



Surface Science Letters

Observation of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction on O-polar ZnO surfacesS.T. King^a, S.S. Parihar^a, K. Pradhan^a, H.T. Johnson-Steigleman^{a,b}, P.F. Lyman^{a,*}^a Department of Physics and Laboratory for Surface Studies, University of Wisconsin, P.O. Box 413, Milwaukee, WI 53211, USA^b Department of Physics, State University of New York at Brockport, Brockport, NY 14420, USA

ARTICLE INFO

Article history:

Received 29 January 2008

Accepted for publication 4 September 2008

Available online 24 September 2008

Keywords:

Low energy electron diffraction
 X-ray photoelectron spectroscopy
 Interface dipole
 Surface relaxation and reconstruction
 Zinc oxide
 Low index single crystal surfaces
 Semiconducting surfaces

ABSTRACT

Low energy electron diffraction shows a $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction on O-polar ZnO surfaces after a tube furnace annealing process commonly used to create atomic-height steps. This reconstruction is also produced in situ under conditions having an extremely low hydrogen background. X-ray photoelectron spectroscopy suggests H stabilizes the (1×1) termination that has been extensively reported. The $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction is stable against H_2 , N_2 , and air, although its formation is suppressed when preparation occurs under a H_2 background. Therefore, caution must be taken when using annealed O-polar ZnO substrates, as reconstruction will affect the nature of the surface and, thus, the growth interface.

© 2008 Elsevier B.V. All rights reserved.

Recently, interest in ZnO has been revitalized due to its large bandgap of 3.3 eV, and because its high exciton binding energy (60 meV) and high optical gain (300 cm^{-1}) at room temperature make it a promising material for blue and ultraviolet light-emitting and laser diodes [1]. Furthermore, ZnO has proven to be an ideal substrate for the epitaxial growth of other wide-bandgap semiconductors, in particular GaN, due to the shared structural symmetry and small lattice mismatch (1.9% and 0.4% for the *a*- and *c*-axes, respectively) between these two materials [2]. While the bulk properties of ZnO are well understood, knowledge of its surface properties is more crucial to understanding the nature of the interface between the ZnO substrate and any other material.

The mechanism by which ZnO crystals lower the high energy of their polar surfaces is of fundamental importance [3]. A currently accepted stabilization method to explain observed (1×1) surfaces suggests partial charge transfer between unreconstructed Zn- and O-polar faces, resulting in metallic surface states [4]. Conversely, reconstructions on clean, polar ZnO surfaces have been observed [5,6], and it has been suggested that the (1×1) surface results from H-stabilization [6,7]. While a vibrational spectroscopy study has suggested that the O-polar ZnO surface can be largely cleansed of H [8], the results have been questioned due to the poor sensitivity of HREELS to H on ZnO surfaces and the difficulty in obtaining reliable quantitative coverages using that technique [7,9]. Furthermore, calculations have shown that the existence of a H-free sur-

face is energetically unfavorable for typical partial pressures of H_2 found in most vacuum systems [10]. Based on this extensive body of work, some have gone so far as to say that a H-free, O-polar ZnO- (1×1) surface does not exist [7]. Determining the conditions under which clean ZnO surfaces reconstruct is of utmost importance since reconstruction alters the surface density of states, affecting any interface made with the ZnO surface.

In this letter we investigate a $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface reconstruction observed by low energy electron diffraction (LEED) on O-polar ZnO ($ZnO(000\bar{1})$) single-crystal surfaces prepared both by in-situ Ar^+ sputtering and annealing cycles in ultra-high vacuum (UHV) as well as by ex-situ tube furnace annealing in an ambient atmosphere. X-ray photoelectron spectroscopy (XPS) shows that the intensity of the hydroxyl shoulder (located to the higher binding energy side of the $O1s$ peak) decreases drastically for in-situ-prepared $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstructions compared to either as-inserted or (1×1) surfaces. Interestingly, samples prepared via the ex-situ method also show a decrease in the intensity of this shoulder. Annealing experiments show the reconstruction, once formed, is stable under a H_2 background, but such a background inhibits ordering from the (1×1) . Therefore, we suggest that $ZnO(000\bar{1})$ surfaces exhibit the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction only when they are significantly free of H.

Double-sided polished ZnO single crystals (obtained from both MTI and CrysTec Corporations) were ultrasonically cleaned in acetone and methanol and then blown dry with inert gas. After cleaning, samples were either loaded into a UHV preparation and analysis system equipped with LEED and XPS or sandwiched between two ZnO wafers and loaded into a closed-end tube furnace.

* Corresponding author. Tel.: +1 414 229 4626; fax: +1 414 229 5589.
 E-mail address: plyman@uwm.edu (P.F. Lyman).

Details of the diffusion-pumped UHV system may be found elsewhere [11].

Samples to be prepared in situ were mounted to a Ta sample holder with W clips, inserted into UHV, and degassed at 400 °C for 15 min. Temperatures were monitored with an optical pyrometer during resistive heating. After degassing, samples were reduced to room temperature, Ar⁺-sputtered for 30 min, then annealed at 650 °C for 15 min. After this initial cycle of sputtering and annealing, samples were sputtered an additional 15 min followed by another 15 min anneal. After one to three such cycles, a crisp, reconstructed LEED pattern was observed¹.

Samples to be prepared ex situ were placed between two ZnO wafers, which were then placed into an alumina crucible. The crucible was loaded into a closed-end tube furnace and annealed to 1100 °C for varying amounts of time. After annealing, samples were either examined by ex-situ atomic-force microscopy (AFM) or mounted to a UHV sample holder for LEED and XPS analysis.

Fig. 1 shows the LEED patterns from an in-situ-prepared ZnO sample after the initial sputter and anneal cycle (Fig. 1a) and after three additional cycles (Fig. 1b) with the corresponding unit cells indicated by polygons. After the initial degassing, Ar⁺ sputtering for 30 min, and annealing at 650 °C for 15 min, the ZnO surface shows a crisp (1 × 1) LEED pattern (Fig. 1a). After three additional sputter and anneal cycles, fractional order spots are observed within the (1 × 1) unit cell (Fig. 1b), corresponding to a ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction.

To probe the chemical environment of the ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction, we have employed XPS using Al-K α radiation (spectra were acquired prior to LEED observations). Survey spectra show features pertaining to only O and Zn, indicating a clean surface. Presented in Fig. 2 are O1s spectra taken at normal emission and obtained as a sample was prepared from: as inserted, to a clean (1 × 1) reconstruction, to the resultant ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction. Upon close examination of the shoulder (attributed to a combination of O near O-vacancies [12] and hydroxyl termination of the ZnO surface [13]) to the high-binding-energy side of the main feature obtained for the as-inserted sample, one notices that the intensity of this shoulder is drastically decreased upon preparation of the (1 × 1) surface, consistent with removing a surface contamination layer. Upon forming the ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction, the intensity of the shoulder decreases even further from that of the (1 × 1). This is suggestive that the (1 × 1) surface may still be hydroxyl terminated and the remaining asymmetry in the lineshape for the reconstructed surface may stem primarily from O near O-vacancies. Note that this feature is unlikely to be attributed solely to O-vacancies, as a decrease in such a feature with the sputtering required to form the ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction would not be expected.

H stabilization of polar oxide surfaces has been shown to occur for such materials as MgO(111)–(1 × 1) [14,15], and is also suggested to stabilize the ZnO(000 $\bar{1}$)–(1 × 1) surface [6,7,9]. While a vibrational spectroscopy study suggests that a nearly H-free (1 × 1) surface may be prepared [8], He-atom scattering experiments, also capable of probing the presence of H on the surface, have shown that a (1 × 3) reconstruction forms on H-free ZnO(000 $\bar{1}$) surfaces while H-terminated surfaces always exhibit a (1 × 1) termination [6,7,9]. These results are very suggestive of the influence that ambient H₂ has on stabilizing the ZnO(000 $\bar{1}$)–(1 × 1) surface. As H₂ is the main constituent of the residual gases found in typical UHV systems, H-stabilization may be the reason why few clean, reconstructed ZnO surfaces have been observed.

Why would a ZnO(000 $\bar{1}$) surface reconstruction then be observed in a UHV He atom scattering system? The answer may lie

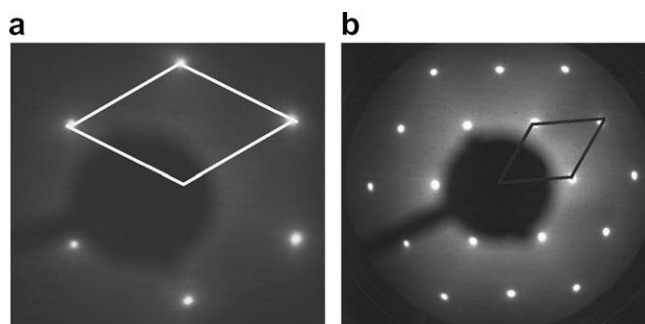


Fig. 1. LEED patterns taken at 60 eV showing (a) a ZnO(000 $\bar{1}$)–(1 × 1) reconstruction and (b) a ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction. The respective unit cells are indicated.

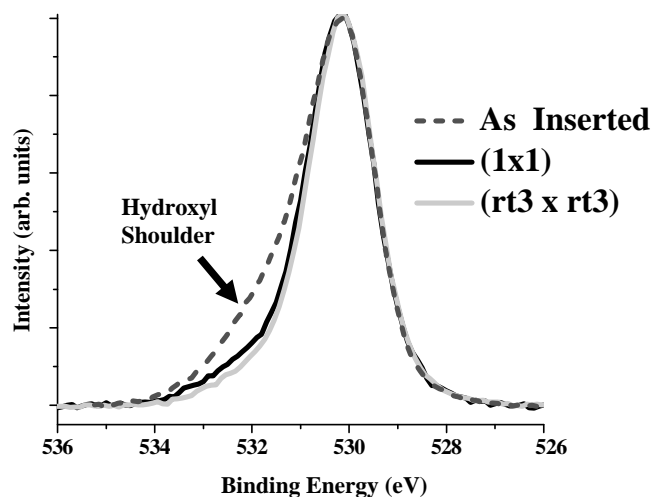


Fig. 2. XPS O1s spectra taken at normal emission for an as-inserted sample, a (1 × 1) reconstruction, and a ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction.

with the need for these systems to pump large loads of light gases. Efficient He pumping yields efficient H₂ pumping, which results in a H₂ background substantially less than that of an ion- or turbo-pumped system.

Since the UHV system used in this study is pumped by twin diffusion pumps, a series of experiments was carried out under an intentional H₂ background of 10^{−7} torr to test the effect H has on preparing the ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction. Initially, a sample was prepared with a ($\sqrt{3} \times \sqrt{3}$)R30° reconstruction, per our usual in-situ process, after which the sample was sputtered until the ($\sqrt{3} \times \sqrt{3}$)R30° was completely removed. Next, a leak valve was opened, a H₂ background of 10^{−7} torr was introduced, and sample preparation resumed from the beginning of the process. After sputtering and annealing multiple times under a H₂ background, only a (1 × 1) pattern was observed by LEED. Further cycles included raising the annealing temperature from 600 °C to 800 °C in 50 °C steps, but no reconstruction was observed.

After the H₂ experiments were performed, the leak valve was closed and the system was pumped until the partial pressure of H₂ returned to normal levels. After the system recovered, the sample was once again prepared using the standard procedure, and a ($\sqrt{3} \times \sqrt{3}$)R30° was once again observed. Moreover, our attempts to prepare a reconstructed surface in a conventional ion-pumped system failed. These results strongly suggest that the H₂ background suppresses the ability of the clean ZnO(000 $\bar{1}$) surface to reconstruct.

Many studies have shown the surface morphology of both polarities of ZnO drastically improves after ex-situ tube-furnace

¹ The LEED pattern did not change upon translating the sample, indicating that the pattern observed was not caused by electron beam damage.

Download English Version:

<https://daneshyari.com/en/article/5424435>

Download Persian Version:

<https://daneshyari.com/article/5424435>

[Daneshyari.com](https://daneshyari.com)