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Experimental observation of bulk band dispersions in the oxide semiconductor ZnO using soft x-ray angle-resolved photoemission spectroscopy

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The electronic structure of the oxide semiconductor ZnO has been investigated using soft x-ray angle-resolved photoemission spectroscopy (ARPES). The obtained band dispersions within the k_x-k_y planes reflect the symmetry of the Brillouin zone and show no surface-state-derived flat bands. Band dispersions along the k_z direction have also been observed. The obtained band dispersions qualitatively agree with band-structure calculations except for the bandwidth. The observations provide experimental evidence that soft x-ray ARPES enables us to study the bulk band structure of semiconductors. © *2009 American Institute of Physics.* [DOI: 10.1063/1.3116223]

I. INTRODUCTION

ZnO is one of the most promising oxide semiconductors for applications in oxide electronics. ZnO crystallizes in the hexagonal wurtzite structure, is an *n*-type semiconductor, has an optical band gap of ~3.4 eV, and has a large exciton binding energy of ~60 meV. Their inexpensiveness and environmental safety are also advantages for practical applications. Recently, *p*-type ZnO has been successfully prepared and ZnO-based light-emitting diode has demonstrated violet electroluminescence at room temperature.[1] Moreover, quantum Hall effect in polar $ZnO/Mg_xZn_{1-x}O$ heterostructure has been demonstrated.[2] In addition, ZnO-based diluted magnetic semiconductors are candidates for transparent ferromagnets.[3] Therefore, ZnO has attracted considerable attentions as materials for future technologies.[4]

In order to obtain a fundamental understanding of the physical properties of ZnO and devices using ZnO, it is desired to reveal the bulk electronic structure. Information about the occupied electronic states will be useful for *p*-type ZnO (Refs. 5 and 6) and for device design such as quantum wells using ZnO.[7] Reflecting the wurtzite structure, the Brillouin zone of ZnO has hexagonal symmetry, as shown in Fig. 1. So far, the electronic states of ZnO surfaces have been investigated by angle-resolved photoemission spectroscopy (ARPES) using photons in the ultraviolet region ($h\nu < 150$ eV),[8–10] in which photoelectron escape depth is several angstroms. It has recently been pointed out the usefulness of photoemission spectroscopy (PES) using higher photon energies ($h\nu$) for probing the bulk electronic properties of materials.[11] Actually, the three-dimensional Fermi surfaces of a heavy Fermion compound $CeRu_2Ge_2$ have been determined by means of soft x-ray (SX) ARPES.[12] In this work, we have performed a SX-ARPES study on a ZnO thin film in order to study the bulk electronic properties. We have succeeded in observing clear band dispersions in ZnO without bands due to surface states.

II. EXPERIMENTAL

A single crystalline ZnO thin film was homoepitaxially grown on a ZnO(0001) substrate by the pulsed laser deposition technique using an ArF excimer laser. During the deposition, the substrate was kept at 400 °C in an oxygen pressure of 0.1 Pa. The total thickness of the deposited ZnO layer
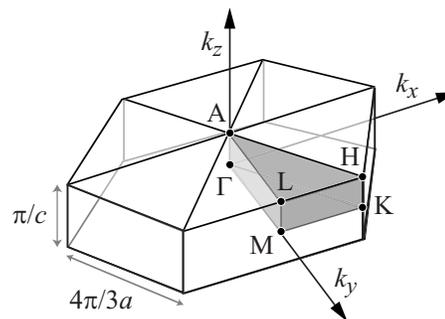

FIG. 1. Brillouin zone of ZnO: circles show high symmetry points. The shaded area is the primitive unit cell of the Brillouin zone. The lattice constants *a* and *c* are 3.25 and 5.21 Å, respectively.

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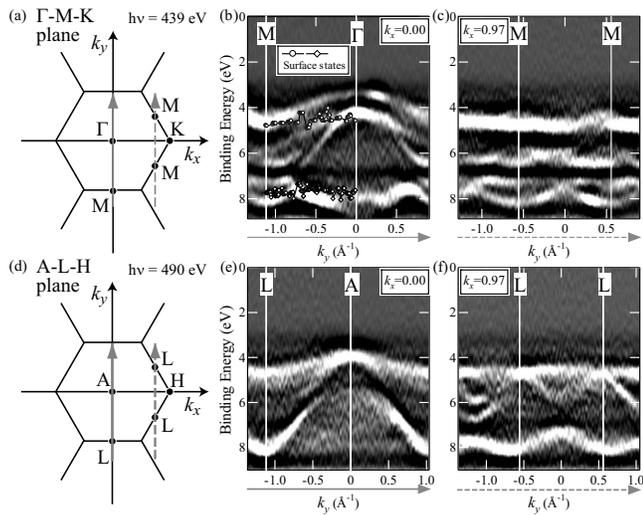
FIG. 2. k_y scans in hexagonal planes of the ZnO Brillouin zone: photon energies of $h\nu$=439 and 490 eV were chosen so as to study the Γ-M-K and A-L-H planes, respectively. (a) The Γ-M-K plain. The arrows denote sliced directions. (b) The intensity plot of the second derivative EDC in E-k space along the Γ-M and M-M directions with k_x=0.00 Å. The surface bands have been reproduced from Ref. 8. (c) The intensity plot of the second derivative EDC in E-k space along the M-M direction with k_x=0.97 Å. The same graphs for the [(d)–(f)] A-L-H plane as those for the [(a) –(c)] Γ-M-K plane.

FIG. 3. Constant-energy contour plots of the photoemission intensity in the (a) Γ-M-K plane and the (b) A-L-H plane. The solid lines are the Brillouin-zone boundaries.

was $\sim$100 nm. The lattice constant c is estimated to be $\sim$5.20 Å from x-ray diffraction measurements.

ARPES measurements were performed at the SX beamline BL23SU of SPring-8.[13] The sample was kept at 100 K during the measurements. The monochromator resolution was $E/\Delta E > 10\,000$. The total resolution of the ARPES measurements including temperature broadening was $\sim$130 meV. The sample surface was cleaned by repeated Ar$^+$-ion sputtering and subsequent annealing in an oxygen atmosphere. Cleanliness of the sample surface was checked by the absence of a high binding-energy shoulder in the O 1s core-level photoemission spectrum and the C 1s core-level signal from contamination. The position of the Fermi level (E_F) was determined by measuring the PES spectra of evaporated gold, which was electrically in contact with the sample.

First-principles calculations of the electronic structure of ZnO were performed by applying the relativistic linearized augmented-plane-wave method based on the relativistic Dirac equation.[14] In the calculations, the exchange and correlation potentials were used within the local-density functional formalism, and the potentials and the charge densities were calculated in the muffin-tin approximation. Here, the experimental lattice constants a and c were chosen as 3.25 and 5.21 Å, respectively.

III. RESULTS AND DISCUSSION

Figure 1 shows the Brillouin zone of ZnO. In Fig. 2, the second derivative of energy distribution curves (EDCs) is plotted in $E-k_y$ space for various curves in the Brillouin zone. The valence-band maximum is located at the binding energy $E_B \sim 3.0$ eV. The E_F is considered to be located near the bottom of conduction band due to the n-type semiconducting nature of ZnO. The Zn 3d band appears at the bind-
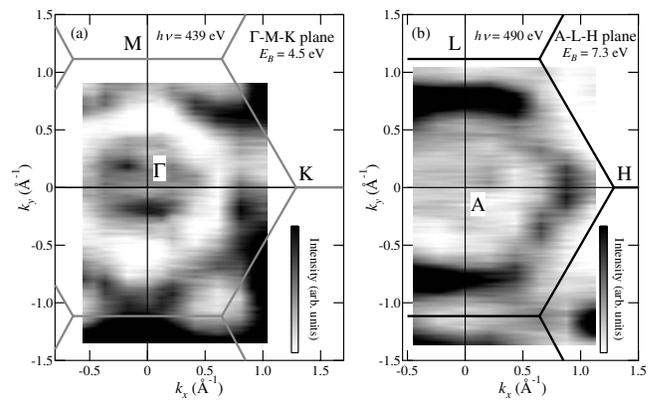
ing energy (E_B) around $\sim$10.5 eV. The clear dispersive features in the O 2p band indicate that the thin film is a highly oriented single crystal.

In Fig. 2, we show band dispersions in $k_x - k_y$ planes including the Γ point (Γ-M-K plane) and the A point (A-L-H plane). Many dispersive bands along the Γ-M direction have been observed, as shown in Fig. 2(b). Each of the bands has a different dispersive bandwidth, but these bands have common periodicity in crystal momentum k corresponding to the symmetry of the Brillouin zone. In fact, the dispersions along the M-M direction crossing the two boundaries have shorter periodicity, as shown in Fig. 2(c), than these along the Γ-M one. Although the dispersive features of the bands in the A-L-H plane, which is a $k_x - k_y$ plane including the A point [Fig. 2(d)], differ from those in the Γ-M-K one, the symmetry is the same between the two planes, as shown in Figs. 2(e) and 2(f). It is important to remark here that dispersion less (or flat) bands due to the surface states reported in Ref. 8 were not observed [see Fig. 2(b)], suggesting that the surface atomic structure, if they exist, hardly affects the ARPES spectra measured by SX APRES because of the bulk sensitivity.

In order to confirm the overall symmetry of the bands, constant-energy intensity contours at the Γ-M-K and A-L-H planes are plotted in Fig. 3. In the contour plot of the Γ-M-K plane at E_B=4.5 eV [Fig. 3(a)], the shape of band around Γ point is hexagon, the same as the Brillouin zone, and the second band shows hexagonal feature rotated by $\pi/6$ compared with the Brillouin zone. The contour plot of the A-L-H plane at E_B=7.3 eV [Fig. 3(b)] demonstrates that the bands in the A-L-H plane also have hexagonal symmetry. Therefore, all the contours reflect the hexagonal symmetry of the Brillouin zone independent of k_z or $h\nu$ and E_B, indicating that the obtained band dispersions are originated from the electronic structure of ZnO. It follows from the observations that we have succeeded to probe the bulk electronic structure of ZnO by SX ARPES.

Besides the in-plane measurements, we have also measured the k_z dependence of the band dispersions by turning $h\nu$. Figure 4 shows the k_z dependence of the band dispersion along the direction parallel to the Γ-M line. The dispersions taken with $h\nu$=430 eV are almost the same as those with
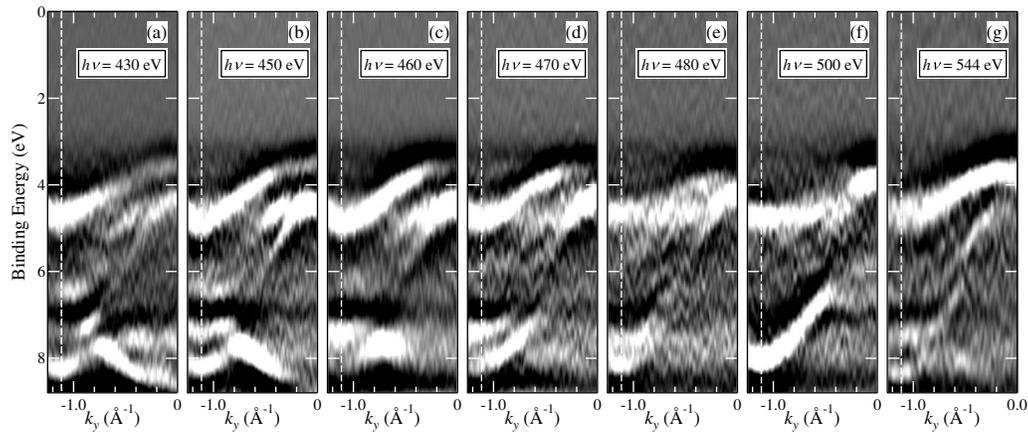
FIG. 4. k_y scan along the lines parallel to the Γ-*A* direction. [(a)–(g)] k_y−*E* intensity plot along the Γ-*M* direction to the *A-L* direction taken with $h\nu$=430, 450, 460, 470, 480, 500, and 544 eV. Dashed lines are the boundary of the Brillouin zone (*M-L* line).

$h\nu$=450 eV, as shown in Figs. 4(a) and 4(b). In addition, the dispersions taken with $h\nu$=480 eV are similar to those with $h\nu$=500 eV, as shown in Figs. 4(e) and 4(f). Collecting photoelectrons emitted in the surface normal direction k_z of photoelectron is given by

$$k_z = \frac{\sqrt{2m_0}}{\hbar}\sqrt{(h\nu - \phi - E_B) + V_0}, \qquad (1)$$

where m_0 is electron rest mass, ϕ is the work function, and V_0 is the inner potential. One can estimate the value of V_0 from the periodicity in k_z in units of π/c. The inner potential has been thus derived to be ~13.5 eV, consistent with the previous measurements.[8] Indeed, dispersive features in the ARPES spectrum taken with $h\nu$=544 eV [Fig. 4(g)], which correspond to the Γ point in the higher Brillouin zone (k_z $=\pi/c$) estimated from the value of V_0, are similar to that with $h\nu$=439 eV [Fig. 2(b)] although there are differences in the intensity. The observations also suggest that no surface states-induced band is observed by SX ARPES because the surface band is independent of k_z.

Finally, we summarize the obtained band dispersions and compare them with local-density approximation (LDA) calculations. Figure 5(a) shows the band dispersions in ZnO along the high symmetry lines of the Brillouin zone. All the bands are smoothly connected with each other at the zone boundaries, suggesting the high accuracy of the measurements. Figure 5(b) shows the LDA band-structure calculations along the high symmetry lines, and the origin of energies is chosen at the conduction-band minimum (CBM). The LDA calculations qualitatively well reproduce the experimental dispersive features, while there are quantitative differences in the bandwidth between the experiment and calculated dispersions. The experimental and calculated bandwidths are ~5.3 and ~3.9 eV, respectively. The LDA calculation underestimates the band gap as ~3.2 eV. The discrepancy between the ARPES spectra and the band structure calculation will be reduced to some extent in the LDA +GW approximation, which expands the bandwidth compared with the LDA calculation.[15,16]

IV. SUMMARY

We have performed SX-ARPES measurements on a ZnO thin film. All the obtained band dispersion reflects the hexagonal Brillouin zone of ZnO, indicating that we have succeeded in the observation of bulk electronic structure. The first-principles calculations qualitatively well explain the obtained band dispersion. We believe that the present work opens a way to understand semiconductors from the electronic structure points of view.
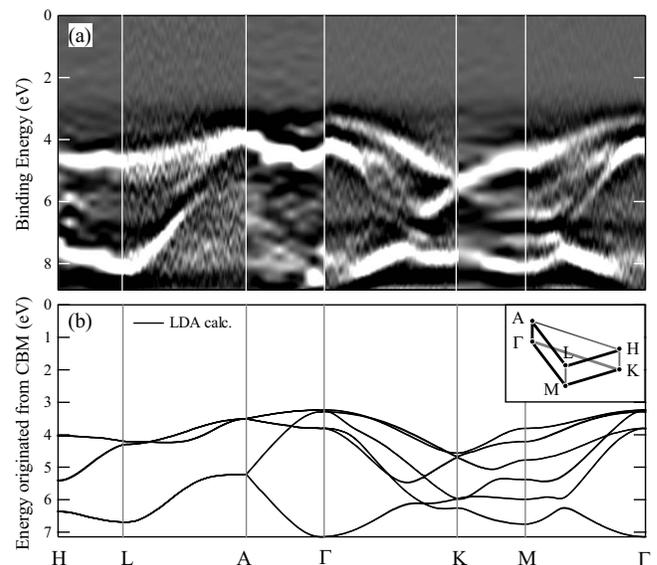
FIG. 5. Band dispersions of ZnO along the high symmetry lines of the Brillouin zone shown by bold lines in the inset. (a) Experiment. (b) Band structure calculation. The origin of energy is chosen at the CBM.

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