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Unoccupied surface states of $LaB_6(001)$ studied by *k*-resolved inverse photoemission

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We have measured *k*-resolved inverse photoemission spectra of $LaB_6(001)$ to study unoccupied surface states. The surface states are observed near the Fermi level (E_F) and at 6.8 eV above E_F, which are originated from La 5*d* and La 4*f* states, respectively. The surface state near E_F shows energy dispersion along the Γ–M direction of the surface Brillouin zone, which does not agree with that of a recently reported theoretical calculation. It is deduced that at a $LaB_6(001)$ surface, electrons are transferred from the subsurface to the topmost La layer. This charge redistribution can reduce surface dipole moments.

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I. INTRODUCTION

Lanthanum hexaboride (LaB_6) has been widely used as a high brightness cathode because of its high electron emissivity and low work function, the origins of which are related to high density of states (DOS) at the Fermi level (E_F), structural relaxations at the surface, etc. The crystal structure of LaB_6 is a simple cubic lattice with a La atom at the center of the cube and boron octahedra (B_6) at the apexes. It is stabilized with three types of bonding; covalent, ionic, and metallic bonds. The boron atoms are covalently bonded to each other to form a rigid three-dimensional framework. The B_6 framework is electron deficient and two electrons per unit cell are transferred from the La atom to the B_6 frameworks, which leads to the ionic bonding between La atoms and B_6 frameworks. In addition, valence electrons of La atoms contribute to the metallic bond.[1–3]

The work function of a material generally consists of two components. One is the bulk chemical potential of the electrons relative to the mean interior electrostatic potential and the other is the change in electrostatic potential across a dipole layer at the surface.[4] The latter strongly depends on structural and electronic properties of the surface, and for LaB_6, Lafferty[5] first pointed out the importance of the contribution of the surface La layer to the work function of LaB_6. So far, surface structural and electronic properties of $LaB_6(001)$, (011), and (111) clean surfaces have been investigated by angle-resolved photoemission (ARPES), low energy electron diffraction (LEED), etc., to elucidate the origin of the characteristic properties of LaB_6.[6–9] The results suggested the following model for the surface structures (Fig. 1). The $LaB_6(011)$ surface has the relaxed and reconstructed $c(2\times2)$ structure where the surface layer consists of La atoms displaced outward from the unrelaxed surface. The $LaB_6(001)$ surface has the (1×1) structure with the La-terminated surface, which was confirmed by scanning tunneling microscopy (STM) observation.[10] This structural model suggests the existence of electric dipole moments at the $LaB_6(001)$ and (011) surfaces, which are caused by positive charges of the surface La layer and negative charges of the subsurface B_6 layer. Since the $LaB_6(111)$ surface has the relaxed (1×1) structure where the surface La atoms displace toward the bulk, the electric dipole moments are not likely to exist. Hence it is suggested that the origin of the low work functions of the (001) and (011) surfaces could be interpreted as the electric dipole moments at the surfaces, while the higher work function of the (111) surface reflects mainly a bulk property.[7]

Surface electronic states of LaB_6 have been observed by ARPES at 2 eV below E_F, and they are considered to be originated from B 2*p* dangling bonds.[6,8] Recently, Monnier and Delley[11] have made *ab initio* slab calculations of the surface electronic structure of $LaB_6(001)$ with the La-terminated surface and obtained the energy dispersion of the surface states. The calculation has reproduced well the experimentally obtained surface band dispersion originated from the B 2*p* dangling bonds and the low work function. They have also demonstrated that unoccupied surface states lie near E_F and are localized in the outermost La layer, which may contribute to the low work function and the high electron emissivity. Such surface states could appear near E_F to stabilize a polar surface without reconstruction such as

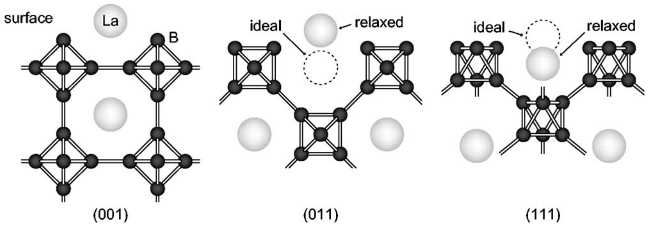

FIG. 1. Surface structures of the $LaB_6(001)$, (011), and (111) clean surfaces. The figures show the side views of the surfaces. In the (011) and (111) surfaces, the topmost La atoms are displaced from the ideal lattice plane upward by 1.66 Å and downward by 1.2 Å, respectively (Ref. 7).

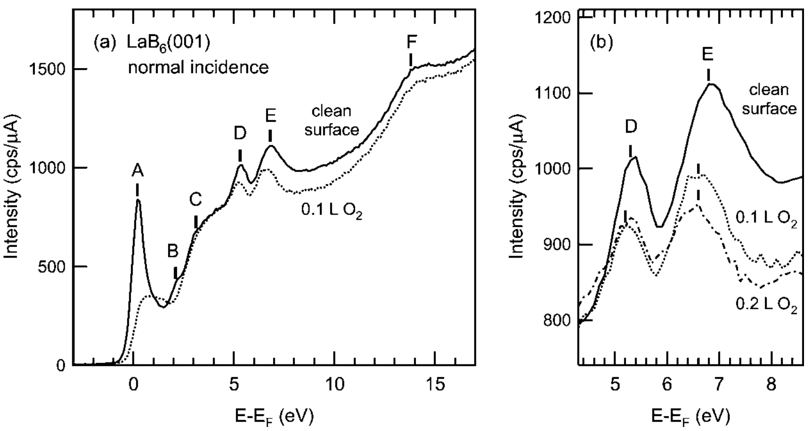

FIG. 2. Normal incidence IPES spectra of a clean $LaB_6(001)$ surface and ones after oxygen adsorption. The spectra intensities are normalized to sample impinging current. (a) The solid line is a spectrum from a clean surface. The dotted line is from the surface exposed to 0.1 L of oxygen. (b) The dashed-dotted line is a spectrum from the surface exposed to 0.2 L of oxygen.

$LaB_6(001)$. Similar properties of the surface states have been observed in TiC(111).[12–14]

So far, numerous studies have been performed on occupied electronic states of LaB_6. The bulk electronic structure of LaB_6 observed by ARPES showed good agreement with band calculation,[15,16] and it has been shown that the surface structures and electronic states play a crucial role for the low work function of LaB_6. However, the existence of surface relaxation of $LaB_6(001)$ is not clear yet despite high resolution electron energy loss spectroscopy (HREELS) experiments,[17] and relationships between the occupied and unoccupied surface electronic states are not fully understood. Especially, the experimental observation of the energy dispersion of the surface states across E_F would be crucial to confirm the theoretical expectation of the surface states of $LaB_6(001)$.

In the present study, we report momentum or *k*-resolved inverse photoemission (KRIPES) spectra of the $LaB_6(001)$ surface and discuss the surface electronic states of $LaB_6(001)$.

II. EXPERIMENT

The experiments were performed in an ultrahigh vacuum system with a base pressure of 1×10^{-10} Torr. The system is equipped with an Auger electron spectrometer (AES), a LEED apparatus, and a newly designed and constructed KRIPES spectrometer. The KRIPES spectrometer has a low energy electron gun (5–30 eV) and an ultraviolet photon detector of a bandpass filter type. The electron gun consists of a 90° spherical deflector and a three-element focusing lens system. The electron source used in this experiment was a BaO thermionic cathode. The electron beam is collimated within an angular divergence of 2° and the beam diameter is about 3 mm in the energy range from 5 to 30 eV. The photon detector consists of a SrF_2 entrance window and a KCl coated photocathode, which function as low and high pass filters, respectively. The energy of the detected photons is about 9.3 eV and the energy resolution of the photon detector is 0.46 eV in full width at half maximum (FWHM). Since the cross sections of IPES are much lower than those of PES, we designed the photon detector with a large collection solid angle (1.2 sr) to improve the efficiency of the spectrometer. As a result, we have achieved an excellent intensity of 600 cps for 1 μA of incident electrons at the peak top near E_F of a gold film. The overall energy resolution of the KRIPES spectrometer is 0.6 eV (FWHM).

The LaB_6 single crystal was grown by the floating zone method. The sample surface was mechanically polished with alumina paste to form an optically flat (001) surface, and then cleaned by flash-heating at about 1400 °C repeatedly in an ultrahigh vacuum. The pressure was kept below 1×10^{-9} Torr during the heating. The cleanliness and long-range order of the surface were confirmed by AES and LEED measurements. To maintain a clean surface, the sample was flash-heated every 2–3 h. After the cleaning procedures impurities such as sulfur, carbon, and oxygen were below the detection limit of AES, and clear (1×1) LEED patterns were observed.

III. RESULTS AND DISCUSSION

Figure 2 shows normal incidence inverse photoemission (IPES) spectra of a clean $LaB_6(001)$ surface and ones measured after 0.1 L ($L=10^{-6}$ Torr s) and 0.2 L oxygen exposures. In Fig. 2(a), six spectral features are discernible for clean $LaB_6(001)$ at the energies of 0.2 eV (*A*), 2.1 eV (*B*), 3.1 eV (*C*), 5.3 eV (*D*), 6.8 eV (*E*), and 13.8 eV (*F*) above E_F, respectively. Upon the oxygen exposure of 0.1 L, the peaks *A* and *B* disappear, while the reduction of the intensities of the other peaks is not so remarkable as compared with the peak *A*. Since surface states are more sensitive to oxygen adsorption than bulk states, the result indicates that the features *A* and *B* are originated from surface electronic states of $LaB_6(001)$. From the comparison between the observed spectra and band calculations,[11,16] the feature *A* is considered to be the surface states localized in the outermost La layer of $LaB_6(001)$. The existence of the surface states with high DOS near E_F is partly related to the high electron emissivity of LaB_6. Since the peak *B* is located just below the work function of $LaB_6(001)$ of 2.3 eV,[7] it can be assigned to a surface image state, which is usually observed in a metallic surface. The result agrees well with surface properties of $LaB_6(001)$ proved by STM.[10] The intensity of the feature *E* reduces gradually with the increase of oxygen exposure and its peak shifts by 0.2 eV toward E_F [Fig. 2(b)]. This reveals

TABLE I. Characteristics of each feature in the IPES spectra of $LaB_6(001)$.

Features					
A	*B*	*C*	*D*	*E*	*F*
Surface La 5*d*	Surface image state	Bulk La 5*d*	Bulk La 4*f*	Surface La 4*f*	Bulk B *sp*

that the feature E has a characteristic of surface states.

According to the partial DOS derived from band calculation,[18] La 5*d* states are located in 3–4 eV above E_F, and B *sp* antibonding states are spread over a wide energy range and have relatively high DOS around 13 eV above E_F. La 4*f* states with a prominent peak structure lie a few electron volts above E_F although band calculations usually reveal lower energies for unoccupied 4*f* levels.[19] In addition, La 5*d* states form a broad peak, or a shoulder peak similar to the feature C in IPES spectra of La metal and La compounds.[20,21] Hence, the features C and F are assigned to the La 5*d* and B *sp* antibonding states, respectively. As is known well, 4*f* states have much larger cross sections in bremsstrahlung isochromat spectroscopy (BIS, $\hbar\omega \sim 1486$ eV) than in IPES ($\hbar\omega$=9.3 eV). Consequently, one might expect that 4*f* states could not be observed with IPES. In fact, 4*f* states were not observed in IPES spectra ($\hbar\omega$ =12 eV) of Eu metal. However they were observed in IPES spectra ($\hbar\omega$=10.2 eV) of La metal[21] since the number of f holes of La atom is twice as large as that of Eu atom. In considering the energy of 4*f* states in IPES, it is important to recall that an IPES spectrum shows the energy difference between the total energies of a final state with $N+1$ electrons and of an initial state with N electrons. So the energies represented by IPES spectra do not necessarily agree with those of band calculations. Especially, the energy of localized 4*f* states could shift from one-electron band calculations. As for the energy of the 4*f* states of LaB_6, Mori *et al.*[22] carried out BIS experiments and have shown that the La 4*f* states lie at 5.2 eV above E_F. Since the energy agrees well with that of the peak D, it can be assigned to La 4*f* bulk states. In La metal, 4*f* features have been observed as two split components of the low energy (4.6 eV) and high energy (5.2 eV) peaks, which are attributed to surface and bulk states, respectively.[23] Since the feature E has an appearance similar to feature D and shows a characteristic of surface states, feature E is considered to be La 4*f* surface states by analogy with La metal. Its corresponding peak was not observed in BIS of a scraped LaB_6 surface.[22] The characteristics of each feature in the IPES spectra are summarized in Table I.

The energy shift of the surface state of $LaB_6(001)$ is significantly larger in magnitude than that of La metal and the opposite direction to it. This reveals that the origin of the energy shift in $LaB_6(001)$ is different from that in La metal. In $LaB_6(001)$, a surface La atom is coordinated by four B_6 frameworks and five La atoms, while one in the bulk is coordinated by eight B_6 frameworks and six La atoms. The reduced coordination number at the surface could lead smaller electron transfer to B_6 frameworks since a La atom plays as an electron donor in LaB_6, and hence could make the La atoms in the surface layer more negative compared with those in the bulk. Therefore, we simply attribute the origin of the energy shift to the charge redistribution at the surface: in the surface La layer of $LaB_6(001)$, the electron density at a La atom is larger than that in the bulk due to the charge redistribution at the surface, and consequently the surface 4*f* states are located at the higher energy relative to the bulk ones.

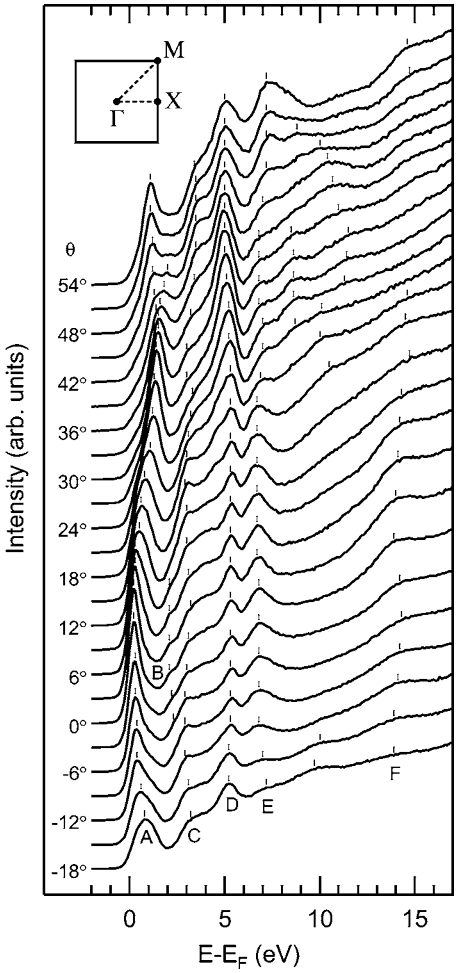

FIG. 3. KRIPES spectra of a clean $LaB_6(001)$ surface varying angles of electron incidence from −18° to 54° by 3° along the Γ–M direction. The angle of incidence θ is measured relative to the surface normal. The inset shows the surface Brillouin zone of $LaB_6(001)$ and the small vertical rods represent the peak positions. The peak A at $\theta \sim 45°$ and the peak E at $\theta \sim 33°$ correspond to the M point.

To obtain the energy dispersion of the surface states, we have measured KRIPES spectra (Fig. 3) of a clean $LaB_6(001)$ surface along the Γ–M direction of the surface Brillouin zone (SBZ). In the figure, we can observe two broad features around 10 eV, apart from the feature F, which correspond to the B *sp* antibonding states. The surface state A near E_F shows considerable energy dispersion, while peaks D and E do not show energy dispersion. This characteristic of peaks D and E agrees well with that of localized 4*f* states.

Figure 4 shows the energy dispersion of the surface state A. From the comparison with the recent slab calculation[11]

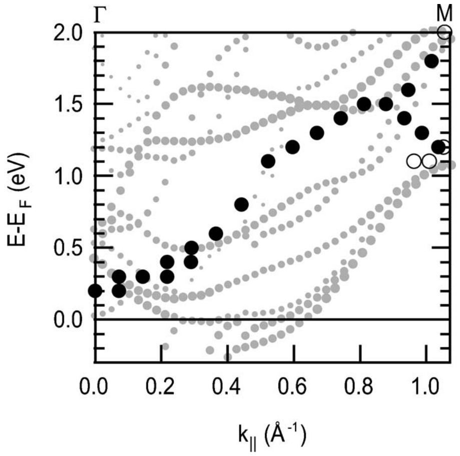

FIG. 4. The energy dispersion of the surface state (peak *A* in Fig. 3) of $LaB_6(001)$. The closed black circles show the band in the first Brillouin zone and the open circles are reduced from the second zone to the first zone. The gray circles show the calculated surface bands of $LaB_6(001)$, which are strongly localized in the outermost La layer (Ref. 11).

shown by the gray circles in the figure, it is obvious that the energy dispersion of the surface state obtained by KRIPES does not agree with those of the theoretical calculation. In the calculated energy dispersion, the surface states which are localized in the outermost La layer of $LaB_6(001)$ cross E_F in the middle of the Γ–M line of SBZ and the bandwidth is about 1 eV. Our observation shows that the energy dispersion has the minimum energy at the Γ point and the maximum energy near the M point of SBZ and does not cross E_F, at least near the middle of the Γ–M line. Moreover the bandwidth is much larger than that of the calculation. In the slab calculation, the interlayer spacing between the surface La layer and the subsurface B layer of $LaB_6(001)$ is estimated to be reduced by 44%. One may think this causes the discrepancy between the KRIPES experiment and the calculation. Although the surface relaxation of $LaB_6(001)$ is not experimentally confirmed yet, it is convincing from the fact that a polar surface without reconstruction such as $LaB_6(001)$ is so unstable that relaxation usually appears to stabilize the surface. In fact, HREELS experiments of $LaB_6(001)$ indicate that the boron octahedra at the surface are expanded in the direction parallel to the surface.[17] This naively suggests that the interlayer spacing between the topmost La layer and the subsurface layer is reduced. Hence, we consider the discrepancy to be an intrinsic property in the method of the calculation rather than to be the improper estimate of the surface relaxation in the calculation. The band structures obtained by local density functional theory tend to give relatively lower energies for unoccupied bands.[19] Consequently, the slab calculation could not reproduce well the surface states above E_F, while it can do well the occupied surface states.

Since the surface state observed in IPES is very close to E_F at the Γ point and surface resonance states have been observed just below E_F in ARPES spectra of $LaB_6(001)$,[6,15] the surface state is partly occupied in the neighborhood of the Γ point. Theoretical considerations[11,24] suggest that the surface states near E_F are originated from La 5*d* states. On the other hand, we observe the bulk La 5*d* states around 3 eV above E_F. This indicates that the La 5*d* states are pulled down toward E_F at the surface. This suggests that the origin of the surface state near E_F is the charge redistribution at the surface, which screens the long-range electric field produced by the polar structure and stabilizes the polar surface. The similarity occurs in a TiC(111) surface, which has the (1×1) structure with the Ti-terminated surface, and unoccupied Ti 3*d* states are pulled down toward E_F.[12–14]

It has been considered that the low work function of $LaB_6(001)$ is caused by the surface electric dipole moments produced by positive charges of the surface La layer and negative charges of the subsurface B_6 layer.[6,7] Our results show that the electron density of a surface La atom is larger than that of a bulk La atom due to the charge redistribution at the surface, which can reduce the surface dipole moments. Since the work function of a material is the difference between the surface dipole moment contribution and the bulk chemical potential,[4] this may suggest that the surface dipole moments make only a small contribution to the work function of $LaB_6(001)$. In fact, using the calculation by Lang and Kohn,[4] Nishitani *et al.*[7] estimated the bulk chemical potential of LaB_6, i.e., the bulk component of the work function to be 2.6 eV, which is close to the work function of $LaB_6(001)$ of 2.3 eV. Hence, contrary to the previous model for the work function, it seems that the low work function of $LaB_6(001)$ can be attributed mainly not to the surface dipole moments but to the low bulk chemical potential of LaB_6.

IV. CONCLUSIONS

We measured KRIPES spectra of $LaB_6(001)$ and found the surface states near E_F and at 6.8 eV above E_F, which are assigned to La 5*d* and La 4*f* states, respectively. The energy dispersion of the surface state near E_F does not agree with that expected by the band calculation. From the energy dispersion of the surface state and the ARPES experiments, it was shown that the surface state near E_F is partly occupied in the neighborhood of the Γ point. We deduced that in $LaB_6(001)$, electrons are transferred from the subsurface to the surface La layer, and consequently the electron density at a La atom in the surface layer is larger than that in the bulk.

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