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ARPES study of the O 2p dangling-bond band on ZnO(10-10)

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Introduction

Zinc oxide (ZnO) is one of the most important oxide semiconductors because of a wide variety of its applications such as catalysts, chemical sensors, piezoelectric transducers, varistors, etc. The (10-10) surface of wurtzite ZnO is of particular interest among low-index surfaces from the view point of the surface electronic structure, since the (10-10) surface is composed of alternating rows of O and Zn atoms with occupied and unoccupied dangling bonds (DB), respectively, along the [1-210] direction. Theoretical studies of the electronic structure of this surface have indicated that the O 2p DB band is formed at around the top of the valence band [1,2]. However, the energetic position of the band relative to the projected bulk bands has been controversial because it largely depends on the methods employed in the calculations. The present study offers an experimentally determined band structure of the O 2p DB state and compares it with the theoretically predicted band structures.

Experimental

Angle-resolved photoelectron spectroscopy (ARPES) measurements were carried out at beam line 11C, where synchrotron light was dispersed by a Seya-Namioka monochromator. Photoelectrons were collected by an electron energy analyzer of the 180° hemispherical-sector type with an acceptance angle of 1°.

Results and Discussions

Figure 1 shows a two-dimensional band structure of the O 2p DB state determined from a series of off-normal emission spectra. The DB state locates at 3.7 eV at the Γ point and shifts to the higher binding energy (BE) side towards the X and X' points by 1.2 and 0.4 eV, respectively. The state further shifts to the higher BE side by 0.9 eV from X' to M. Along the XM axis, band dispersion is almost negligible. Larger dispersion along the ΓX and X'M axes than along the ΓX' and XM axes is well understood by the difference in the degree of the overlap between the neighboring O 2p DB orbitals, which should reflect the neighboring O-O distances in the [1-210] and [0001] directions (0.3253 versus 0.5211 nm).

Hatched areas in both panels indicate the region of the bulk bands projected onto the (10-10) surface obtained from the empirical tight-binding calculation (top panel) [1] and the ab initio calculation (bottom panel) [2]. The experimentally determined O 2p DB band lies within the projected bulk band region along the four high symmetry axes of the surface Brillouin zone (SBZ). On the other hand, the theoretically determined DB band enters a fundamental gap as shown by solid lines in both panels. Such a discrepancy results from a larger dispersion width and a deeper lying of the DB band found in the experiment than in the theoretical studies, i.e. these theoretical calculations could tend to estimate less neighboring interaction between the O 2p DB orbitals.

In conclusion, we have investigated the band structure of the O 2p DB state on ZnO(10-10) utilizing ARPES. In contradiction to the theoretical results, no gap state by the DB band has been observed and the band overlaps with the projected bulk bands along the major high symmetry axes of the SBZ.

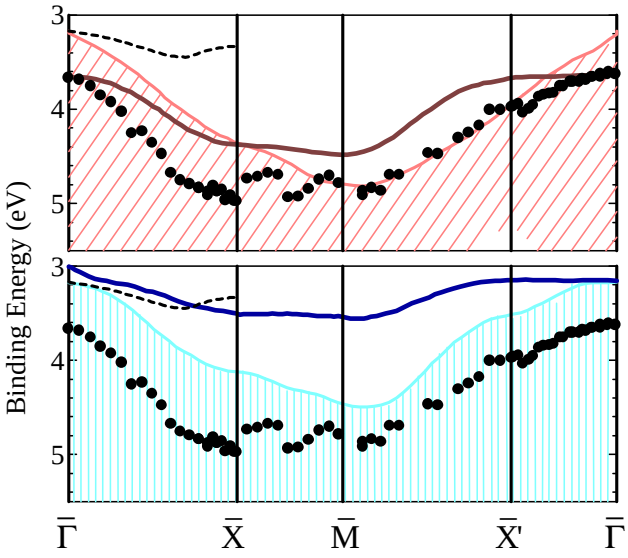

Figure 1. Experimentally determined O 2p dangling bond band structure (dot), which is compared with the results by the empirical tight-binding calculation (top panel) [1] and the ab initio calculation (bottom panel) [2]. Hatched areas in both panel indicate the bulk band regions projected onto the (10-10) surface and solid lines the O 2p DB band by the theoretical studies. Dashed line along the ΓX axis shows the valence band onset obtained from the ARPES spectra.

References

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[2] P. Schroer et al., Phys. Rev. B 47, 6971 (1994).

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