

## Polarity-dependent photoemission spectra of wurtzite-type zinc oxide

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The polar surfaces of wurtzite-type zinc oxide (ZnO) were characterized by x-ray photoemission spectroscopy to identify the origin of the polarity dependence of the valence band spectra. A characteristic sub-peak always appeared in the valence band spectra of the (0001) face regardless of the surface preparation conditions. It also appeared in the valence band spectra of the (10 $\bar{1}$ 2) face, but only when the photoelectron take-off angle was parallel to the *c*-axis of ZnO. Our analysis demonstrates that this take-off angle dependency originates not from the surface state, photoelectron diffraction, or the presence of surfactants but from the crystal polarity. © 2012 American Institute of Physics. [doi:10.1063/1.3673553]

Crystal polarity is an important consideration in the industrial applications of wurtzite-type (WZ-type) semiconductors.<sup>1-3</sup> For example, in WZ-type zinc oxide (ZnO), crystal polarity is the reason for the much higher chemical stability of the (0001) face compared with the (000 $\bar{1}$ ) face,<sup>1</sup> the formation of a two-dimensional electron gas in ZnO-based heterostructures,<sup>2</sup> and the higher probability for incorporation of donor-like defects on the (000 $\bar{1}$ ) facet than on the (0001) facet during crystal growth.<sup>3</sup> These effects on surface and interfacial properties are also significant in GaN based light-emitting diodes (LEDs), where considerable attention has been devoted to charge separation by the internal electric field along the *c*-axis, which reduces device efficiency.<sup>4</sup> Indeed, the electronic structure and physical phenomena in polar semiconductors are crucial for the development of a wide range of optoelectronic devices.

Recently, x-ray photoemission spectroscopy (XPES) has been found to be a useful probe for characterization of the polar surfaces of WZ-type semiconductors,<sup>5-7</sup> because their valence band spectra exhibit polarity dependence. In fact, an as-yet unexplained characteristic sub-peak appears in the valence band spectra of the (0001) surface but not in those of the (000 $\bar{1}$ ) surface; typical profiles of sub-peaks in the valence band spectra are shown later in this report as well as in Refs. 5-7. Previously, it was attributed to the presence of surfactants such as indium (In) adatoms on the (0001) face of indium nitride (InN).<sup>5</sup> However, this explanation is rather unlikely, because the sub-peak still appeared for an as-deposited ZnO surface formed by physical deposition and on a well-polished single-crystal surface.<sup>6,7</sup>

To further pursue the origin of this polarity dependence, we extensively investigated the valence band spectra of ZnO

by XPES with two excitation sources: conventional monochromated aluminum K $\alpha$  (Al K $\alpha$ ) radiation (soft x-ray XPES, or SXPES) and synchrotron radiation, specifically, highly monochromated 6-keV x-rays (hard x-ray XPES, or HXPES). Because of the difference in the photoelectron inelastic mean free path (IMFP) between SXPES and HXPES, the results are surface sensitive and bulk sensitive, respectively.<sup>6</sup>

The SXPES measurements were performed using a  $\Sigma$  Probe spectrometer (Thermolectron Co. Ltd., Yokohama, Japan), and the HXPES measurements were performed at the National Institute for Materials Science (NIMS) contract beamline (BL15XU) at SPring-8, Japan. The instrumental setup at the BL15XU facility is described elsewhere.<sup>8</sup> The XPES studies were performed using the (0001), (10 $\bar{1}$ 2), (000 $\bar{1}$ ), and ( $\bar{1}$ 01 $\bar{2}$ ) faces of ZnO single crystals. The surfaces were prepared by chemical mechanical polishing (CMP)<sup>9</sup> if not otherwise specified. Note that the ZnO surfaces prepared by CMP showed relatively strong near-band-edge (NBE) emission in their photoluminescence spectra, which indicates low defect concentrations. Additionally, to examine the effect of surface preparation, we also characterized mechanically ground wafers and wafers etched by *in situ* Ar ion sputtering.

As seen in the typical valence band spectra obtained normal to the surface in Fig. 1, a sub-peak centered at about 4.8 eV in binding energy ( $E_b$ ) appeared in the valence band spectra for the (0001) face and not the (000 $\bar{1}$ ) face. Note that the overall shapes of the SXPES and HXPES spectra differ because of the excitation energy dependence of the partial photoionization cross-section. Furthermore, because HXPES is not surface sensitive but bulk sensitive, this comparison indicates that origin of the sub-peak is not highly localized to the topmost surface.<sup>8</sup> Furthermore, Allen *et al.*<sup>10</sup> reported very recently that the sub-peak was not obvious when using

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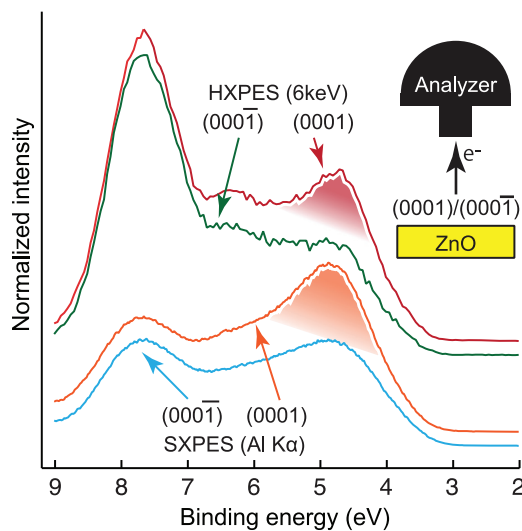


FIG. 1. (Color online) Valence band spectra of the (0001) and (000 $\bar{1}$ ) surfaces from single-crystal ZnO prepared by CMP. The sub-peaks are denoted by filling.

very soft x-rays ( $h\nu < 0.5$  keV), which also supports our idea that the sub-peak originated neither from surface states nor from adsorbates.

However, one may still consider the contribution of adsorbates via interactions with defects in ZnO through charge compensation phenomena, as it is known that the (0001) and (000 $\bar{1}$ ) facets differ in chemical properties.<sup>1</sup> To answer this question, we compared the XPES spectra obtained after using different surface preparation techniques, as shown in Fig. 2. The figure shows that the sub-peak persisted even after any adsorbed carbonate, water, and/or hydroxide was removed by *in situ* ion etching with a 5-keV Ar ion beam. The figure also shows a clear sub-peak for the obviously rough surfaces (inset to Fig. 2) prepared by mechanical grinding.

Here, we first assume that mechanical grinding and CMP leave different kinds and concentrations of adsorbates on the ZnO surface because of the obvious difference in sur-

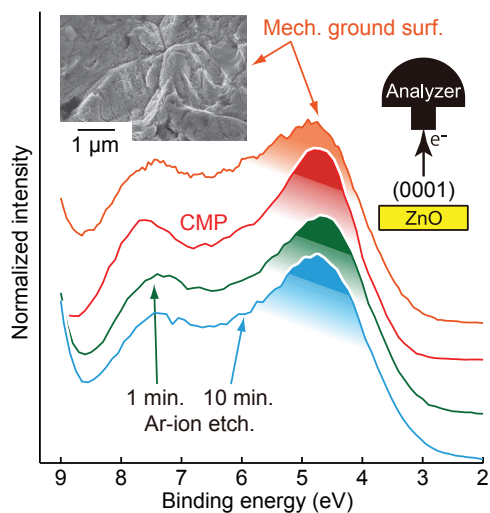


FIG. 2. (Color online) Valence band spectra of the (0001) face of ZnO prepared by CMP, mechanical grinding, and Ar ion sputtering for 1 or 10 min, measured using Al K $\alpha$  radiation. The inset shows a scanning electron micrograph of the mechanically ground surface.

face area and morphology. We also assume that the former process introduces a relatively huge concentration of defects, since the luminescence properties of ZnO were suppressed completely after grinding.<sup>9</sup> However, regardless, the sub-peak was found in the valence band spectra for the (0001) face and not the (000 $\bar{1}$ ) face. In addition, note that mechanical grinding and ion etching afforded a broader sub-peak than CMP. This broadening is attributed to the degradation in crystallinity caused by these methods. Thus, we can safely conclude that the appearance of the sub-peak cannot be explained by surface contamination, defect concentration, or surface roughness.

As mentioned, for WZ-type InN,<sup>5</sup> the appearance of the sub-peak was previously attributed to excess In on the (0001) face, because the (In 3d)/(N 1s) peak intensity ratio in the XPES spectra for the (0001) face was different from that for the (000 $\bar{1}$ ) face. Similar facet dependence has also been reported for the (Zn 2p)/(O 1s) peak intensity ratio.<sup>10</sup> However, such facet dependence observed in ZnO core-level peak intensities has been attributed to x-ray photoelectron diffraction (XPD) rather than non-stoichiometry.<sup>11</sup> Thus, in the current state of knowledge, we must assume that the facet-dependent appearances of the sub-peak and variation in core-level peak intensity have different origins.

In fact, we must consider XPD as the principal reason for the variations in peak intensity, particularly for single-crystal samples. Furthermore, it is possible that the appearance of the (0001) face sub-peak is due to the XPD process, assuming forward scattering. To investigate this, we performed angle-resolved XPES (ARXPES) measurements on the (0001) face. Further details of the ARXPES results and the procedure for evaluation of the relative areal sub-peak intensities are described elsewhere.<sup>12</sup> As shown in Fig. 3, the relative sub-peak intensity gradually decreased with increasing polar angle ( $\theta$ ), and the sub-peak disappeared for  $\theta > 40^\circ$ . A comparison with previously published XPD patterns for the Zn 2p<sub>3/2</sub> and O 1s core-level peaks<sup>11</sup> indicates that the observed  $\theta$  dependence of the sub-peak intensity is

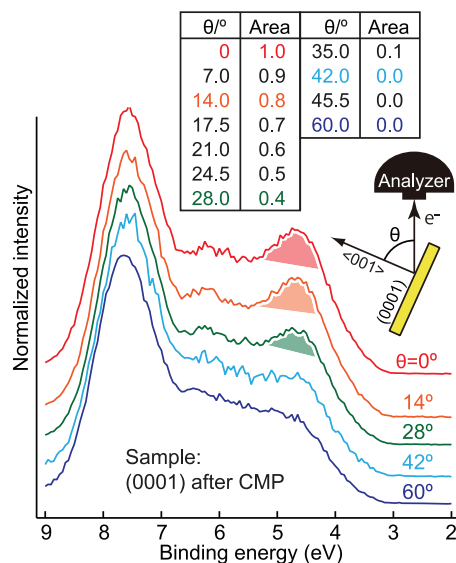


FIG. 3. (Color online) Angle-resolved valence band spectra from the (0001) face of ZnO measured with 6-keV synchrotron radiation. The inset lists the relative sub-peak areas at the measured  $\theta$ .

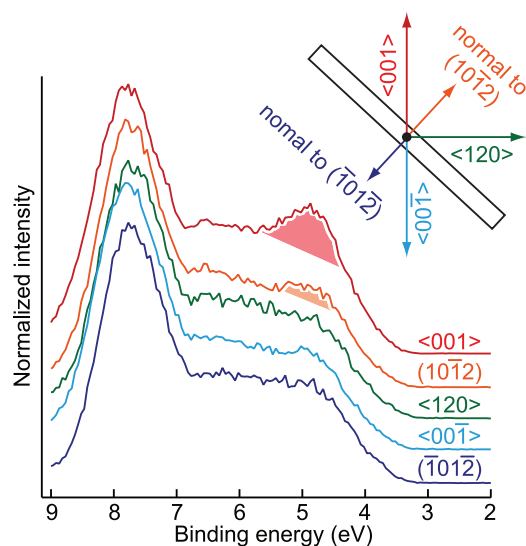


FIG. 4. (Color online) Angle resolved valence band spectra from the  $(10\bar{1}2)$  and  $(\bar{1}01\bar{2})$  faces of CMP-processed ZnO, measured using 6-keV synchrotron radiation. The inset denotes the photoelectron take-off angle for each spectrum.

not explained by the XPD mechanism. Note that the acceptance angle of the electron energy analyzer used in the HXPES study was about  $7^\circ$ . Consequently, we must conclude that the very broad  $\theta$  dependence was caused not by instrumental broadening but by the nature of the sample. Thus, the sub-peak was due purely to the crystal polarity.

Finally, we discuss the ARXPES results for the  $(10\bar{1}2)$  face, as shown in Fig. 4. The intensity of the sub-peak in the valence band of the  $(10\bar{1}2)$  face exhibited  $\theta$  dependence, and the highest sub-peak intensity appeared when the photoelectron take-off angle was parallel to the  $c$ -axis of ZnO. Note that the sub-peak was not observed from the  $(\bar{1}01\bar{2})$  face even when the take-off angle was parallel to the  $\langle 001 \rangle$  direction. Thus, the intensity of the sub-peak in the valence band peaked when the take-off angle of photoelectrons was normal to the  $(0001)$  plane, regardless of the facet orientation of the substrate. Hence, this peak cannot be attributed to any surface phenomenon.

In summary, a sub-peak appeared in the valence band spectra not only for the  $(0001)$  face but also the  $(10\bar{1}2)$  face when the take-off angle was parallel to the  $\langle 001 \rangle$  direction. Moreover, the sub-peak appeared for both  $(0001)$  and  $(10\bar{1}2)$  faces regardless of the surface preparation. Thus, we can safely conclude that appearance of sub-peak is a characteris-

tic of XPES spectra obtained with a take-off angle parallel to the  $\langle 001 \rangle$  direction. These results indicate that the sub-peak is not induced by facet orientation, surface states, or defects in the ZnO bulk. The polarity dependence of the valence band spectra is likely an intrinsic characteristic of polarization in WZ-type crystals. With these results, although the true origin of the sub-peak remains unknown, we may safely conclude that analysis of such polarity-dependent features is critical to understanding the physics and chemistry of polar semiconductors.

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<sup>12</sup>See supplementary material at <http://dx.doi.org/10.1063/1.3673553> for angle resolved XPES profile.