Electronic States of NbB₂(0001), TaB₂(0001) and ZrB₂(0001) Surfaces Studied by Angle-resolved Ultraviolet Photoelectron Spectroscopy*

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(Received 4 November 2005; Accepted 14 December 2005; Published 19 January 2006)

We have investigated the surface electronic structures of transition-metal diboride (0001) surfaces by angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) and ab-initio calculations based on the slab model with 13 layers. In the spectra of NbB₂ and TaB₂, the peaks near -1 eV below E_F are derived from the π band of their surface graphitic boron layer. As compared with graphene, the dispersion curves of the π bands are greatly modulated by the hybridization of B- π orbits with the metal d orbits. On the other hand, the similar peaks were not observed in spectra of ZrB₂, of which the surface is terminated with Zr atoms. [DOI: 10.1380/ejssnt.2006.100]

Keywords: transition-metal diboride; angle-resolved ultraviolet photoelectron spectroscopy; ab-initio calculations; electronic structure

I. INTRODUCTION

A transition metal diboride (MB₂) has unique features: high hardness, high melting point, and metallic conductivity. It has been used as a thin film resistor, a diffusion barrier layer in micro devices, hard coating, and so on. It is also expected to be used for a cold electron emitter, a catalyst, or a substrate for growth of epitaxial GaN films [1, 2]. The materials of MB₂ compose an AlB₂-type crystal structure as shown in Fig. 1, which consists of alternate stacking of a graphitic B layer and a close-packed metal layer. According to previous works, there are strong covalent bonds between B atoms in the B layer, and metallic bonds exist between metal atoms. In addition, there are not only ionic but also covalent bonds between metal and B [3].

The surface properties have been widely investigated experimentally and theoretically [4–7]. The surfaces of ZrB₂(0001) and HfB₂(0001) are terminated with the metal layer [8, 9], and the surfaces of NbB₂(0001) and TaB₂(0001) are terminated with the B layer [8, 10]. Why are the surface structures different between M_{IV}B₂ and M_VB₂? Here, M_{IV} and M_V mean the metal atoms of group IV and group V in the periodic table, respectively. In previous work, Yamamoto *et al.* indicated theoretically that the surface termination is closely related to the amount of valence electrons of the metal atom [4]. While the electronic structure of TaB₂(0001) surface has been

investigated by Kawanowa *et al.* [5], however, the surface electronic structures of M_{IV}B₂(0001) have not been investigated. No discussion based on the experimental data was reported for the electronic origin of the different termination. In this work, therefore, the ARUPS results of NbB₂(0001), TaB₂(0001), and ZrB₂(0001) are presented and differences in the band structure between M_{IV}B₂(0001) and M_VB₂(0001) surfaces are reported.

II. EXPERIMENTAL SETUP AND THEORETICAL CALCULATIONS

The experiments were carried out in an ultrahigh vacuum chamber equipped with optics of low-energy electron diffraction (LEED), an ultraviolet discharge lamp, an X-ray source and a hemispherical energy analyzer on a rotatory table for angle-resolved photoemission. The

FIG. 1: The crystal and surface structures of (a) NbB₂(0001), TaB₂(0001) and (b) ZrB₂(0001), which are oblique views. Red circles represent metal atoms and blue circles represent B atoms.

*This paper was presented at International Symposium on Surface Science and Nanotechnology (ISSS-4), Saitama, Japan, 14-17 November, 2005.

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FIG. 2: ARUPS spectra measured along (a) the $[11\bar{2}0]$ and (b) the $[10\bar{1}0]$ azimuth of the $\text{NbB}_2(0001)$ surface terminated with a graphitic B layer.

FIG. 3: The electronic dispersion curves of $\text{NbB}_2(0001)$ surface terminated with a graphitic B layer. Red circles represent experimental data points. Black circles represent the calculations for NbB_2 bulk crystal and blue circles represent calculations for NbB_2 slab with 13 layers.

unpolarized HeI ($h\nu = 21.2$ eV) resonance line was used for angle-resolved ultraviolet photoelectron spectroscopy (ARUPS). Single crystal rods of NbB_2 , TaB_2 and ZrB_2

FIG. 4: The theoretical electronic dispersion curves of a graphene. Red solid lines represent π branches, and black solid lines represent σ branches.

were grown by a floating-zone technique [11]. The specimen of 1mm thickness was cut from the rod after the Laue alignment within the accuracy of 0.5° from the $[0001]$ direction. The specimen surface was mechanically polished with diamond paste to a mirror finish. The specimen

FIG. 5: ARUPS spectra measured along (a) the $[11\bar{2}0]$ and (b) the $[10\bar{1}0]$ azimuth of the $\text{TaB}_2(0001)$ surface terminated with a graphitic B layer.

FIG. 6: The electronic dispersion curves of $\text{TaB}_2(0001)$ surface terminated with a graphitic B layer. Red circles represent experimental data points. Black circles represent calculations for TaB_2 bulk crystal and blue circles represent calculations for TaB_2 slab with 13 layers.

was heated by electron back bombardment. The polished $\text{NbB}_2(0001)$ surface was first annealed up to 1100 K in

1.3×10^{-5} Pa of oxygen ambient for 5 hours to remove the carbon contamination. After that, it was heated up to 1500 K to remove the oxygen contamination. The polished $\text{TaB}_2(0001)$ surface was heated up to 1900 K several times to obtain a clean surface. In the case of ZrB_2 , the surface was heated up to 1800 K several times to obtain a clean surface.

In this work, we have also calculated dispersion curves of their electronic energy bands based on their slab model with 13 layers. This calculation is based on ab-initio (DACAPO package) with in the framework of the density functional theory (DFT) [12].

III. RESULTS AND DISCUSSION

Figure 2 shows ARUPS spectra of $\text{NbB}_2(0001)$ excited by a HeI resonance line along the $\bar{\Gamma}-\bar{K}$ and the $\bar{\Gamma}-\bar{M}$ directions of two-dimensional Brillouin zone. The horizontal axes express the binding energy (E_B), which is referred from Fermi energy (E_F). The emission angle, θ , referred to the surface normal is denoted for each spectrum. There appear well-developed four peaks at 1, 2.5, 4, and 7 eV in the normal emission spectrum. The intensities of the peaks at the Fermi edge decrease as the emission angle increases, so that the branch disperses toward the empty state. Two weak peaks at 2.5 eV and 4 eV show no dispersion in both directions of the $\bar{\Gamma}-\bar{K}$ and the $\bar{\Gamma}-\bar{M}$ symmetry axes. The peaks around 7 eV show no dispersion at low emission angles, and disperse toward 10 eV at high emission angles.

In Fig. 3, we plotted the binding energies of the observed peaks of $\text{NbB}_2(0001)$ versus the wave vector parallel to the surface ($k_{||}$) obtained by the following formula:

FIG. 7: ARUPS spectra measured along (a) the $[11\bar{2}0]$ and (b) the $[10\bar{1}0]$ azimuth of the $\text{ZrB}_2(0001)$ surface terminated with a Zr layer.

$k_{||} = [2m(h\nu - \phi - E_B)/\hbar^2]^{1/2} \sin \theta$ where m is the rest mass of an electron, $h\nu$ is the photon energy for excitation, and ϕ is the work function. In addition, we depicted theoretical dispersion curves of $\text{NbB}_2(0001)$ calculated on the basis of the slab model in Fig. 3. Most of the experimental data points agreed with the theoretical curves. The exception is the branch at 2.5 eV, which was not reproduced. The branch at 1 eV is derived from the graphitic surface B layer for the following reason. It was observed in the spectra of $\text{NbB}_2(0001)$ and $\text{TaB}_2(0001)$, but not in those of $\text{ZrB}_2(0001)$ as discussed later. It was well known that the topmost layers of NbB_2 and TaB_2 are the graphitic B layer and ZrB_2 is terminated with Zr atom layer. In addition, it agreed with the surface states of π bond of the graphitic surface B layer in the theoretical curves, which are labeled by S in Fig. 3. As compared with the dispersion curves of a graphene in Fig. 4, the dispersion curve of the π bond is greatly changed. A parabolic dispersion curve with large dispersion exists in graphene, but an unparabolic dispersion curve with small dispersion exists in the graphitic surface B layer. This relates with the fact that the in-plane overlapping of the wave function of B- p_z is weaker than that of graphene, which originates from the difference of atomic distance. The nearest neighbor atomic distance is 1.79 Å in B layer, and that is 1.42 Å in a graphene. The branches below 5 eV are assignable to the bonds of the bulk and surface B layers. The dispersion curves of B- σ bonds are also different from that of a graphene. In a graphene, two up convex dispersion curves of the σ bonds exist as shown in Fig. 4, but in the B layers, one of the dispersion curves of the B- σ bonds

corresponding to that of a graphene is a down convex curve and the other is an up convex curve. Therefore, the electronic structure of the graphitic surface B layer cannot be interpreted by a rigid band model based on a graphene because of the strong interaction between the graphitic surface B layer and the second Nb layer. The reason why the branch around 2.5 eV was not reproduced theoretically is presumably due to the inhomogeneous mixture of the surface phase. In previous experiments, the intensive peaks at 2.5 eV were often observed on the surface exhibiting a $\sqrt{7} \times \sqrt{7}$ LEED pattern. Hence, the area of the $\sqrt{7} \times \sqrt{7}$ structure presumably remains partially on the surface.

Figure 5 shows the spectra of $\text{TaB}_2(0001)$ excited by a HeI resonance line along the $\bar{\Gamma}-\bar{K}$ and the $\bar{\Gamma}-\bar{M}$ axes of two-dimensional Brillouin zone. The emission angle referred to the surface normal is denoted for each spectrum. The observed spectra are similar to those of NbB_2 except a few peaks; one can clearly observe the peaks around 4 eV in the spectra of $\theta = 0 - 10^\circ$ of NbB_2 , but not in those of TaB_2 . The present result on $\text{TaB}_2(0001)$ agreed well with the previous report by Kawanowa *et al.* [5] Figure 6 shows the experimental and theoretical dispersion curves of $\text{TaB}_2(0001)$. The result of $\text{TaB}_2(0001)$ is similar to that of $\text{NbB}_2(0001)$, except for the branch around 2.5 eV. The surface state of $\text{TaB}_2(0001)$ shows almost the same feature as that of $\text{NbB}_2(0001)$.

Figure 7 shows the spectra of $\text{ZrB}_2(0001)$ excited by a HeI resonance line along the $\bar{\Gamma}-\bar{K}$ and the $\bar{\Gamma}-\bar{M}$ axes of two-dimensional Brillouin zone. The emission angle referred to the surface normal is denoted for each spectrum.

FIG. 8: The electronic dispersion curves of $\text{ZrB}_2(0001)$ surface terminated with Zr layer. Red circles represent experimental data points. Black circles represent calculation ones for ZrB_2 bulk crystal and blue circles represent calculations for ZrB_2 slab with 13 layers.

There appear well-developed three peaks at 0.5, 3, and 7 eV in the normal emission spectrum. The intensive peak at 0.5 eV in the normal emission spectrum disappears as the emission angle increases, so that the branch would disperse toward the empty state. The peak around 3 eV shows the dispersion to the high binding energy and weakens in the intensity as the emission angle increases. After this peak disappears once at 24° , it appears again and dis-

perses to the lower binding energy. The peak around 7 eV disperses slightly to the lower binding energy from 0° to 24° . At emission angles 24° or more, this peak disperses to the higher binding energy.

Figure 8 shows the experimental and theoretical dispersion curves of $\text{ZrB}_2(0001)$. The experimental plots agreed well with the theoretical curves based on the Zr terminated slab model. The observed peaks around E_F agreed with the surface states in the theoretical ones labeled by S in Fig. 8. This surface state is derived from the surface Zr atom. On the other hand, no surface state originating from surface B layer was found in both the experimental and theoretical curves. The dispersion curves of the B- σ bonds, which are designated by arrows, are similar to those of M_VB_2 . However, the binding energy of the B- σ bonds of ZrB_2 is about 1 eV lower than that of M_VB_2 . The feature relates to the valence number of the metal atom; the number of valence electrons of Zr is four, and that of Nb and Ta is five. Even if $\text{ZrB}_2(0001)$ is terminated with B layer, the surface state of the B- π band cannot be filled, because it lies around 1 eV below E_F in the dispersion curves of NbB_2 and TaB_2 . Therefore, one can say that the surface termination is determined by the occupation of the B- π bonding state.

IV. CONCLUSIONS

We have investigated the surface electronic structures of $\text{NbB}_2(0001)$, $\text{TaB}_2(0001)$ and $\text{ZrB}_2(0001)$. In the spectra of $\text{NbB}_2(0001)$ and $\text{TaB}_2(0001)$, we found the surface states of the B- π bonds in surface B layer around the E_F , but not in that of $\text{ZrB}_2(0001)$. The binding energies of the B- σ bonds of $\text{ZrB}_2(0001)$ is about 1 eV lower than those of $\text{NbB}_2(0001)$ and $\text{TaB}_2(0001)$, which are related with the difference of the E_F level. The surface electronic structures of $\text{MB}_2(0001)$ observed in this work were consistent with the surface structures determined experimentally, and the theoretical results by Yamamoto *et al.* [4].

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