Electronic State Analysis of ZrB_2, NbB_2(0001) Surface Termination by Two-Dimensional Photoelectron Spectroscopy

Rie Horie[1)], Fumihiko Matsui[1)], 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) and Niobium diboride (NbB_2) are attractive materials for many applications. They have high melting points over 3000°C, high electric conductivities, and high corrosion resistance. Interestingly, ZrB_2 and NbB_2 have the same crystal structure as MgB_2, which is an AlB_2-type, where honeycomb boron (boraphene) sheets and close-packed metal layers are stacked alternately. However, the clean surface of ZrB_2(0001) terminates with a Zr layer, whereas the clean NbB_2(0001) surface terminates with a B layer [1]. The electronic structures of ZrB_2(0001) and NbB_2(0001) have been studied experimentally by ARUPS (angle-resolved ultraviolet photoelectron spectroscopy) [2] and theoretically [3]; however, the detailed electronic structures of these diborides have not been clarified yet. The band structures of ZrB_2 and NbB_2 are almost the same, but we can see a difference at Γ-point between them as indicated by a red circle in **Fig. 1**. In this study, we focused on this difference at Γ-point and investigated both electronic states including surface states in view of atomic orbitals constituting the electronic states by using two-dimensional photoelectron spectroscopy (2D-PES). We obtained some knowledge about the origin of this interesting difference of termination between ZrB_2(0001) and NbB_2(0001).

2. Experiment

The experiment was performed at BL-7 of the SR center at Ritsumeikan University [4]. A NbB_2(0001) sample was heated up to 1000 °C at first for degassing in the preparation chamber. After recovery of the vacuum, the sample was heated up to 1000 °C for 3 to 8 min several times under the O_2 gas pressure of $\sim 5 \times 10^{-4}$ Pa. After the sample was flash-annealed at 1500 °C for a few seconds several times, the surface quality was checked by low energy electron diffraction (LEED) and Auger electron spectroscopy. 2D-PES measurements of these

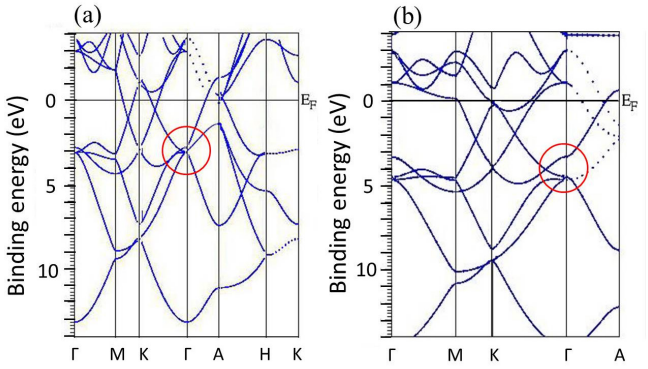

Fig. 1 Band structures of (a) ZrB_2 and (b) NbB_2 calculated by WIEN2k.

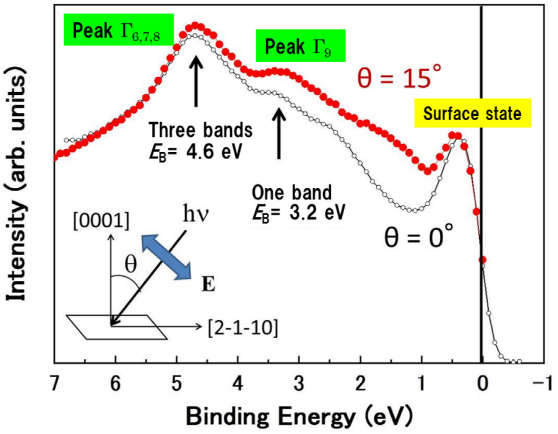

Fig. 2 Polarization dependence of angle-resolved photoelectron spectra around the $\bar{\Gamma}$-point in $NbB_2(0001)$.

samples were performed at room temperature under an ultrahigh vacuum of $\sim 1 \times 10^{-8}$ Pa by using a display-type spherical mirror analyzer (DIANA) [5]. The excitation light was a horizontally linearly-polarized synchrotron radiation (SR), and the photon energy was 40 eV. The total energy resolution was about 400 meV and the angular resolution was about 1°. The work function of DIANA was 4.2 eV.

3. Results and discussion

In **Fig.1**, the band structures of (a) ZrB_2 and (b) NbB_2 calculated by WIEN2k are shown. The band dispersions NbB_2 (b) are almost the same when the binding energies of those of ZrB_2 (a) are shifted downward by 1.5 eV. However there is a difference at the Γ point indicated by red circles, that is ZrB_2 has four degenerated bands at the circle whereas NbB_2 has three degenerated bands and one separated band there. We measured two-dimensional photoelectron intensity angular distribution (PIAD) patterns with different incident angles to analyze atomic orbitals. We extracted the photoelectron intensities around $\bar{\Gamma}$-point from the PIADs measured at polar angles θ = 0° and 15°, and made the polarization dependent angle-resolved photoelectron spectra as seen in **Fig. 2**. We can see a surface state near the Fermi level and two peaks at the binding energies of E_B = 4.6 eV and 3.2 eV. The observed peaks at E_B = 4.6 eV and 3.2 eV correspond to the band structure of NbB_2 in **Fig. 1(b)** at E_B= 4.6 eV (we call this peak as $\Gamma_{6,7,8}$) and 3.2 eV (we call this peak as Γ_9). The peak Γ_9 is stronger in the spectra of θ = 15° than that of θ = 0°. This means that the possible atomic orbital constituting this band is p_z orbital. Hence this band is a bonding band between B layer and metal (Nb) layer [6]. We confirmed experimentally and theoretically that this inter-layer bonds became weaker in NbB_2 than in ZrB_2 because the energy of this band has higher energy than other three-degenerated bands as shown in **Fig. 1(b).**

Figures **3**(a) and (b) show the density-of-states (DOS) of ZrB_2 and NbB_2 [3]. Red rectangles show the DOS of Zr and Nb 4d orbitals, where the DOS of NbB_2 is 1.5 eV lower than that of ZrB_2 as seen in **Fig. 1**. Notice that Nb has one more 4d electron than Zr. The DOS of this electron appears near Fermi level of NbB_2 as shown by a blue rectangle in **Fig. 3**(b). Then the center of gravity of Nb 4d DOS shifts upward a little as shown by a blue arrow in **Fig. 3**(b). This indicates that the B layer is more stable than the metal layer in NbB_2. As discussed above, the metal and B layers are more independent in NbB_2 than those in ZrB_2. In summary the energy of the B layer is deeper than the metal layer in both NbB_2 and ZrB_2, but it is further deeper in NbB_2 than in ZrB_2, which can explain the reason why the B layer terminates on NbB_2(0001) instead of the metal layer.

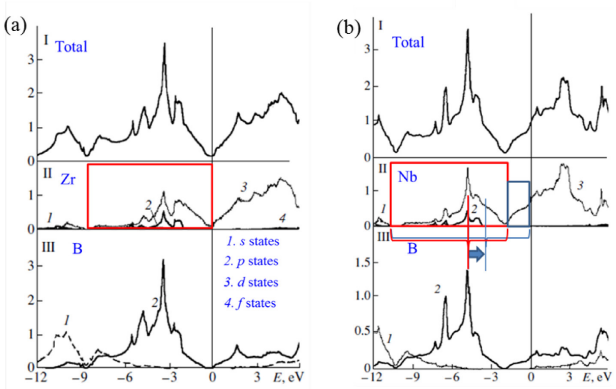

Fig. 3 (I) Total and (II, III) local densities of valence (1) s states, (2) p states, (3) d states, and (4) f states of (II) metal and (III) boron sublattices of (a) ZrB_2 and (b) NbB_2 [3].

4. Conclusion

To obtain a knowledge about the origin of the difference in the surface termination between ZrB_2 and NbB_2 (0001) clean surface in terms of the electronic structure, we measured two-dimensional photoelectron intensity angular distribution (PIAD) patterns by using a display-type spherical mirror analyzer (DIANA) at BL-7 of SR center, Ritsumeikan University. We measured the polarization dependence of the angle-resolved photoelectron spectra of NbB_2 at $\bar{\Gamma}$ point at the binding energies around 4 eV. We found that the bonding between the B layer and the metal layer is weaker in NbB_2 than in ZrB_2, which means the independency of each layer in NbB_2. We concluded that the energy of B layer is deeper than the metal layer in both NbB_2 and ZrB_2, but it is further deeper in NbB_2 than ZrB_2, which can be the reason why the B layer terminates on NbB_2(0001).

References

[1] T. Aizawa, W. Hayami, and S. Otani, *Phys. Rev.* B **65**, 024303 (2001). [2] S. Kumashiro, H. Tanaka, Y. Kawamata, H. Yanagisawa, K. Momose, G. Nakamura, and C. Oshima, and S. Otani, *e-J. Surf. Sci. Nanotech*. Vol. **4**, 100 (2006). [3] I.R. Shein and A.L. Ivanovskii, *Physics of the Solid State* **44**, 1833 (2002). [4] Y. Hamada, F. Matsui, Y. Nozawa, K. Nakanishi, M. Nanpei, K. Ogawa, S. Shigenai, N. Takahashi, H. Daimon and H. Namba, *AIP Conf. Proc.* **879**, 547 (2007). [5] H. Daimon, *Rev. Sci. Instrum*. **59**, 545 (1988). [6] H. Daimon, S. Imada, H. Nishimoto, and S. Suga, *J. Electron Spectrosc. Relat. Phenom*. **76**, (1995) 487.