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# Angle-resolved photoemission study of the valence band structure of ZnO(10 $\bar{1}$ 0)

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## Abstract

The valence band structure of the (10 $\bar{1}$ 0) surface of wurtzite ZnO has been investigated by angle-resolved photoelectron spectroscopy utilizing polarized synchrotron radiation. The energetic position and the dispersion width of the O 2p dangling-bond (DB) state are determined along the high symmetry axes of the surface Brillouin zone (SBZ). The O 2p DB is 3.7 eV below the  $\bar{\Gamma}$  point and disperses to higher binding energies with a total dispersion width of  $\sim 1.2$  eV. Comparison with the projected bulk bands from the earlier theoretical studies reveals that the DB state is a surface resonance in the whole SBZ. Polarization-dependent measurements have also been carried out along the  $\bar{\Gamma}\bar{X}'$  axis suggest that the DB band with odd symmetry with respect to the mirror plane of the crystal surface has a larger dispersion than the band with even symmetry.

## 1. Introduction

Studying the bulk and surface electronic structures of solids is crucial for understanding their physical and chemical properties as well as for designing new functional materials. Zinc oxide (ZnO) is an industrially important metal oxide used in varistors, piezo-electric transducers, chemical sensors, catalysts, etc. ZnO is a potential material for blue light emitters and laser diodes because of its wide direct band gap ( $\sim 3.4$  eV) and large exciton energy ( $\sim 60$  meV), and a successful application of ZnO has recently been reported [1]. Moreover, interest in spin-based electronics has focussed attention on the ferromagnetic behaviour of diluted magnetic semiconductors including Mn-doped ZnO [2]. Information about the bulk and surface electronic structures of ZnO is important for the further exploitation of ZnO-based novel functional materials. However, in contrast to the case for elemental metals and

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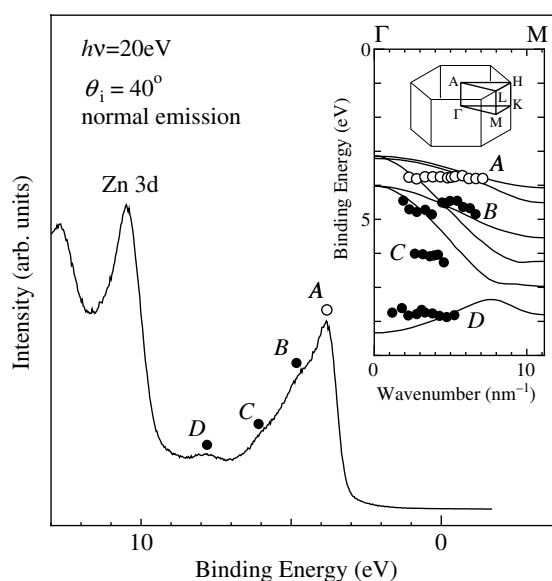
semiconductors as well as other metal oxides such as  $\text{TiO}_2$ , little is known about the valence band structure of ZnO. Previously only the polar ZnO(0001) surface has been investigated using angle-resolved photoemission (ARPES) [3]. In the present paper, we report the surface electronic structure of ZnO(10 $\bar{1}$ 0).

The (10 $\bar{1}$ 0) surface, which is the most stable surface among the low-index surfaces of wurtzite ZnO [4], has a unique surface atomic arrangement, which is characterized by alternating rows of the coordinately unsaturated O and Zn atoms with occupied and unoccupied dangling-bond (DB) orbitals, along the [1 $\bar{2}$ 10] direction. The electronic structure of these DB states is expected to be highly anisotropic. Several theoretical attempts have been made to clarify the electronic structure of ZnO(10 $\bar{1}$ 0) [5–7]. However, a conclusive result has not been obtained, because the theoretical electronic structure depends heavily on the model employed in the calculations. The difference is especially noticeable in the energetic position and the dispersion width of the O 2p DB band. The empirical tight-binding approach by Ivanov and Pollmann failed to reproduce the O 2p DB band with a high density of states at around the centre of the surface Brillouin zone (SBZ) [5]. On the other hand, tight-binding calculations using the so-called  $sp^3$  model yield a DB band whose energy minimum and maximum coincide with the  $\bar{M}$  and  $\bar{\Gamma}$  points, with a total dispersion width of  $\sim 0.8$  eV [6]. A similar dispersion relation of the DB band has been obtained by local density approximation (LDA) calculations [7]. However, the dispersion width is about one half of that deduced from the  $sp^3$  model. Moreover, the O 2p DB band resulting from the LDA calculations lies in the bulk band gap in the whole SBZ, whereas the band overlaps the projected bulk bands along  $\bar{\Gamma X}$  and  $\bar{\Gamma X'}$  according to the  $sp^3$  model.

To settle such discrepancies among the theoretical studies, we carried out ARPES measurements on ZnO(10 $\bar{1}$ 0), and the dispersion of the O 2p DB state have been determined along  $\bar{\Gamma X}$  and  $\bar{\Gamma X'}$  [8]. The DB band is found to be formed below the upper edge of the projected bulk-band region along these high symmetry axes, in good agreement with the result of the  $sp^3$  model. It is also found that the dispersion relation of the DB state along  $\bar{\Gamma X}$  resembles the DB band given by the  $sp^3$  model calculations. However, the overall shape of the 2p DB band has not been clarified experimentally so important information such as the total dispersion width, existence of the gap state in a certain part of the SBZ, etc, remains unknown. Interestingly, the band gap state is predicted along the  $\bar{XM}$  and  $\bar{X'M}$  axes by both  $sp^3$  model [6] and LDA [7] calculations. Moreover, the LDA calculations have indicated that the DB band should split into two branches along  $\bar{\Gamma X'}$ , where the initial state of the band can be classified by symmetry with respect to the mirror plane of the (10 $\bar{1}$ 0) surface [7]. In order to verify these theoretically predicted properties of the O 2p DB state experimentally, we have performed a comprehensive ARPES study on the electronic structure of ZnO(10 $\bar{1}$ 0) along the major high symmetry axes of the SBZ, i.e.,  $\bar{\Gamma X}$ ,  $\bar{\Gamma X'}$ ,  $\bar{XM}$ , and  $\bar{X'M}$ , including polarization-dependent measurements along  $\bar{\Gamma X'}$ .

## 2. Experimental details

The ARPES measurements were performed at Beam Line 11C of the Photon Factory, High Energy Accelerator Research Organization (KEK). Photoelectrons were collected by an electron energy analyser of the 180° hemispherical-sector type with an acceptance angle of  $\pm 1^\circ$ . The total experimental resolution, which was estimated from the Fermi edge in the spectra of the Ta sample holder, was 0.23–0.29 eV at photon energies  $h\nu$  of 20–27 eV. The base pressure of the ultra-high vacuum (UHV) system was  $2 \times 10^{-10}$  Torr. All the measurements were carried out at room temperature.



**Figure 1.** Normal emission spectrum of ZnO(10 $\bar{1}$ 0). The photon energy was 20 eV, and the incidence angle of the light was 40°. The peak positions, determined by taking the second derivative of the measured spectrum, are indicated by open and filled circles, which correspond to the surface and bulk-related features, respectively. The inset shows the dispersion relation of peaks A–D along the  $\Gamma$ M axis of the bulk Brillouin zone. The solid curves are the theoretical bulk bands from Vogel *et al* [12].

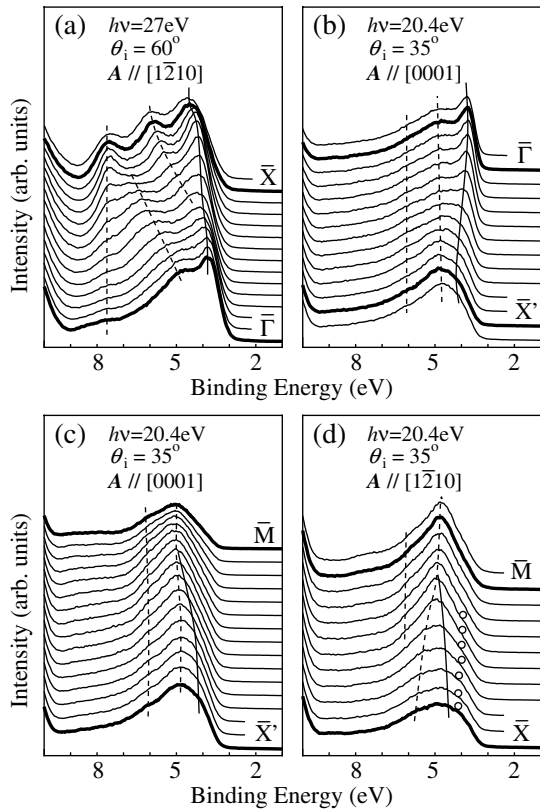
A ZnO crystal with (10 $\bar{1}$ 0) orientation was set so that the incidence plane of the light was parallel to the [0001] or [1 $\bar{2}$ 10] direction, which corresponds to the direction parallel or perpendicular to the mirror plane of the (10 $\bar{1}$ 0) surface, respectively. The incident light was linearly polarized in the incidence plane. The *in situ* preparation to remove surface contamination involved several cycles of Ar<sup>+</sup> sputtering (2–3 kV, 0.5–1  $\mu$ A) and annealing at 1050 K. Then, the sample was annealed at 700 K in an O<sub>2</sub> atmosphere ( $3 \times 10^{-6}$  Torr) for 10 min to restore the surface stoichiometry. Finally, the sample was heated to 650 K to remove possible oxygen adsorbates. The clean surface thus prepared showed a sharp (1  $\times$  1) LEED pattern. The work function  $\Phi$  of the clean surface, measured from the spectrum width from the Fermi level  $E_F$  of the Ta holder to the cut-off of the secondary electron of ZnO(10 $\bar{1}$ 0), was determined to be  $4.5 \pm 0.1$  eV, which is in good agreement with the available literature values of 4.5–5.05 eV [9–11].

In this paper, the incidence angle of the light  $\theta_i$  is given relative to the surface normal. In the ARPES spectra presented below, the electron binding energy is referenced to zero at  $E_F$ . The accuracy of the binding energy is  $\pm 0.1$  eV.

### 3. Results and discussion

#### 3.1. Dispersion relation of the O 2p DB state

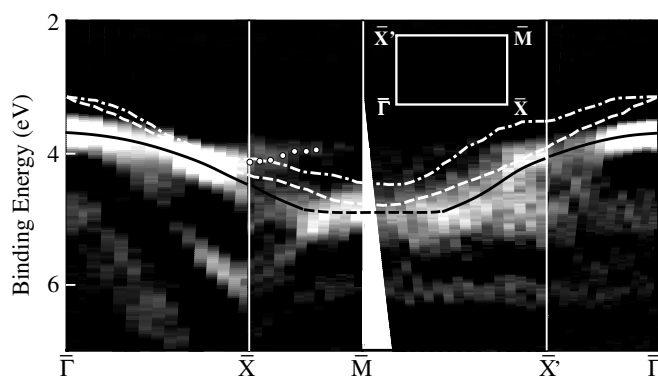
The valence electronic structure of ZnO is characterized by hybrid O 2p and Zn 3d/4sp orbitals, which extend from the valence band maximum at  $\sim 3$  to 8 eV below  $E_F$ , and the Zn 3d states at 10–11 eV. Figure 1 shows a typical example of the normal emission spectrum of clean ZnO(10 $\bar{1}$ 0). Four peaks labelled A–D are identified in the energy region of 3–8 eV. In the previous ARPES study [8], we assigned peak A to the emission from the O 2p DB orbitals on



**Figure 2.** Off-normal emission spectra of the clean surface along the high symmetry axes of (a)  $\overline{\Gamma X}$ , (b)  $\overline{\Gamma X'}$ , (c)  $\overline{X'M}$  and (d)  $\overline{XM}$ .  $A$  denotes the polarization vector of the light, which lies in the plane of incidence. The solid and dashed curves indicate the positions of the O 2p DB peaks and the bulk-band related peaks, respectively.

the surface O atoms, since the peak is sensitively attenuated by adsorption of foreign species (oxygen and potassium) and the peak position is insensitive to changing the excitation photon energy. The other peaks  $B$ ,  $C$  and  $D$ , on the other hand, have been associated with the bulk-band emissions [8]. The inset shows the dispersion relation of these peaks along the  $\overline{\Gamma M}$  axis of the bulk Brillouin zone. Comparison with the theoretical bulk-band structure of Vogel *et al* [12] makes more detailed assignment possible; peaks  $B$  and  $D$  are formed by direct bulk-band transitions, whereas an indirect bulk-band transition should contribute to peak  $C$ . Since peak  $A$  is associated with a surface localized state, it shows a dispersionless feature along the high symmetry axis of the bulk Brillouin zone.

In order to examine the two-dimensional band structure of the O 2p DB state along the high symmetry axes of the SBZ, off-normal emission spectra were measured. Figure 2 shows a series of spectra of ZnO(10 $\overline{10}$ ) along (a)  $\overline{\Gamma X}$ , (b)  $\overline{\Gamma X'}$ , (c)  $\overline{X'M}$  and (d)  $\overline{XM}$ . The solid and dashed curves in figure 2 indicate the positions of the O 2p DB peak and the bulk-related peaks, respectively. The normal emission spectrum in figure 2(a) (bottom curve) exhibits the O 2p DB peak at 3.7 eV and the bulk-related peaks at 5.0 and 7.6 eV, which correspond to peaks  $B$  and  $D$  in figure 1, respectively. The DB state shifts to the higher-binding energy side along the  $\overline{\Gamma X}$  axis and reaches 4.5 eV at  $\overline{X}$  (the surface parallel component of the wavenumber vector  $k_{\parallel} = 9.66 \text{ nm}^{-1}$ ). The bulk-related peak at 5 eV also shows a downward shift, whereas the deep-lying bulk peak stays at 7.6 eV. Another bulk-related peak appears around the middle point of the  $\overline{\Gamma X}$  axis and moves to the higher binding energy side at larger  $k_{\parallel}$ . A downward shift of the O 2p DB peak from  $\overline{\Gamma}$  to the zone boundary is also observed along the  $\overline{\Gamma X'}$  axis (figure 2(b)). Here, the spectra along the axis from  $\overline{X'}$  ( $k_{\parallel} = 6.03 \text{ nm}^{-1}$ ) to  $\overline{\Gamma}$  in the second



**Figure 3.** Intensity plot of the second derivative of the ARPES spectra along four high symmetry axes of the SBZ. The SBZ of the ZnO(1010) surface is indicated in the inset. The black solid curve traces the O 2p DB band, whereas the black dashed curve shows a tentative position of the DB band, which is obscured by the bulk band emission. The white dashed and dash-dotted curves show the upper edge of the projected bulk-band region, which are obtained from the  $sp^3$  model calculations [6] and the LDA calculations [7], respectively. Open circles indicate the position of the bulk-related state which locates above the DB band. The details are described in the text.

SBZ ( $12.06 \text{ nm}^{-1}$ ) are depicted, since a stronger emission from the O 2p DB state is observed in the second SBZ than in the first SBZ. A similar effect has been found for CdS(1010) and CdSe(1010) [13, 14]. The O 2p DB state disperses from 4.1 eV at  $\bar{X}'$  to 3.7 eV at  $\bar{\Gamma}$  in the second SBZ. Although the observed dispersion of the bulk-related peaks along  $\bar{\Gamma}\bar{X}$  and  $\bar{\Gamma}\bar{X}'$  is different from that reported in [8] because of the different measurement condition, an almost identical band structure is obtained for the O 2p DB state, indicating the credibility of the present ARPES measurements.

A general trend of the O 2p DB peak is that its relative intensity to the bulk-related peaks lowers as the DB state is located away from the  $\bar{\Gamma}$  point. Thus, only a weak DB peak is observed along the  $\bar{X}'\bar{M}$  and  $\bar{X}\bar{M}$  axes (figures 2(c) and (d)). In both directions, the DB peak shifts from 4.1 and 4.5 eV at  $\bar{X}'$  and  $\bar{X}$ , respectively, to the higher binding energy side towards the  $\bar{M}$  point. However, the DB state overlaps the bulk-band peak near the  $\bar{M}$  point so that the precise peak position cannot be determined around the  $\bar{M}$  point.

Figure 3 shows a greyscale two-dimensional band map obtained by plotting the spectral weight of the second derivatives of the off-normal emission spectra. Among several branches seen in the band map, the O 2p DB band is indicated by the black solid curve. The black dashed curve around the  $\bar{M}$  point indicates a tentative position of the DB state, which is obscured by the overlap with the strong bulk-band emission. The O 2p DB state at 3.7 eV at  $\bar{\Gamma}$  disperses downwards along  $\bar{\Gamma}\bar{X}$  and  $\bar{\Gamma}\bar{X}'$  and further shifts to reach its minimum at  $\sim 4.9$  eV at  $\bar{M}$ . The dispersion widths are  $\sim 0.8$  eV along the  $\bar{\Gamma}\bar{X}$  and  $\bar{X}'\bar{M}$  axes and  $\sim 0.4$  eV along the  $\bar{\Gamma}\bar{X}'$  and  $\bar{X}\bar{M}$  axes. Such a dispersion relation is well understood on the basis of the difference in the overlap between the neighbouring O 2p DB orbitals in the two directions [1210] and [0001]. Namely, a larger lateral interaction between the DB orbitals is expected along the [1210] direction than along the [0001] direction, reflecting the lattice constant of the crystal surface ( $a = 0.3235$  nm versus  $c = 0.5211$  nm).

The theoretical O 2p DB bands [6, 7] reproduce the experimental band qualitatively as far as the dispersion behaviour is concerned. However, a quantitative comparison signifies significant differences. The total dispersion width of the O 2p DB band is estimated to be 0.7–0.8 eV by the  $sp^3$  model calculations [6], whereas a width of  $\sim 0.4$  eV is given by the

LDA calculations [7]. These values are smaller than the experimental value of  $\sim 1.2$  eV. The larger dispersion compared with the theoretical bands is mainly due to the dispersion along the  $\overline{\Gamma X'}$  and  $\overline{XM}$  axes, where almost flat bands are obtained by both the  $sp^3$  model and LDA calculations. This means that the model calculations underestimate the lateral interactions between the neighbouring O 2p DB orbitals in the [0001] direction. Obviously, the O 2p DB state of ZnO(10 $\bar{1}0$ ) has stronger two-dimensional character than the theoretical studies have predicted.

Regarding the energetic position of the O 2p DB band relative to the projected bulk bands, the difference between theory and experiment becomes more apparent. In figure 3, we indicate the upper edges of the projected bulk-band region obtained by the  $sp^3$  model [6] and LDA [7] calculations by white dashed and dash-dotted curves, respectively. It is clear that the O 2p DB band is located below the calculated upper edge lines, i.e., the DB state is a surface resonance along the major high symmetry axes. Such a result is in sharp contrast to the theoretical predictions. The LDA calculations result in a DB band which lies in the bulk-band gap along all the high symmetry axes [7]. The  $sp^3$  model calculations have also predicted the gap state along  $\overline{XM}$  and  $\overline{X'M}$ , although the DB state overlaps the projected bulk bands along  $\overline{\Gamma X}$  and  $\overline{\Gamma X'}$  [6].

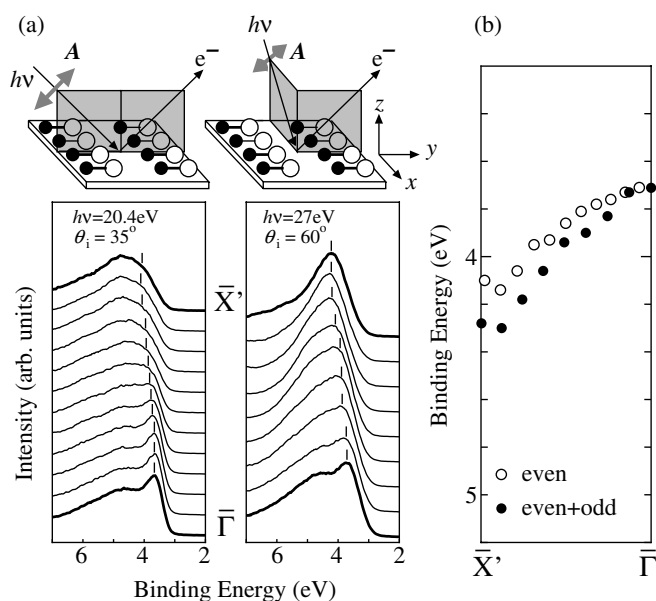
It is worth noting that the absence of a gap state is inferred experimentally. A close examination of the off-normal-emission spectra reveals a shoulder structure at 3.9–4.1 eV along the  $\overline{XM}$  axis (the position is plotted by open circles in figure 2(d)). The shoulder peak is persistent even though the surface is covered with potassium (the result is not shown), and thus it is associated with the bulk-band emission. Since this bulk-related state is located above the O 2p DB state along  $\overline{XM}$ , where the theoretically derived DB state lies above the upper edge of the projected bulk-band region [6, 7], the DB state should overlap the bulk bands. Therefore, we conclude that, unlike the theoretical prediction, there is no gap state on ZnO(10 $\bar{1}0$ ) in the entire SBZ.

### 3.2. Symmetry dependence of the O 2p DB band along $\overline{\Gamma X'}$

Schröer *et al* find from their LDA calculations [7] that the O 2p DB band is separated into two branches along the  $\overline{\Gamma X'}$  axis; one is almost flat and has even symmetry with respect to the mirror plane, and the other is a slightly dispersing band with odd symmetry.

In order to examine such a predicted symmetry dependence of the dispersion width, it is necessary to compare the off-normal-emission spectra measured with a different polarization geometry. The spectra shown in figure 2(b) were obtained by a measurement geometry in which the incidence plane of the light and the detection plane of the photoelectrons were set parallel to the [0001] direction, i.e., to the mirror plane. On the other hand, the incidence plane was parallel to the [1 $\bar{2}$ 10] direction in the previous ARPES study when measuring the spectra along  $\overline{\Gamma X'}$  [8]. These sets of ARPES spectra are compared in figure 4(a). The O 2p DB state shifts to higher binding energies from  $\overline{\Gamma}$  to  $\overline{X'}$  in both geometries. However, a larger shift is seen in the perpendicular geometry (right panel in figure 4(a)) than in the parallel geometry (left panel). We confirmed that several measurements reproduced the same trend. The dispersion of the DB state is depicted as open and filled circles in figure 4(b). The dispersion widths are 0.4 and 0.6 eV in the parallel (○) and perpendicular (●) geometries, respectively.

Since the polarization vector of the light lies in the incidence plane, only the O 2p state with even symmetry with respect to the mirror plane can be detected in the parallel geometry according to the dipole selection rule [15]. Thus, the observed O 2p DB band (○ in figure 4(b)) should be composed of O 2p<sub>y</sub> and 2p<sub>z</sub> orbitals. On the other hand, the O 2p<sub>x</sub> (odd) and 2p<sub>y,z</sub> (even) electrons are excited in the perpendicular geometry, and thus both even and odd



**Figure 4.** (a) Comparison of the ARPES spectra along  $\bar{\Gamma}\bar{X}'$  measured with different polarization geometry, i.e., the incidence plane of the light is set parallel (left panel) and perpendicular (right panel) to the mirror plane of the crystal surface. (b) Measured dispersion of the O 2p DB state with even symmetry (open circles) and even + odd symmetry (filled circles).

bands are observed. Although only a single band is identified as shown by filled circles in figure 4(b), this band should have contributions from both even and odd bands. The larger dispersion of the even + odd band than the band with only the even contribution implies that the odd band has a larger dispersion than the even band, although the actual dispersion of the odd band is not obtained from the present study. The LDA calculations have given a 0.3–0.4 eV dispersion for the odd band and an almost dispersionless even band [7]. Although the theoretical calculations underestimate the interaction between the neighbouring DB orbitals, as discussed in the previous section, the present experimental result supports the predicted splitting of the O 2p DB states depending on symmetry. A similar symmetry dependence of the anion-derived DB band has been found in the earlier ARPES study on the CdS(10 $\bar{1}$ 0) surface, where the S 3p-derived DB state with odd symmetry has a larger dispersion than that with even symmetry along the  $\bar{\Gamma}\bar{X}'$  axis [13, 14], and this result is reproduced by the LDA calculations of Schröer *et al* [7].

In the previous report [8], we have shown that the  $sp^3$  model calculations give an O 2p DB band which reproduces the experimental band along the  $\bar{\Gamma}\bar{X}$  axis. However, such an agreement seems to be accidental, and overall agreement is rather poor considering the entire SBZ. Much larger deviations exist between the experiment and the LDA calculations. Shortcomings of the LDA calculations applied to ZnO are that the band gap is underestimated and that the position of the Zn 3d states in energy is too high [7, 12, 16]. This is because the LDA does not accurately treat the self-interaction correlation (SIC) of the localized 3d electrons. Attempts to include the SIC in the LDA calculations have been made by Vogel *et al* [12] and Dong *et al* [16], and a good improvement in the width of the band gap and the position of the Zn 3d state was obtained for bulk ZnO. Therefore, utilizing the LDA which properly treats the SIC should be a good approach to theoretically examine the valence band structure of the ZnO(10 $\bar{1}$ 0) surface, and the results given in the present paper can be used to assess the model calculations.



#### 4. Summary

The valence electronic structure of the ZnO(10 $\bar{1}$ 0) surface has been investigated by ARPES utilizing linearly polarized synchrotron radiation. The dispersion relation of the O 2p DB state is determined along the major high symmetry axes of the SBZ, i.e., the  $\bar{\Gamma}\bar{X}$ ,  $\bar{\Gamma}\bar{X}'$ ,  $\bar{X}\bar{M}$ , and  $\bar{X}'\bar{M}$  axes. The O 2p DB states located 3.7 eV below  $E_F$  at the  $\bar{\Gamma}$  point and disperses downwards away from  $\bar{\Gamma}$  to reach  $\sim 4.9$  eV at  $\bar{M}$ . The total dispersion width is 1.2 eV, which is much larger than the theoretically determined widths of 0.4–0.8 eV. The larger dispersion is due partly to the net dispersion of 0.4 eV along  $\bar{\Gamma}\bar{X}'$  and  $\bar{X}\bar{M}$ , where the neighbouring O–O distance is rather large ( $c = 0.5211$  nm) so that the theoretically derived DB bands have negligible dispersion. Thus, the O 2p DB state has a more two-dimensional character theory predicts. The energetic position of the O 2p DB band is below the upper edges of the projected bulk-band region along the major high symmetry axes, implying that the state has a resonance character in the whole SBZ. This finding is in sharp contrast to the DB bands found in the theoretical studies utilizing the  $sp^3$  model and LDA, both of which have gap states in the whole or part of the SBZ. Another important finding is that a symmetry dependence of the dispersion exists along the  $\bar{\Gamma}\bar{X}'$  axis; the odd band has a larger dispersion compared with the even band. This is in good agreement with the result of the LDA calculations, although the band dispersion is underestimated.

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