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Chevtchenko, S.A., Moore, J.C., Özgür, Ü., et al. Comparative study of the (0001) and (000 $\bar{1}$) surfaces of ZnO. Applied Physics Letters, 89, 182111 (2006). Copyright © 2006 AIP Publishing LLC.

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Comparative study of the (0001) and (000 $\bar{1}$) surfaces of ZnO

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(Received 31 May 2006; accepted 21 September 2006; published online 1 November 2006)

The authors compare the surface and optical properties of the Zn-polar (0001) and O-polar (000 $\bar{1}$) surfaces of bulk ZnO samples. For optical characterization, steady-state photoluminescence using a He–Cd laser was measured at 15 and 300 K. At room temperature, the (000 $\bar{1}$) surface demonstrates nearly double the near-band-edge emission intensity seen for the (0001) surface. Using scanning Kelvin probe microscopy, the authors have measured surface contact potentials of 0.39 ± 0.05 and 0.50 ± 0.05 V for the (0001) and (000 $\bar{1}$) surfaces, respectively. The resulting small difference in band bending for these two surfaces indicates that charge transfer between the surfaces is not a dominant stabilizing mechanism. Conductive atomic force microscopy studies show enhanced reverse-bias conduction in localized regions on the (000 $\bar{1}$) vs (0001) surface. The differences in surface conduction and band bending between the two polar surfaces can be attributed to their chemical interactions with hydrogen and water in the ambient. © 2006 American Institute of Physics.

[DOI: [10.1063/1.2378589](https://doi.org/10.1063/1.2378589)]

Zinc oxide (ZnO) has attracted substantial attention in recent years due to its use in a wide variety of applications such as sensors and UV photodetectors, where high-quality bulk materials are available at reasonable cost. ZnO has a strong spontaneous polarization along the [0001] direction with a value as high as 0.047 C/m^2 ,¹ which is significantly larger than that for another well-known wide band gap material, GaN (0.029 C/m^2). This spontaneous polarization may induce charges of opposite signs at the (0001) and (000 $\bar{1}$) surfaces, which would depend on the conductivity of the sample and the surface properties. Although extensive reports exist for the bulk properties of ZnO, there are few experimental studies concerning its surface properties. It has been theoretically predicted that hydrogen reacts differently with the (0001) and (000 $\bar{1}$) surfaces,² and that the (000 $\bar{1}$) surface forms Schottky barriers with a smaller barrier height.^{3,4} In this letter, we report a comparative study of the electrical and optical properties of the (0001) and (000 $\bar{1}$) surfaces.

The ZnO samples used in this study were diced from the same bulk crystal prepared by Cermet Inc.⁵ The (0001) and (000 $\bar{1}$) surfaces were obtained by mechanical polishing of the opposite sides of a [0001]-oriented crystal. The samples had a thickness of $\sim 380 \mu\text{m}$ and a carrier concentration of $4.5 \times 10^{16} \text{ cm}^{-3}$ at room temperature, corresponding to a Fermi level of 0.11 eV below the conduction band. This study examined as-received samples and samples that had been annealed in air ambient at 1050 °C for 60 min, with heating and cooling times of 90 min each. Such an ambient heating treatment is known to enhance surface smoothness.

Steady-state photoluminescence (PL) data was obtained using the 325 nm line of a He–Cd laser and collected by a

photomultiplier tube attached to a 0.5 m Spex grating monochromator. The PL signal was measured at 15 and 300 K in a closed-cycle optical cryostat. Scanning Kelvin probe microscopy (SKPM) was used to measure the contact potential difference (V_{cp}) between the ZnO surfaces and a gold-coated tip. The surface band bending was calculated^{6,7} using the work function for Au (5.1 eV), the measured experimental offset (determined by V_{cp} on a Au calibration sample), the sample's Fermi level with respect to the conduction band, and the electron affinity of ZnO (values range from 4.6 to 4.2 eV).^{8–10} Conductive atomic force microscopy (C-AFM) was also performed to measure local electrical properties of the samples. The voltage bias was applied through an Ohmic indium contact to the sample surface, and a Ti/Pt-coated tip acted as a microscopic Schottky contact. In this geometry, a positive bias to the sample corresponds to a reverse bias of the Schottky contact. Both the SKPM and C-AFM data were acquired using a Veeco dimension-3100 atomic force microscope with standard attachments.

Figure 1 shows low-temperature PL data for the as-received (000 $\bar{1}$) surface with the following main transitions indicated:¹¹ free exciton (FX_A), donor bound exciton (D^0X_A), two-electron satellite (TES), donor acceptor pair (DAP), and their LO-phonon replicas. The most intense donor bound exciton transition at 3.359 eV has a full width at half maximum of 1.7 meV, indicating a high-quality sample. We did not observe any significant difference between the low-temperature PL spectra for the (0001) and (000 $\bar{1}$) surfaces. At room temperature, however, a difference in the intensity of the near-band-edge emission was notable. The (000 $\bar{1}$) surface demonstrated a PL intensity 1.8 times higher than that obtained for the (0001) surface. The corresponding spectra are shown in the inset of Fig. 1.

Figure 2 shows tapping-mode AFM images of the surface topography for as-received and annealed ZnO samples.

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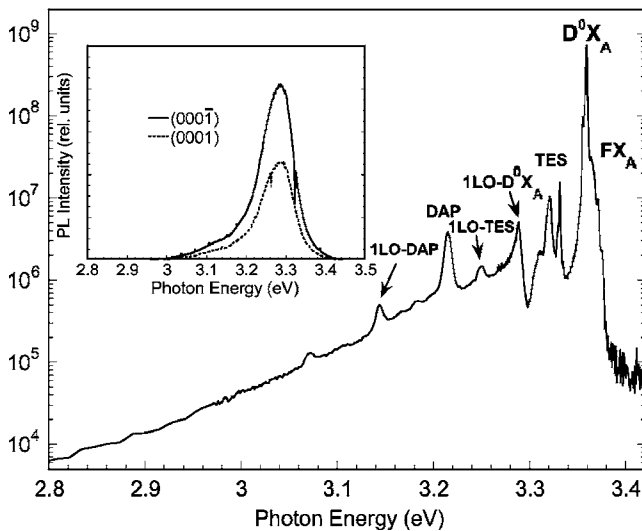


FIG. 1. PL spectrum of an air-exposed ZnO (000 $\bar{1}$) sample measured at 10 K. Free exciton (FX_A), donor bound exciton (D⁰X_A), two-electron satellite (TES), donor acceptor pair (DAP) transitions, and their LO-phonon replicas are marked. Inset shows PL spectra of air-exposed (001) and (000 $\bar{1}$) samples at 300 K.

Before annealing, both the (0001) and (000 $\bar{1}$) surfaces have relatively smooth morphologies with no discernible step-plus-terrace structure. The rms surface roughness of the (000 $\bar{1}$) surface (1.2 nm) is approximately twice that of the (0001) surface (0.64 nm). After annealing, the (0001) surface [Fig. 2(c)] rearranges to form bunched steps with wide terraces, whereas the (000 $\bar{1}$) surface [Fig. 2(d)] forms a uniform distribution of steps. In general, the annealing process improves the ordering of the surface structure. C-AFM data were acquired for both the as-received and annealed sur-

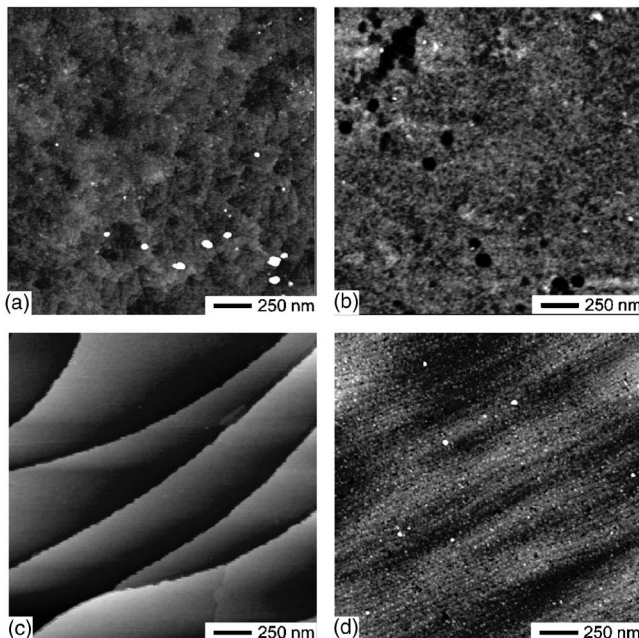


FIG. 2. Tapping-mode AFM images ($2 \times 2 \mu\text{m}^2$) of (a) as-received ZnO (0001) ($\Delta z=5$ nm, $z_{\text{max}}=18$ nm, rms=0.64 nm); (b) as-received ZnO (000 $\bar{1}$) ($\Delta z=8$ nm, $z_{\text{max}}=23$ nm, rms=1.2 nm); (c) annealed ZnO (0001) ($\Delta z=8$ nm, $z_{\text{max}}=8$ nm, rms=1.1 nm, on terrace rms=0.1 nm); and (d) annealed ZnO (000 $\bar{1}$) ($\Delta z=12$ nm, rms=0.6 nm).

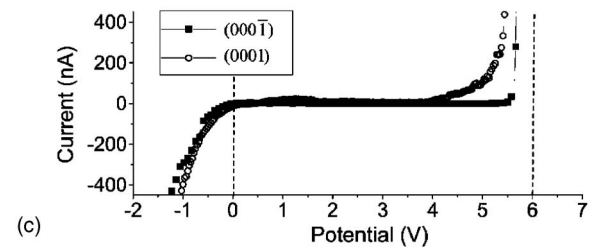
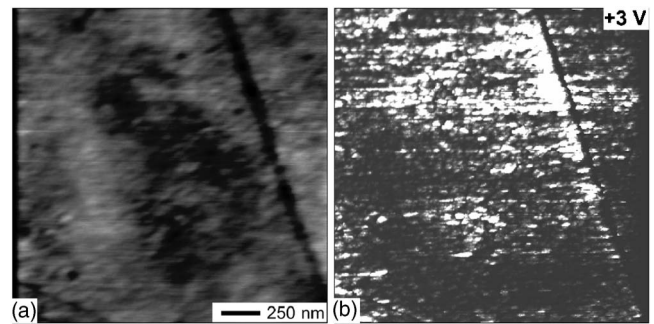


FIG. 3. (a) Contact-mode AFM image ($2 \times 2 \mu\text{m}^2$) of as-received ZnO (000 $\bar{1}$) and (b) simultaneous C-AFM current image at 3 V reverse bias ($\Delta I=100$ nA, $I_{\text{max}}=760$ nA, rms=71 nA). (c) Local I - V spectra measured at low-conductance regions on ZnO (0001) and ZnO (000 $\bar{1}$).

faces. Figures 3(a) and 3(b) show simultaneous contact-mode AFM and current images of an as-received (000 $\bar{1}$) surface. The white areas in the current image indicate local regions having high current leakage at 3 V reverse bias. Such leakage behavior was not observed for the (0001) surface at these relatively low bias voltages. The annealing process did not change this behavior in any significant manner. Figure 3(c) shows representative I - V spectra measured at locations demonstrating no leakage at 3 V on both the (0001) and (000 $\bar{1}$) surfaces. Both surfaces demonstrate reverse-bias conduction between 4 and 6 V at a variety of surface locations. The only distinct difference between the two surfaces is the significantly more abrupt breakdown in reverse bias for the (000 $\bar{1}$) vs (0001) surface.

With regard to surface potential, SKPM images of the as-received samples were uniform with no discernible features. The (0001) and (000 $\bar{1}$) surfaces had average contact potentials of 0.39 ± 0.05 and 0.50 ± 0.05 V, respectively. The corresponding upward band bending was 0.03–0.40 eV for the (0001) surface and –0.08 to 0.29 eV for the (000 $\bar{1}$) surface, depending on the chosen value for electron affinity (4.6–4.2 eV). The unexpectedly negative value for band bending requires a correction for the maximum electron affinity of 0.13 eV, which gives $\chi_{\text{max}}=4.44$ eV. Interestingly, our measured band bending for ZnO is significantly smaller than that observed for polar GaN surfaces (0.9 eV).¹² It should be noted that a recent x-ray photoemission spectroscopy/ultraviolet photoemission spectroscopy study⁴ found a downward band bending of 0.9 eV for n -type, untreated ZnO(0001) surfaces ($n \sim 10^{17} \text{ cm}^{-3}$), which indicates the presence of an accumulation layer not found in our studies. The SKPM of the annealed samples indicated that the difference in band bending between the (0001) and (000 $\bar{1}$) surfaces remains the same, while the absolute value of the band bending increases by ~ 0.1 eV. The difference in band

bending for the two ZnO surfaces is consistent with room temperature PL, where the lower band bending for the (000 $\bar{1}$) surface corresponds to its stronger intensity for near-band-edge emission at room temperature. Such a correlation was previously observed for GaN and was attributed to the difference in the density of surface states acting as centers of nonradiative recombination.¹³ Therefore, the density of surface states appears to be lower on the (000 $\bar{1}$) than on the (0001) surface.

There are a number of proposed stabilization mechanisms for ZnO polar surfaces, including charge redistribution between the (0001) and (000 $\bar{1}$) surfaces,¹⁴ surface reconstructions in the absence of hydrogen,^{15,16} and hydroxylated surfaces in the presence of hydrogen.^{15–17} Concerning the last case, ZnO surfaces have been reported to show large reactivity to molecular hydrogen and water, making this material useful as a hydrogen sensor.¹⁸ In our studies, a relatively small value of surface band bending for both surface orientations indicates the absence of charged surfaces and does not support a charge redistribution mechanism. Given that the surfaces are exposed to ambient, some type of hydroxide layer should be present. The observed differences in band bending and conduction behavior between the (0001) and (000 $\bar{1}$) surfaces may therefore indicate differences in the adsorbed surface states resulting from the formation of a hydroxide layer. Theoretically, it has been shown that formation of OH groups on the (0001) surface results in a nonmetallic behavior, whereas H adsorption on the (000 $\bar{1}$) surface results in a metallic behavior.² Our C-AFM studies show increased conduction in localized regions on the (000 $\bar{1}$) vs (0001) surface. This result may indicate localized reactivity of the surface with hydrogen in the ambient (H₂ or H₂O) to form hydroxyl species. The difference in surface conduction for the two polar surfaces is also consistent with the observed difference in band bending. The lower band bending observed for the (000 $\bar{1}$) vs (0001) surface indicates the formation of a narrower depletion layer, which should result in increased conduction for the (000 $\bar{1}$) surface.

In conclusion, we have compared surface and optical properties of the (0001) and (000 $\bar{1}$) surfaces of a bulk ZnO sample. The absolute value of the band bending was determined to be in the range from 0.05±0.05 to 0.29±0.05 eV

for the (000 $\bar{1}$) surface, corresponding to an electron affinity in the range of 4.44–4.20 eV. Band bending for the (0001) surface was found to be 0.11 eV higher than that for the (000 $\bar{1}$) surface. This relatively small difference in band bending for ZnO with a strong spontaneous polarization along [0001] indicates that charge redistribution between the (0001) and (000 $\bar{1}$) surfaces is not a dominant contributor. Using C-AFM, we have also observed higher reverse-bias conduction on the (000 $\bar{1}$) vs (0001) surface. This difference can be accounted for by different surface reactivities with air, in particular with water and hydrogen, and/or as a result of different band bendings.

This work is supported by the NSF and AFOSR (G. L. Witt and K. Reinhardt). The authors would like to thank V. Avrutin for useful discussions.

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