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## Electronic behavior of the Zn- and O-polar ZnO surfaces studied using conductive atomic force microscopy

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We have used conducting atomic force microscopy (CAFM) to study the morphology and electronic behavior of as-received and air-annealed (0001) Zn- and (000 $\bar{1}$ ) O-polar surfaces of bulk ZnO. Both polar surfaces exhibit relatively flat morphologies prior to annealing, which rearrange to form well-defined steps upon annealing in air at 1050 °C for 1 h. Long-term exposure to air results in surface layer pitting and the destruction of steps for both the as-received and air-annealed (000 $\bar{1}$ ) surfaces, indicating its enhanced reactivity relative to the (0001) surface. CAFM *I-V* spectra for polar surfaces are similar and indicate Ohmic to rectifying behavior that depends on the maximum applied ramp voltage, where higher voltages result in more conducting behavior. These data and force-displacement curves suggest the presence of a physisorbed H<sub>2</sub>O layer, which is removed at higher voltages and results in higher conduction. © 2009 American Institute of Physics.  
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The wide-bandgap material zinc oxide has attracted attention due to its use in a variety of sensor and optoelectronic applications and the relatively low cost for high-quality bulk material.<sup>1</sup> ZnO has a hexagonal wurtzite crystal structure with a strong spontaneous polarization along the  $\langle 0001 \rangle$  and  $\langle 000\bar{1} \rangle$  directions.<sup>2</sup> Several groups report that both the Zn-polar (0001) and O-polar (000 $\bar{1}$ ) surfaces react in ambient with water to form a hydroxide surface layer,<sup>3</sup> which can increase the surface conductivity via the formation of an accumulation layer.<sup>4</sup> *In situ* scanning tunneling spectroscopy studies by Dulub *et al.*<sup>5</sup> show semiconductorlike behavior for polar surfaces of ZnO single crystals. Previous *ex situ* conducting atomic force microscopy (CAFM) and scanning Kelvin probe microscopy studies show rectifying behavior for both polar surfaces; however, enhanced reverse-bias conduction and a larger surface contact potential are observed for the (000 $\bar{1}$ ) surface presumably due to increased chemical reactions with ambient water.<sup>6</sup> In this study, we use CAFM to examine the morphology and electronic behavior of the polar (0001) and (000 $\bar{1}$ ) surfaces. Specifically, we discuss the tip-induced desorption of surface water layers, which causes a change in the local electrical behavior.

The ZnO samples used in this study were diced from a bulk crystal prepared by Cermet, Inc. using a melt growth method described previously.<sup>1</sup> The (0001) and (000 $\bar{1}$ ) surfaces were obtained by mechanical polishing of the opposite sides of a bulk [0001]-oriented crystal. Samples had thicknesses 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. Samples designated “as-received” underwent no further treatment, whereas

annealed samples were heated in air at 1050 °C for 1 h. For CAFM data acquisition, Ohmic contacts were formed on all samples using indium solder, and a microscopic Schottky contact occurred between the metallized (Ti/Pt alloy) CAFM tip and sample. Bias voltages were applied to the sample with the tip at ground, and current measurements were obtained using a current amplifier module with a range of 5 pA–500 nA. Unless noted otherwise, each *I-V* curve represents the average of ten consecutive spectra. When indicated, the surface water layer thickness was determined using force-displacement curves<sup>7</sup> taken using Si cantilevers having a relatively low force constant ( $\sim 0.15 \text{ N/m}$ ).

Prior to annealing, both the Zn- and O-polar surfaces display relatively smooth morphologies albeit with pits. Large hexagonal pits ( $\sim 1 \mu\text{m}$  diameter, 20–800 nm deep) are observed on the Zn-polar surface [see Fig. 1(a)] and smaller pits ( $\sim 120 \text{ nm}$  diameter,  $\sim 15 \text{ nm}$  deep) are seen for the O-polar surface [see Fig. 1(b)]. Pit densities for the (000 $\bar{1}$ ) surface ( $5 \times 10^8 \text{ cm}^{-2}$ ) are approximately five times that of the (0001) surface ( $1 \times 10^8 \text{ cm}^{-1}$ ). After annealing, both surfaces show a step-plus-terrace structure, where the (0001) surface rearranges to form bunched steps with  $\sim 600 \text{ nm}$  wide terraces [see Fig. 1(c)] and the (000 $\bar{1}$ ) surface has shorter  $\sim 25 \text{ nm}$  wide terraces [see Fig. 1(d)]. This type of surface ordering and observed step formation following annealing has been observed in previous studies<sup>8,9</sup> with scanning tunneling microscopy (STM) images of ZnO(000 $\bar{1}$ ) annealed *in situ* at  $\sim 1200 \text{ °C}$  showing steps with flat terraces.<sup>10</sup>

Sample aging in ambient results in surface layer pitting and a disruption of the step-plus-terrace morphology for the air-annealed samples of both polarities. Figures 1(e) and 1(f) show the atomic force microscopy (AFM) topography images of the air-annealed (0001) and (000 $\bar{1}$ ) surfaces, respec-

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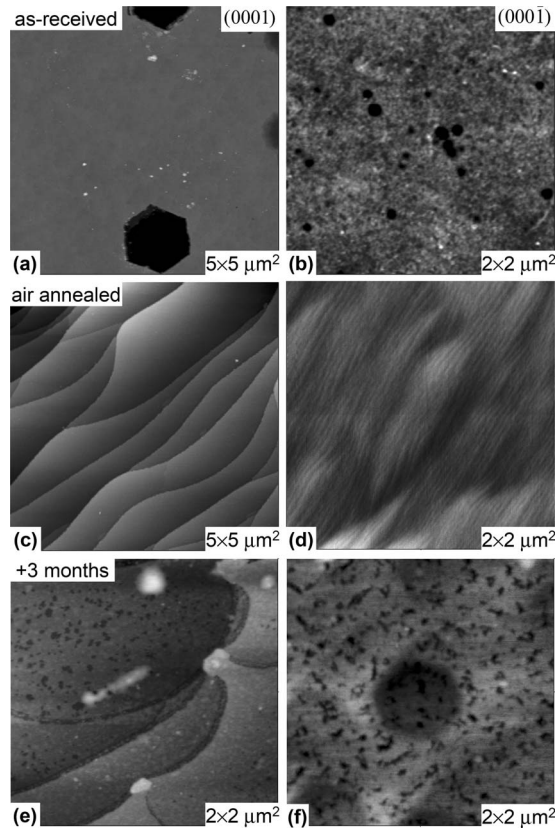


FIG. 1. Tapping-mode AFM topography images of the as-received (a) Zn-polar (0001) (grayscale range=50 nm) and (b) O-polar (000 $\bar{1}$ ) (grayscale range=8 nm) ZnO surfaces. Air-annealed (0001) and (000 $\bar{1}$ ) surfaces are shown in (c) and (d) immediately after treatment, respectively, and (e) and (f) after several months of exposure to ambient (grayscale ranges=20, 5, 20, and 25 nm, respectively).

tively, imaged after  $\sim 3$  months of storage in ambient. For both polarities, surface layer pitting is observed where small irregularly shaped pits ( $\sim 100$  nm diameter, 3–15 nm deep) decorate the surface. For the (0001) surface, the stepped morphology is retained, whereas for the (000 $\bar{1}$ ) surface individual steps are no longer visible and the surface exhibits shallow hexagonal pits (650 nm diameter, 10 nm deep) that are likely etch pits at dislocations.<sup>11</sup> The as-received (000 $\bar{1}$ ) surface exhibits a similar morphology after several months to that of the aged annealed surface. In contrast, the as-received (0001) surface shows a little change in morphology with time, which may be related to its lower step density with respect to the (000 $\bar{1}$ ) surface. This difference in aging behavior suggests a more reactive (000 $\bar{1}$ ) surface, which is consistent with other studies.<sup>11–13</sup>

CAFM current images for the as-received (0001) and (000 $\bar{1}$ ) surfaces show no significant correlation between topographical features and local conduction for both forward and reverse biases, which is consistent with previous studies.<sup>6</sup> However, local  $I$ - $V$  spectra show an interesting dependence on the maximum applied ramp voltage. As seen in Fig. 2, the conduction appears rectifying for ramps at or below  $\pm 5$  V and Ohmic at or above  $\pm 9$  V. The inset in Fig. 2(a) shows the  $I$ - $V$  behavior for the as-received (0001) surface that is initially Ohmic (filled circles) immediately after a

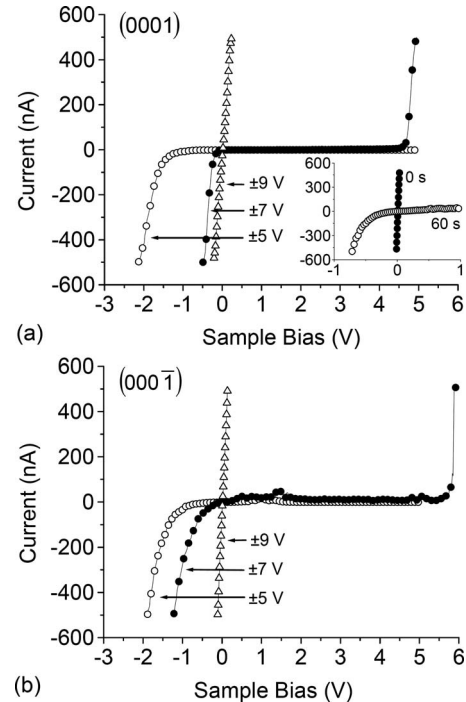


FIG. 2. CAFM  $I$ - $V$  spectra for the as-received (a) Zn-polar (0001) and (b) O-polar (000 $\bar{1}$ ) surfaces for ramp ranges of  $\pm 5$  V (hollow circles),  $\pm 7$  V (filled circles), and  $\pm 9$  V (hollow triangles). The curves in (a) are averages of ten consecutive spectra and in (b) are individual spectra. The inset shows the spectra for the (0001) surface acquired immediately after a  $\pm 12$  V ramp (filled circles) and after 60 s of continuous ramping at  $\pm 1$  V (hollow circles). Note that currents over 500 nA are railed.

ramp at  $\pm 12$  V but becomes rectifying (hollow circles) after 60 s of continuous ramping at  $\pm 1$  V. For positive sample bias the (0001) and (000 $\bar{1}$ ) surfaces typically show conduction for potential ramps at or above  $\pm 7$  V. For negative sample bias, conduction occurs at increasingly smaller values as the potential ramp is increased, eventually appearing Ohmic at or above  $\pm 9$  V. The only notable difference between the two surfaces is the stability of the  $I$ - $V$  spectra, where the (000 $\bar{1}$ ) surface demonstrates more significant fluctuations. After annealing, both polar surfaces show similar electronic behavior to the as-received surfaces; however, no Ohmic behavior was observed at the highest biases. This observation is consistent with studies that have shown annealing in air generates defects in the surface region that can produce an insulating layer.<sup>14</sup>

These changes in  $I$ - $V$  behavior as a function of maximum applied ramp voltage and exposure to air may be attributed to the presence of surface water. Figure 3(a) shows the  $I$ - $V$  spectra acquired for the as-received (0001) surface after aging for several months in ambient with its native water layer. AFM force-displacement measurements indicate an upper limit for the water-layer thickness in ambient of  $\sim 4$  nm (relative humidity of  $\sim 70\%$ ). Similar to  $I$ - $V$  spectra shown in Fig. 2, the turn-on voltage for conduction at negative sample bias decreases as the maximum ramp value is increased. It should be noted, however, that there are differences in the  $I$ - $V$  behavior for the ambient-aged sample which include smaller reverse breakdown voltages, larger forward turn-on voltages, and an absence of Ohmic behavior. Such

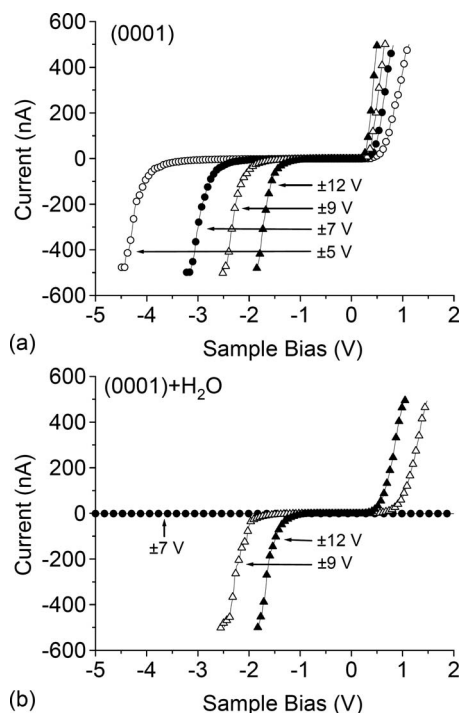


FIG. 3. CAFM  $I$ - $V$  spectra of the as-received (0001) surface after several months of exposure for (a) ambient conditions and (b) after introduction of an excess water layer for ramp ranges of  $\pm 5$  V (hollow circles),  $\pm 7$  V (filled circles),  $\pm 9$  V (hollow triangles), and  $\pm 12$  V (filled triangles).

changes in conduction behavior for aged samples are likely due to sample reactions with the ambient over time, which change the amount and types of defects present in the near-surface region. Figure 3(b) shows the  $I$ - $V$  spectra acquired for the same (0001) surface after the intentional introduction of a thicker water layer. A small drop of de-ionized water was placed on the sample surface and then removed using a cloth wipe. This procedure produced a surface water layer of  $\sim 8$  nm thick. The thicker water layer now leads to an insulating junction for a ramp value at or below  $\pm 7$  V but appears to have a negligible effect for ramps at or above  $\pm 9$  V. Such insulating behavior for ramp values that were previously conducting is also observed for several other ZnO surfaces with thicker water layers.

The presence of water at the tip-surface junction therefore has a measurable effect on the  $I$ - $V$  behavior. We propose that water is removed at the tip-surface junction for sufficiently high ramp voltages. Possible mechanisms for water removal may be either tip-induced electron stimulated desorption<sup>15,16</sup> or field-induced desorption.<sup>17</sup> Previous He-scattering studies suggest that  $H_2O$  physisorbs on the (000 $\bar{1}$ ) surface with a binding energy of 53 kJ/mol (or 0.55 eV).<sup>3</sup> Local removal of this layer may expose the conducting tip to the underlying hydroxide, resulting in Ohmic or weakly rectifying conduction for both polar surfaces in agreement with  $I$ - $V$  studies completed *in situ*.<sup>4</sup> This increased conduction at higher ramp voltages during CAFM  $I$ - $V$  ceases in less than 1 min if the ramp voltage is decreased below  $\sim \pm 5$  V. Therefore, the water layer in ambient must be continuously re-

moved at the tip-surface junction in order to observe enhanced conduction.

In summary, the surface morphology and current conduction for the (0001) and (000 $\bar{1}$ ) polar surfaces of ZnO have been studied both before and after annealing, as well as after storage in ambient. These surfaces exhibit similar surface morphologies that are flat prior to annealing. After annealing, the (0001) and (000 $\bar{1}$ ) surfaces form well-defined steps that are either bunched with wide terraces or uniformly distributed with short terraces, respectively. Long-term exposure to air results in morphological and electronic changes to the surface. Surface layer pitting for both annealed samples and the disordering of steps for the (000 $\bar{1}$ ) surface are observed with increased air exposure. Ohmic surface conduction is seen after minimal exposure to ambient, whereas weakly rectifying behavior is seen after longer exposure, which may be due to the generation of surface defects. Furthermore, CAFM  $I$ - $V$  data suggest that tip-induced desorption of a physisorbed  $H_2O$  layer leads to increased surface conduction. This would be consistent with the qualitatively similar  $I$ - $V$  behavior observed at increasing ramp voltages for as-received, air-annealed, and ambient-aged surfaces, regardless of differences in surface morphological features.

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