Valence-Band Atomic-Orbital Analysis of ZrB_2 by Two-Dimensional Photoelectron Spectroscopy

Rie Horie[1)], Fumihiko Matsui[1)], Masaru Takizawa[2)], Takashi Aizawa[3)], Shigeki Otani[3)], Hidetoshi Namba[2)], and Hiroshi Daimon[1)]

1) Graduate School of Materials Science, Nara Institute of Science and Technology, Ikoma, Nara 630-0192, Japan.

2) Department of Physical Sciences, Faculty of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan.

3) National Institute for Materials Science, Namiki, Tsukuba, Ibaraki 305-0044, Japan

1. Introduction

Zirconium diboride (ZrB_2) is an attractive material for wide applications. It has a high melting point, high electric conductivity, and high corrosion resistance. ZrB_2(0001) surface is a promising substrate for the GaN(0001) epitaxial thin film growth too. Moreover, MgB_2 is a novel superconductor at exceptionally high critical temperature (39 K) [1], which has the same crystal structure as ZrB_2, but ZrB_2 has no superconductivity at such a high temperature. Therefore, to investigate the difference of the electronic structure between ZrB_2 and MgB_2 is very important to understand the property of superconductors. Therefore, the understanding of the surface electronic structure of ZrB_2 is significant for both basic science and application. Although it has been studied by angle-resolved ultraviolet photoelectron spectroscopy [2], the orbital character of the energy band has not been studied. In this study, we have measured two-dimensional photoelectron intensity angular distributions (PIADs) by using a horizontally linearly-polarized synchrotron radiation (SR) and a display-type spherical mirror analyzer (DIANA) [3]. The purpose of this research is to analyze the atomic orbitals constituting each band from these PIADs which show specific symmetry originating from transition matrix.

2. Experiment

The experiment was performed at BL-7 of SR center, Ritsumeikan University [4]. The sample was heated up to 1000℃ at first for degassing in the preparation chamber. After recovery of the vacuum, the sample was flash-annealed at 1500℃ for a few seconds several times. The surface quality was checked by low energy electron diffraction and Auger electron spectroscopy. The two-dimensional photoelectron spectroscopy (2D-PES) measurements were performed at room temperature under the ultrahigh vacuum of ~1×10^{-8} Pa by using DIANA.

The photon energy of SR was 40 eV. The total energy resolution was about 400 meV and the angular resolution was about 1°.

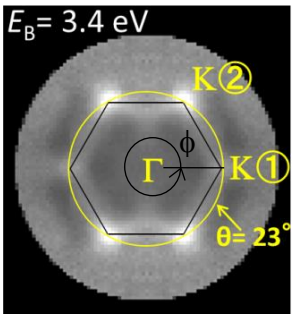

Fig. 1 PIADs of ZrB_2(0001) valence band at E_B = 3.4 eV. The arrow shows angle ϕ in Fig.2.

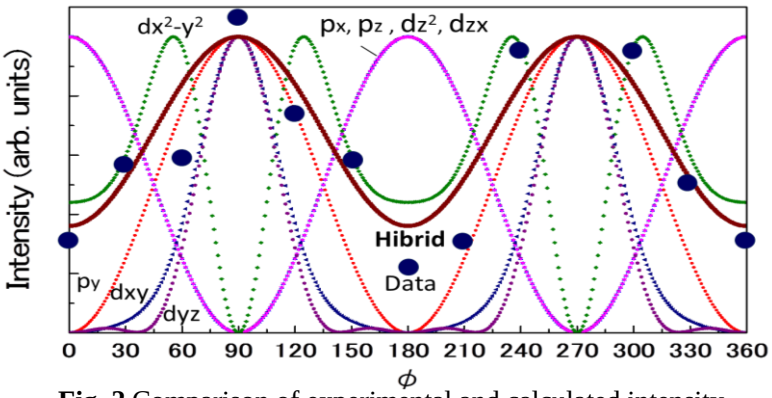

Fig. 2 Comparison of experimental and calculated intensity angular-distribution at θ = 23°.

3. Results and discussion

Figure 1 shows a PIAD pattern of ZrB_2(0001) valence band at the binding energy E_B of 3.4 eV excited by a horizontally lineary-polarized light. The original pattern was averaged by horizontal and vertical mirror symmetry operation considering the symmetry of the crystal and the excitation light. The hexagon in Fig. 1 indicates the first Brillouin zone (BZ) of ZrB_2. We can see the transition matrix element effect in this 2D-PIAD pattern. That is, the intensity of photoelectron at K② is stronger than that at K①. This difference is the transition-matrix-element effect when the atomic orbitals consisting of each band are excited by a linearly-polarized light. Thus, we have obtained the useful data to analyze the atomic orbital. We calculated ZrB_2 band structure with a first-principles calculation software, WIEN2k. From this calculation, we obtained the ratio of atomic orbitals which compose the K-points. This calculation result suggests that the electronic state at K-point at the binding energy of about 3.4 eV is a hybrid orbital consisting of p_z orbital of B, d_{yz} and d_{zx} orbitals of Zr. The circles, solid and dashed lines in Fig. 2 show the angular distribution of experimental data, the calculated intensity of the hybrid orbital and atomic orbitals, respectively. Experimental data are approximately reproduced by the calculation for the hyblid orbital as shown in Fig. 2. We concluded that the band at the K point at the binding energy of 3.4 eV consists of p_z, d_{yz}, and d_{zx} orbitals.

4. Conclusions

We have measured two-dimensional PIADs from ZrB_2(0001) by using a horizontally linearly-polarized synchrotron radiation and DIANA. Comparing the experimental data to the calculation result, we concluded that the band at the K point at the binding energy of 3.4 eV consists of p_z, d_{yz}, and d_{zx} orbitals.

References

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