPES and HAXPES. Especially, the peak around binding energy region 0-2.5 eV is higher than the peak around binding energy region 2.5-6 eV for SXPES, on the other hand, the former is almost same height as the latter for HAXPES. It is known that cross section of 6s state is relatively larger in HAXPES than in SXPES [3]. Furthermore, among 6p_{1/2} and 6p_{3/2} states, the cross section of the former is relatively larger in HAXPES Therefore, the peak intensity ratio between [3]. SXPES and HAXPES indicates that Bi 6s, 6p_{1/2}, 6p_{3/2} bands are located around binding energy region of 7.5-14 eV, 2.5-6 eV, and 0-2.5 eV. In order to discuss the valence band structure, it is necessary to compare with detailed full-relativistic band calculation.

Since the differences in core-level and valence band photoemission spectra between SXPES and HAXPES were well explained by photoionization cross-section, difference between surface and bulk electronic structure for pure bismuth was small in the present results.

4. Conclusions

The photoemission experiments show that the plasmon loss satellites were observed in Bi 4d and 5d core-level photoemission spectra, the plasmon energy of which was found to be 15 eV. The characteristic difference between SXPES and HAXPES in valence band photoemission spectra was explained by photoionization cross-section, and the difference suggests that Bi 6s, $6p_{1/2}$, and $6p_{3/2}$ bands are located around binding energy regions of 7.5-14, 2.5-6, and 0-2.5 eV.

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