

A Comparative Study of the Valence Band Structure of the Polar ZnO Surfaces

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Introduction

Zinc oxide (ZnO) crystallizes in the hexagonal wurtzite structure with Zn and O planes alternatively stacked along the c axis. Thus, differently terminated ZnO surfaces, i.e., a Zn-terminated (0001) surface (ZnO-Zn) and an O-terminated (000 $\bar{1}$) surface (ZnO-O), are obtained when the crystal is cleaved perpendicular to the c axis. Since Zn atoms and O atoms of ZnO are positively and negatively charged, respectively, these surfaces are electrically polarized. In principle, such polar surfaces are unstable because of a nonvanishing dipole moment perpendicular to the surface plane, and surface reconstruction is often induced to quench the surface dipole. However, it is known that the polar ZnO surfaces exhibit (1x1) low-energy electron diffraction patterns, implying that the surfaces are truncated by the Zn and O atoms with (1x1) structures on ZnO-Zn and ZnO-O, respectively. Therefore, it is interesting to know how the difference in the atomic composition of these surfaces affects the surface electronic structure.

In the present angle-resolved photoemission spectroscopy (ARPES) study, we have carried out comparative measurements of the valence electronic structure of ZnO-Zn and ZnO-O. It is found that two bulk-related bands are observed between 4 and 8 eV. They exhibit different dispersion widths depending on the polar surfaces. A possible effect of surface morphology of polar ZnO is discussed.

Experimental

The ARPES measurements were carried out at beam line 28A using SCIENTA SES2002 electron energy analyzer. ZnO-Zn and ZnO-O samples were cleaned by an Ar⁺ bombardment and annealing at 1050-1100 K.

Results and Discussions

Fig. 1 shows intensity plots of the ARPES spectra of ZnO-O and ZnO-Zn measured at photon energy of 220 eV. Bright and dark areas correspond to high and low spectral intensity regions, respectively. Two bands are observed on both surfaces; one at 4 eV with small dispersion widths and the other at the higher binding energy side with large dispersion widths. It is clear that

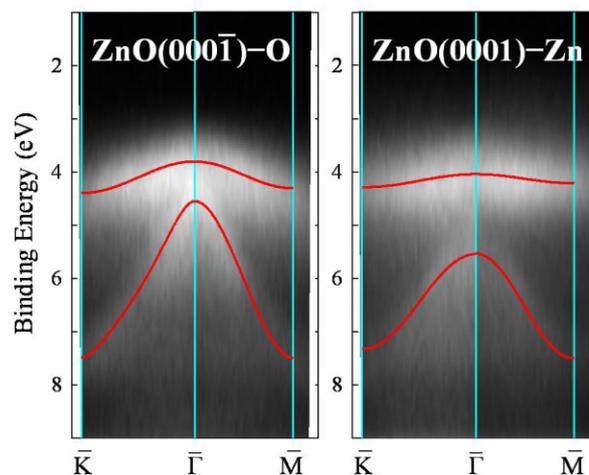


Fig. 1. Intensity plots of the ARPES spectra of the ZnO-O and ZnO-Zn surfaces. Bulk-related valence bands, which are shown by solid lines, are observed along the high symmetry axes of the surface Brillouin zone.

the bands on ZnO-O exhibit larger dispersion widths than those on ZnO-Zn. Such a difference in the band structure is peculiar, because the observed bands are still observable on the Cu-covered surfaces and, hence, are attributed to the bulk-related bands. It is worth noting, however, that the bands reflect the electronic structures of the relatively shallow region because of the limited escape depth of the photoelectrons.

Recent scanning tunneling microscopy (STM) studies have revealed that, on ZnO-Zn, nanoscale triangular pits and islands cover the (1x1) terraces so that the step density on the surface is quite high, whereas the density of steps is much lower on ZnO-O [1]. It is possible that morphology of the polar surfaces affect the valence electronic structures in the near-surface region. Therefore, difference in the dispersion widths of the bands depending on the polar surfaces is considered to arise from different surface morphology.

Reference

[1] O. Dulub et al., *Surf. Sci.* **519**, 201 (2002).

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