“Magic” Vicinal Zinc Oxide Surfaces

Hao Zheng,[1] Markus Gruyters,[1,*] Eckhard Pehlke,[2] and Richard Berndt[1]
[1]*Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany*
[2]*Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany*
(Received 2 May 2013; published 19 August 2013)

The structure of (0001) oriented ZnO single crystal surfaces is investigated by scanning tunneling microscopy. Depending on the preparation conditions, faceting of the crystals into large areas of $\{10\bar{1}4\}$ surface orientation occurs. This restructuring of the surface is shown to be a consequence of dipole compensation and charge neutralization. A new stabilization mechanism of polar oxide surfaces is found which is based on the formation of vicinal surfaces with special electronic and structural properties.

DOI: 10.1103/PhysRevLett.111.086101 PACS numbers: 68.35.B−, 68.37.Ef, 68.47.Gh

Many oxide crystals may be viewed as being composed of alternately charged planes of ions. A neutral crystal with surfaces matching such planes exhibits a net electric dipole moment. The electrostatic energy of these so-called polar surfaces of a bulk-terminated crystal is infinite or, for finite crystals and thick films, very large [1–3]. Thus, according to classical electrostatics, the bulk termination of a polar oxide surface is unstable. However, polar oxide surfaces may be stabilized by modifications of the charge density in the outer layers which compensate the surface charge density due to the polarity [1,3]. Possible mechanisms are the removal of surface atoms, electronic charge transfer, or adsorption of charged species. An alternative mechanism is faceting of the polar surface into nonpolar crystal planes. Considering the great variety of experimental results [1,4,5], it appears to be difficult to conclude which mechanism is the most relevant.

Zinc oxide crystallizes in the wurtzite structure. Its (0001) surface is a prototype for studying the physics and chemistry of polar oxide surfaces. In the [0001] direction, the crystal consists of alternating Zn and O planes [left in Fig. 1(a)]. As a result, the bulk-truncated (0001) surface is unstable. Various stabilization mechanisms have been suggested which depend on conditions such as sample preparation procedure and gas environment. Among these mechanisms are the removal of Zn surface atoms [6–8], charge transfer from the Zn-terminated to the O-terminated surfaces [9], and the formation of hydroxides [10]. While being a model system, ZnO also has many technological applications [4,11].

Here, we report on a novel stabilization mechanism of ZnO(0001), which is, in the bulk region, based on compensation of the microscopic dipole moments perpendicular to the surface and, in the surface region, on charge neutrality. These criteria are fulfilled only for a certain orientation of the surface with a high step density, i.e., a vicinal surface [right in Fig. 1(a)]. We present experimental evidence of such a vicinal surface for ZnO and hint that similar structures should occur on other polar crystal surfaces with wurtzite structure.

Experiments were performed in an ultrahigh vacuum (UHV) apparatus providing a base pressure below 2×10^{-10} mbar. ZnO(0001) single crystals (Mateck GmbH, Germany) were prepared by cycles of Ar ion sputtering and annealing for a duration of 0.5–2 h at different temperatures. Au tips were cut from a polycrystalline wire and *in situ* annealed prior to transfer to the scanning tunneling microscope (STM). The home-built STM was operated at a temperature of 5 K. All STM images were recorded in constant current mode. V indicates the voltage applied to the sample.

A STM image of the surface of a (0001) oriented ZnO single crystal prepared by several cycles of Ar ion sputtering and annealing to temperatures of $\approx 700\,^\circ\mathrm{C}$ is shown in Fig. 2. The surface consists of triangular islands and pits of different sizes. Steps between neighboring terraces are of one Zn-O double layer height. This type of Zn-terminated ZnO(0001) surface structure is known to be characteristic for moderate annealing temperatures [6,12]. On the grounds of STM measurements and density functional theory calculations [6,13], it has been suggested to consist of O-terminated step edges and an overall decrease of Zn atom surface density, leading to polarity compensation.

The surface structure of a (0001) oriented ZnO single crystal drastically changes for higher annealing temperatures of $\approx 850\,^\circ\mathrm{C}$ (Fig. 3). A strong roughening of the surface occurs. Two different types of facets exist, facets of high step density and facets with terraces of small width covered by triangular islands. The latter exhibit a (0001) surface orientation. As the duration of the annealing is extended from 0.5 h [Fig. 3(a)] to 2 h [Fig. 3(b)], the fraction of the former increases drastically.

The relative orientation of the “highly stepped” facets with respect to the “triangular island” facets is given by an angle $\varphi \approx 22^\circ$ as determined from profiles of STM images (Fig. 4). The experimental value is similar to the angle between the (0001) and $(10\bar{1}4)$ surfaces, which is equal to $\arctan[c/(4(\sqrt{3}/2)a)] = 24.8^\circ$ for bulk lattice parameters $a = 3.250$ Å and $c = 5.207$ Å [14].

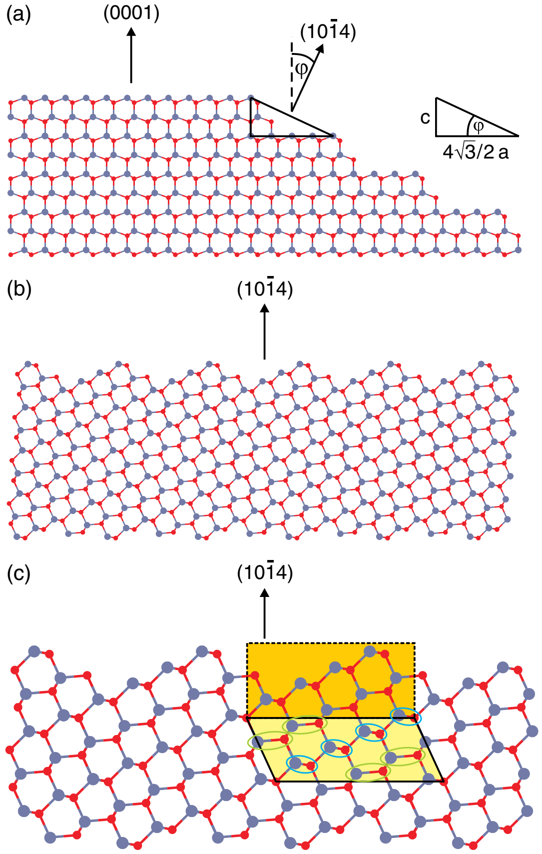

FIG. 1 (color online). Schematic side views of the atomic structure of different configurations of ZnO surfaces. (a) Faceted ZnO with (0001) and $(10\bar{1}4)$ surface orientations on the left and right, respectively. (b) Rotated $(10\bar{1}4)$ surface. (c) Zoom into the $(10\bar{1}4)$ surface with bulk unit cell (yellow background) and the additional surface region (orange background) for an illustration of dipole moments and charge neutrality. Zn and O atoms are shown as grey and red circles, respectively.

The assignment of a $(10\bar{1}4)$ surface orientation to one of the facet types is supported by information from height profiles within the highly stepped surface area (Fig. 5). Neighboring step edges exhibit an average distance of ≈ 12.5 Å which corresponds well to the distance $d = \sqrt{c^2 + [4(\sqrt{3}/2)a]^2} = 12.4$ Å calculated from the bulk lattice parameters.

The atomic structure of the stepped surface area with $(10\bar{1}4)$ orientation is illustrated in Fig. 1(b). In order to provide a planar perspective, the surface is rotated by the angle φ with respect to Fig. 1(a). In Fig. 1(b), the shortest lateral distance between the topmost Zn atoms is equal to the step-edge distance d. This view corresponds to the STM data shown in Fig. 5(b). There are thus two strong experimental indications for a $(10\bar{1}4)$ orientation of the stepped surface area, the step-edge distance of ≈ 12.5 Å and the inclination angle of $\approx 22°$.

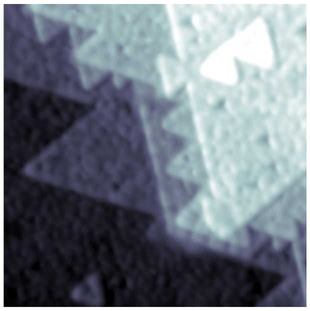

FIG. 2 (color online). Constant current STM image of the surface of a (0001) oriented ZnO single crystal for annealing at $\approx 700\,°\mathrm{C}$ ($25 \times 25\ \mathrm{nm}^2$, $V = +2.5$ V, $I = 0.1$ nA). The height range covers five Zn-O double layer distances.

In Fig. 1(a), both types of surface areas are shown together: on the left, the low-index (0001) orientation, and, on the right, the $(10\bar{1}4)$ orientation. The $(10\bar{1}4)$ surface can be interpreted as being misaligned from the (0001) surface by the angle φ. Such so-called *vicinal* surfaces are characterized by regularly spaced steps, which, for $(10\bar{1}n)$

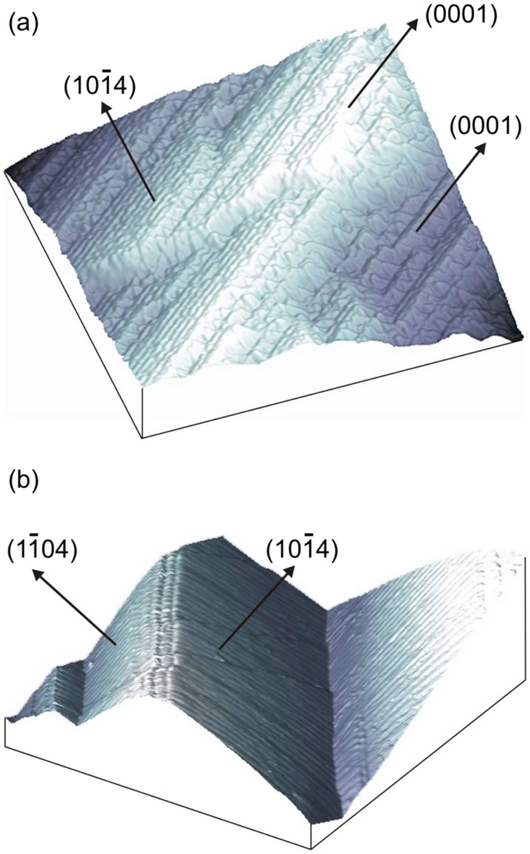

FIG. 3 (color online). Constant current STM images of the faceted surface of a (0001) oriented ZnO single crystal for annealing at $\approx 850\,°\mathrm{C}$ (pseudo-three-dimensional presentation). (a) $70 \times 70\ \mathrm{nm}^2$ area after 0.5 h annealing time ($V = +1.5$ V, $I = 0.1$ nA). (b) $200 \times 180\ \mathrm{nm}^2$ area after 2 h of annealing ($V = +3.5$ V, $I = 0.1$ nA).

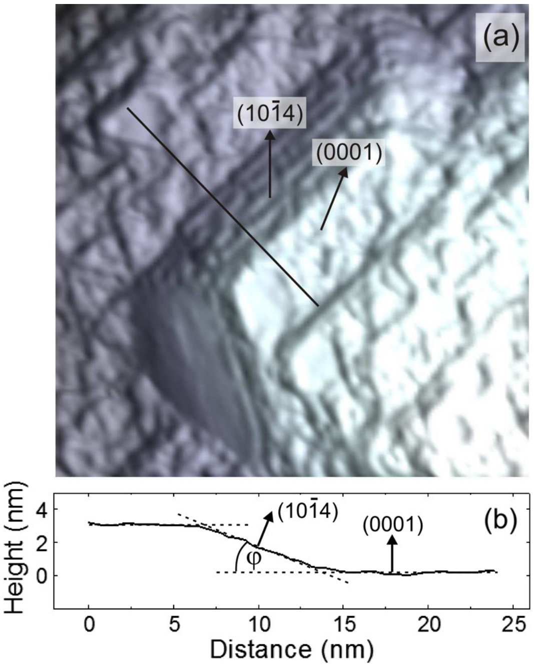

FIG. 4 (color online). (a) Similar to Fig. 3(a) for a smaller surface area (40×40 nm^2, $V = +1.5$ V, $I = 0.1$ nA). (b) Height profile along the black line in (a).

vicinals, lead to a terrace width $n(\sqrt{3}/2)a$. For small n, the terrace width is small and the step density is high. Only for $n = 4$ is good agreement between our STM data and the structural parameters of ZnO obtained.

We summarize that for annealing temperatures of $\approx 850\,^\circ$C, the (0001) surface facets and $\{10\bar{1}4\}$ oriented facets appear on the surface [Fig. 1(a)]. The former is characterized by the presence of triangular islands, the latter by a high step density. Starting with a surface of predominant (0001) orientation, a highly stepped surface is obtained after several cycles of sputtering and subsequent annealing at higher temperatures. A surface of predominant (0001) orientation is reestablished by multiple (10 to 20) cycles of sputtering and subsequent annealing at moderate temperatures of $\approx 700\,^\circ$C. For these different preparation procedures, two different atomic surface structures are stabilized.

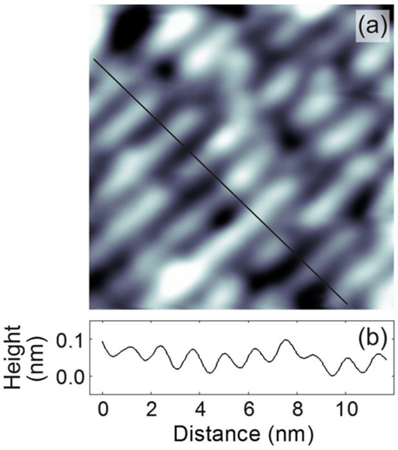

FIG. 5 (color online). (a) Similar to Fig. 3(a) for a zoom into a surface area of only (10$\bar{1}$4) surface orientation (10×10 nm^2, $V = +1.0$ V, $I = 0.1$ nA). (b) Height profile along the black line in (a).

Next, we suggest a mechanism explaining the stability of the (10$\bar{1}$4) vicinal surface. We apply the ionic model, which has proven successful in explaining the triangular pit reconstruction of the clean ZnO(0001) surface [6,13]. Recently, the triangular reconstruction and disorder of the ZnO(0001) surface have been investigated by Monte Carlo simulations based on an empirical Buckingham potential augmented by the Coulomb interaction of the ions [15]. The results corroborate our approach.

Because of the polarity of the partially ionic zinc-oxygen bond, a dipole moment arises within each Zn-O double layer. In the case of a thick crystal slab terminated by (0001) and (000$\bar{1}$) surfaces, the polarization due to this dipole has to be compensated by surface charges. Within the ionic model, this can be achieved, for instance, by removing an equivalent of $\approx 1/4$ ML of the Zn atoms from the ZnO(0001) surface, i.e., by a variation of the surface stoichiometry. In this way, a vanishing average electric field is accomplished within the bulk [1,5,16]. We consider an analogous procedure applied to the (000$\bar{1}$) surface. For simplicity, and as the argument applies to a larger class of materials, we take the ideal wurtzite structure with a ratio of the lattice constants $c/a = \sqrt{8/3} = 1.633$ and $u = 3/8 = 0.375$ [14]. The parameter u is a measure of the relaxation within the bulk unit cell of the wurtzite structure. The Zn-O interlayer spacing amounts to cu. For comparison, experimental values are $c/a = 1.602$ and $u = 0.382$ [14]. The small deviations of these parameters from the ideal case lead to a negligible variation of the results.

Figure 1(c) shows a model of the ZnO(10$\bar{1}$4) surface. The unit cell of the wurtzite structure leads to a vanishing component of the total dipole moment perpendicular to the (10$\bar{1}$4) surface. This is due to a compensation of contributions from the two Zn-O pairs of atoms, which are encircled in blue and green. There are eight pairs within each unit cell. The surface region defined with respect to this bulk unit cell contains as many zinc as oxygen atoms (seven each for the area indicated by the orange background) and is thus charge neutral. Hence, the average electric field vanishes within the bulk. This means that the ZnO(10$\bar{1}$4) surface fulfills the stability criterion of the ionic model without the need of any additional charged defects on the terraces. For this particular orientation, the surface energy of the vicinal surfaces is expected to assume a local minimum. From our experimental observations, we further conclude that the surface energy of the ZnO(10$\bar{1}$4) is sufficiently low to drive faceting of the ZnO(0001) surface. We emphasize that for the discussion of the charge neutrality condition, the precise shape of the step does not play a role as long as zinc and oxygen atoms are added or removed as Zn-O pairs.

The surface also fulfills the electron counting rule [17,18], which states that a semiconductor surface is stable only if all anion dangling bonds are fully occupied while all cation dangling bonds are empty. Keeping in mind that the oxygen atoms at the bottom of the step edge expose two dangling bonds, we find that the number of zinc and oxygen dangling bonds is equal, allowing for a complete charge transfer from the Zn to the O dangling bonds. This charge transfer occurs within the surface and thus does not change the total charge of the surface region. It thus does not affect our above electrostatic arguments.

It has to be mentioned that a different surface structure of ZnO(0001) has recently been reported for annealing to considerably higher temperatures of $\approx 1120\,^{\circ}\mathrm{C}$ [7]. Using scanning force microscopy, a tendency toward faceting at the step edges has been observed. Low-energy Zn-O double layer high steps have been found to consist of $\{10\bar{1}0\}$ nanofacets which are alternately straight or form a sawtoothlike step-edge structure. This type of nanofaceting at step edges is substantially different from the faceting into $(10\bar{1}4)$ surfaces reported here. However, at the elevated temperatures used in Ref. [7], significant sublimation of dissociated ZnO occurs [19–23]. Using published sublimation energies, we estimate a rate of ≈ 6.5 atomic layers (AL) per second [19]. In other words, the surface is under nonequilibrium conditions during preparation due to a rapid loss of material. At the lower temperature used here, $T = 850\,^{\circ}\mathrm{C}$, the calculated sublimation rate is only ≈ 0.007 AL per second and the surface structure is more likely to reflect an equilibrium situation. Because the sublimation proceeds stoichiometrically [21] at a small rate, the resulting surface structure is reproducible under UHV conditions. Moreover, the novel faceted surface structure is energetically favorable compared to the triangular structure obtained at lower temperatures. Otherwise, there would not be a driving force for faceting. As in the case of triangular surface structures, the relatively rough morphology and high step density of the faceted surface structure are intrinsic properties of the surface rather than a result of the specific preparation procedure.

It should also be mentioned that the present study is restricted to UHV conditions for two main reasons: Most of the experimental studies on the structural and chemical properties of polar oxide surfaces such as ZnO(0001) refer to these conditions, which allows for a comparison and general conclusions on the stabilization mechanism. In phase diagrams [6,24,25], UHV corresponds to rather H-poor and O-poor conditions. Hydroxide formation, which is often discussed as a stabilization mechanism [10,25], can therefore be excluded. Experimental UHV studies of the surface structure under H-rich and O-rich conditions are difficult to interpret because thermal equilibrium appears to be difficult to establish, as discussed in detail by Valtiner *et al.* [25].

In summary, the ionic model predicts a unique surface orientation in the wurtzite structure for which the occurrence of a low-energy vicinal surface may be expected. For polar crystals, the "magic" orientation is determined by the electrostatic criterion of vanishing field within the bulk. The surface also fulfils the electron counting rule. Faceting of the ZnO(0001) surface into $\{10\bar{1}4\}$ "magic" surfaces is observed experimentally by STM. Similar faceting may be expected for other polar semiconductors crystallizing in the wurtzite structure.

Financial support by the Deutsche Forschungsgemeinschaft through SFB 855 is acknowledged.

---

[*] Corresponding author.
gruyters@physik.uni-kiel.de

[1] C. Noguera, J. Phys. Condens. Matter **12**, R367 (2000), and references therein.

[2] P. W. Tasker, J. Phys. C **12**, 4977 (1979).

[3] R. W. Nosker, P. Mark, and J. D. Levine, Surf. Sci. **19**, 291 (1970).

[4] C. Wöll, Prog. Surf. Sci. **82**, 55 (2007), and references therein.

[5] J. Goniakowski, F. Finocchi, and C. Noguera, Rep. Prog. Phys. **71**, 016501 (2008), and references therein.

[6] O. Dulub, U. Diebold, and G. Kresse, Phys. Rev. Lett. **90**, 016102 (2003).

[7] F. Ostendorf, S. Torbrügge, and M. Reichling, Phys. Rev. B **77**, 041405 (2008).

[8] S. Torbrügge, F. Ostendorf, and M. Reichling, J. Phys. Chem. C **113**, 4909 (2009).

[9] A. Wander, F. Schedin, P. Steadman, A. Norris, R. McGrath, T. S. Turner, G. Thornton, and N. M. Harrison, Phys. Rev. Lett. **86**, 3811 (2001).

[10] M. Valtiner, S. Borodin, and G. Grundmeier, Phys. Chem. Chem. Phys. **9**, 2406 (2007).

[11] C. W. Litton, D. C. Reynolds, and T. C. Collins, *Zinc Oxide Materials for Electronic and Optoelectronic Device Applications*, Wiley Series in Materials for Electronic and Optoelectronic Applications (Wiley, New York, 2011).

[12] H. Zheng, J. Kröger, and R. Berndt, Phys. Rev. Lett. **108**, 076801 (2012).

[13] G. Kresse, O. Dulub, and U. Diebold, Phys. Rev. B **68**, 245409 (2003).

[14] U. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S. J. Cho, and H. Morkoç, J. Appl. Phys. **98**, 041301 (2005).

[15] H. Meskine and P. A. Mulheran, Phys. Rev. B **84**, 165430 (2011).

[16] W. A. Harrison, J. Vac. Sci. Technol. **16**, 1492 (1979).

[17] M. D. Pashley, Phys. Rev. B **40**, 10 481 (1989).

[18] M. H. Du, S. B. Zhang, J. E. Northrup, and S. C. Erwin, Phys. Rev. B **78**, 155424 (2008).

[19] ZnO dissociates on sublimation [20–23], leading to a sublimation rate which is given by $r_{\mathrm{sub}}^{\mathrm{Zn}} = r_{\mathrm{sub},0}^{\mathrm{Zn}} \exp(-E_{\mathrm{sub}}^{\mathrm{Zn}}/RT)$ [21], where $r_{\mathrm{sub}}^{\mathrm{Zn}}$ is the sublimation rate of Zn atoms and $E_{\mathrm{sub}}^{\mathrm{Zn}}$ the corresponding sublimation energy. For the (0001) surface, $r_{\mathrm{sub},0}^{\mathrm{Zn}}$ and $E_{\mathrm{sub}}^{\mathrm{Zn}}$ have been experimentally determined to $\approx 1.41 \times 10^{28}$ atoms per cm^2 s and ≈ 327 kJ/mole, respectively [20]. For $T = 1120\,^\circ\mathrm{C}$, this leads to $r_{\mathrm{sub}}^{\mathrm{Zn}}$ of 7.15×10^{15} atoms per cm^2 s, which corresponds to ≈ 6.5 AL per second (with 1.1×10^{15} atoms per cm^2 AL being the surface atom density). At $T = 850\,^\circ\mathrm{C}$, the calculated rate is 0.007 AL per second.

[20] W. Hirschwald and F. Stolze, Z. Phys. Chem. Neue Folge **77**, 21 (1972).

[21] W. Göpel, Z. Phys. Chem. Neue Folge **106**, 211 (1977).

[22] D. Kohl, M. Henzler, and G. Heiland, Surf. Sci. **41**, 403 (1974).

[23] J. E. McVicker, R. A. Rapp, and J. P. Hirth, J. Chem. Phys. **63**, 2646 (1975).

[24] M. Valtiner, M. Todorova, G. Grundmeier, and J. Neugebauer, Phys. Rev. Lett. **103**, 065502 (2009).

[25] M. Valtiner, M. Todorova, and J. Neugebauer, Phys. Rev. B **82**, 165418 (2010).