

Stability of the polar surfaces of ZnO: A reinvestigation using He-atom scattering

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A reinvestigation of the O-terminated, polar surface of zinc oxide, O-ZnO(000 $\bar{1}$), using scattering of thermal energy He atoms reveals the presence of a (1 \times 3) reconstruction for the clean surface. This finding is at variance with the results of previous works, where the same surface was found to be unreconstructed. Results for the hydrogen saturated H(1 \times 1) O-ZnO(000 $\bar{1}$) surface, which has also been investigated, suggest that the presence of H atoms has a strong impact on the structure of the O-terminated ZnO surfaces.

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Metal oxides represent a special case of ionic crystals, where electrostatic interactions can cause surface instabilities. When the projection of the electric dipole moment of the (bulk) unit cell on the surface normal has a nonvanishing component, the corresponding surface can be shown to be unstable. For most metal oxides this prediction¹ (Taskers rule) is fulfilled, but in case of ZnO previous research has failed to clearly identify such instabilities for the two polar surfaces, ZnO(0001) and ZnO(000 $\bar{1}$). Instead, a general agreement has emerged in that the polar ZnO surfaces exhibit a (1 \times 1) unreconstructed top layer. The reason for this apparent violation of Taskers rule has not been fully understood, but already in very early work it had been proposed² that the polar surfaces may be stabilized by a charge transfer from the O-terminated side to the Zn-terminated side. In recent theoretical studies employing density-functional methods results were obtained, which support this hypothesis.^{3,4} The experimental evidence for the apparent stability of the polar ZnO surfaces comes from diffraction techniques using either low-energy electron diffraction (LEED),⁵⁻⁷ or, recently, x-ray photons at grazing incidence (grazing incidence x-ray diffraction, GXRD).⁴ Both types of probe particles used in these previous studies, electrons and x-ray photons, suffer from a rather low cross section for hydrogen atoms present on a surface. Because of the large stability of OH species, however, the question about the presence of hydrogen atoms on metal oxide surfaces is pertinent. H atoms adsorbed on metal oxide surface are not only important for chemical properties but may also severely affect the structural properties. For many other materials it has been observed that adsorption of H atoms can lift reconstructions present for the clean, hydrogen-free surfaces. The most prominent case is the (111)-oriented surface of Si, where both reconstructions of the clean surface, the (2 \times 1) and the (7 \times 7) are lifted upon exposure to hydrogen.⁸ For the (111)-oriented surface of diamond a similar scenario is seen.⁹ Unfortunately, because of the low cross section of electrons and x-ray photons for protons the detection of adsorbed H atoms with standard surface science diffraction techniques, e.g., LEED or XRD, is rather difficult and, as a result, the question about the presence of hydrogen atoms on metal oxide surfaces is rarely addressed. Previous studies using infrared (IR) spectroscopy (see, e.g., Ref. 10) have unambiguously demonstrated that exposure of ZnO powders to hydrogen leads to the formation of both, Zn-H and O-H species. Un-

fortunately, because of the low reflectivity of ZnO surfaces in the infrared, IR investigations of species adsorbed on these surfaces have so far not been reported. In addition, the application of the other standard tool for surface vibrational spectroscopy, electron energy-loss spectroscopy, is hampered by the dominance of the Fuchs-Kliewer modes on this substrate,¹¹ which has made observations of adsorbate induced features on this surface very difficult. As a result, the formation of H adlayers on ZnO single-crystal surfaces has remained largely unexplored.

Here we present results obtained using probe particles with a unique sensitivity towards hydrogen atoms adsorbed on a surface, namely, thermal energy He atoms. Scattering of He atoms has in the past already contributed significantly to the structural analysis of hydrogen overlayers on metal surfaces,^{12,13} and also for the two cases discussed above, hydrogen overlayers on Si and diamond surfaces, the application of the technique has been very successful.^{8,9} The potential of He-atom scattering for the investigation of hydrogen adlayers on metal oxide surfaces could be demonstrated recently for the case of the Zn-terminated polar ZnO surface.¹⁴ There it could be demonstrated that exposure to molecular and atomic hydrogen leads to the formation of a well-defined (1 \times 1) overlayer that could easily be removed by heating the substrate.¹⁴ More importantly, it was found that under certain conditions the sticking coefficient for hydrogen molecules can become rather large and exceed 1×10^{-3} , which is an unexpectedly large value.

The measurements have been carried out using an ultra-high vacuum (UHV) molecular beam system that has been described in detail elsewhere.¹⁵ Several additional experiments were carried out using a standard x-ray photoelectron spectroscopy (XPS) apparatus equipped with several standard surface science techniques (including LEED and ion scattering spectroscopy), which has been described in previous papers.¹⁴ The O-terminated ZnO substrates were first oriented to within 0.2° and subsequently polished mechanically. After installation in the UHV chamber the samples were first cleaned by cycles of Ar⁺ sputtering (800 V, $\sim 1 \mu\text{A}$, 4–12 h, $T_s = 650 \text{ K}$) and annealing (800 K). After about 20 preparation cycles the XP-spectra revealed contamination levels of less than 0.05 ML for carbon containing species and the O-ZnO surfaces exhibited a LEED pattern comparable to those published before.⁵⁻⁷ The He-atom diffraction patterns recorded directly after the final heating procedure revealed a

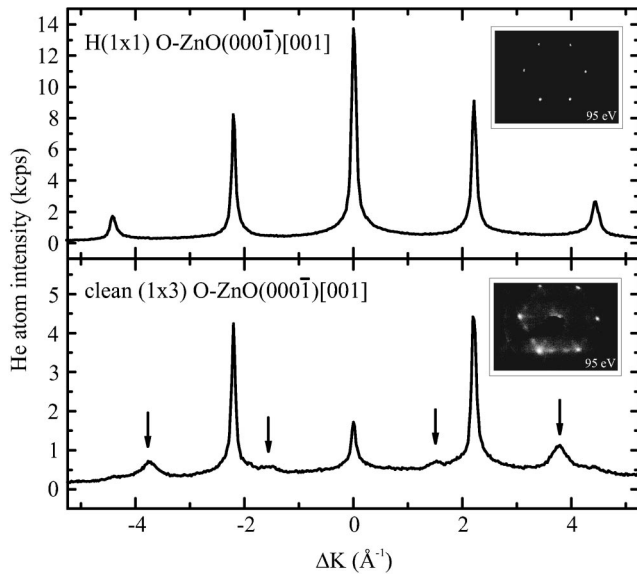


FIG. 1. Main panel: He-atom angular distributions recorded for the clean and the H-saturated O-ZnO surfaces at a surface temperature of 200 K ($E_i = 30.1$ meV). The arrows indicate the additional diffraction peaks related to the (1×3) structure. Insets: LEED pattern corresponding to the He-atom scans.

(1×3) pattern (see below). The general quality of the He atom diffraction pattern, however, was found to be rather poor. This apparent discrepancy results from the fact that He atoms are significantly more sensitive to surface defects and imperfections than electrons. In order to obtain high-quality He-atom diffraction patterns the preparation procedures had to be optimized. Judging from the intensity of the specular diffraction peak and the overall quality of the diffraction pattern the best results were obtained by applying a rather extensive preparation procedure involving annealing in oxygen (1×10^{-6} mbar, $T_s \sim 850$ K, 5–10 min) and a final flash in UHV ($T_s = 830$ – 850 K, 1–2 min). In earlier work it had been reported that the annealing in oxygen is crucial in reducing the number of oxygen vacancies at the surface.¹⁶ Typically, two sputtering cycles with subsequent annealing were followed by one cycle with annealing in oxygen. Note, however, that for the clean, hydrogen-free O-ZnO surface the He-atom diffraction pattern always showed a (1×3) pattern (also before the O_2 treatment).

Due to the mechanical stress generated by these extensive preparation procedures (~ 50 cleaning cycles) the rather brittle crystals had to be replaced after about 3 months of measuring time. In the course of the present study a total of three different substrates have been used, two of them were studied with He-atom scattering. The exposure to atomic hydrogen was carried out by placing a hot tungsten filament at a distance of approx 5 cm from the specimen after backfilling the UHV chamber with H_2 at a pressure of 1×10^{-6} mbar.

In the lower panel of Fig. 1 we show a He-atom angular distribution recorded for the O-terminated ZnO surface along the $[001]$ azimuth. The He-atom diffraction scan clearly shows peaks at positions different from those expected for a

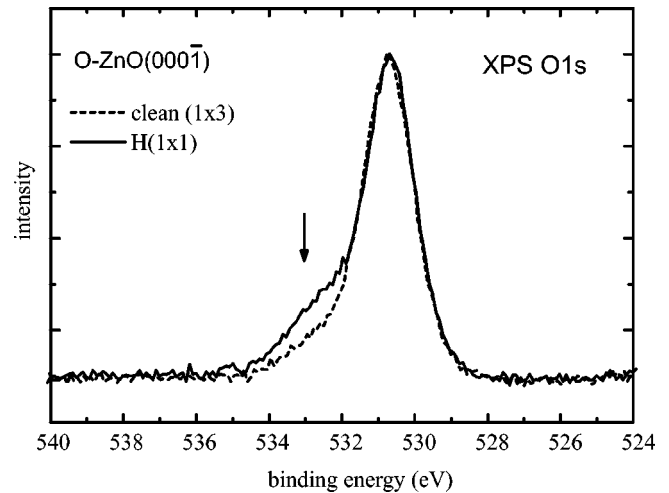


FIG. 2. O 1s XPS of the clean (1×3) (dashed line) and hydrogen saturated (1×1) (solid line) surface, respectively, of O-ZnO. (Take-off angle of the photoelectrons equals 20° .) The two spectra were normalized to yield the same peak heights.

(1×1) unreconstructed surface. All these additional peaks (marked by a vertical arrow) reveal the presence of a (1×3) reconstruction. The findings from the He-atom diffraction are corroborated by the LEED results shown as an inset in the lower part of Fig. 1. Also in this case weak (1×3) spots are visible. These extra spots are detectable, however, only in a rather narrow electron energy regime around 95 eV. More importantly, the extra spots could only be observed in LEED after using the extensive oxygen treatment described above. For crystals with poor quality no (1×3) spots could be observed in the LEED patterns, even though the corresponding He-atom diffraction scans clearly showed (1×3) superlattice peaks similar to those shown in Fig. 1, lower part.

As a reference, we also provide He-atom diffraction data observed after saturating the surface with either atomic or molecular hydrogen. The corresponding results are shown in the upper part of Fig. 1. The results clearly reveal the presence of a (1×1) surface, thus indicating the formation of a (1×1) H-atom overlayer, similar to the case of the Zn-terminated polar surface of ZnO.¹⁴ Note, that the LEED pattern recorded for the H-saturated surface is very similar to that recorded for the clean surface (see inset in upper part of Fig. 1), with the exception of the weak (1×3) extra spots visible for electron energies of 95 eV. When using other electron energies the LEED patterns for the clean (1×3) and the (1×1) surface were virtually identical.

In order to independently verify the presence of OH groups at the surface we have carried out experiments using x-ray photoelectron spectroscopy using Al $K\alpha$ radiation (1486.6 eV). For the clean surface the results shown in Fig. 2 reveal the presence of a well-defined O 1s line at 530.7 eV. Exposing the surface to H atoms (or molecules) leads to the formation of a pronounced shoulder at higher binding energies, indicating the presence of OH groups at the surface. At the same time the $H(1 \times 1)$ diffraction pattern is observed in He-atom scattering (see above).

The adsorption of hydrogen on the surface was found to be reversible, heating the substrate to temperatures above

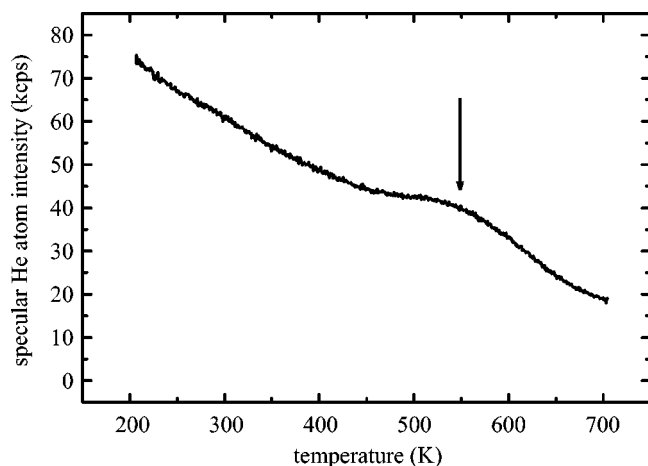


FIG. 3. Specular He-atom intensity as a function of surface temperature after saturating the surface with atomic hydrogen at 200 K. The heating rate amounted to 1 K/s.

600 K leads to desorption of the hydrogen and the reappearance of the diffraction peaks of the (1×3) reconstructed, clean surface. H desorption could be studied in a semiquantitative fashion by monitoring the He reflectivity of the surface as a function of surface temperature, a typical result is shown in Fig. 3. In contrast to the Zn-ZnO surface¹⁴ only one distinct structure could be observed which is assigned to H desorption from OH species formed by adsorption of hydrogen on the O-ZnO surface. Assuming a preexponential factor that is typical for a recombinative (second order) desorption of hydrogen [$(10^{21} \text{ cm}^2/(\text{mol s}))$, see e.g., Ref. 17] and a desorption temperature of 547 K (see arrow in Fig. 3) we yield an activation energy for H_2 -desorption of 141 kJ/mol. This value is almost exactly the same as that reported for the activation energy for desorption of H atoms from OH groups on the Zn-ZnO surface.¹⁴ After heating to 700 K and then quickly (within 20 min) cooling back to surface temperatures

of 200 K, LEED and He-atom scattering clearly reveal the presence of a (1×3) reconstruction of the clean surface (see Fig. 1).

Altogether, these results are the first unambiguous evidence that the clean O-terminated ZnO-surface shows a reconstruction as required by Taskers rule for a polar surface. The fact that this reconstruction has not been observed in earlier work is believed to result from two reasons: (1) whereas in He-atom scattering the difference in the diffraction patterns between the clean (1×3) and the $\text{H}(1 \times 1)$ surface is very pronounced (see Fig. 1) the extra spots in the LEED pattern revealing the presence of the (1×3) reconstruction are rather weak and can be seen only in a rather narrow energy range (92–98 eV). In addition, we were only able to observe the LEED (1×3) spots for high-quality surfaces after many preparation cycles. (2) The polar O-ZnO(0001) surface exhibits an unexpectedly large reactivity towards molecular hydrogen and water. We observed that without special precautions a sample in UHV with a background pressure of 5×10^{-10} mbar (where a significant amount of H_2 and H_2O is always present in the residual gas) can adsorb an amount of H atoms sufficient to remove the (1×3) reconstruction of the clean surface within 30 min. Note, that unexpectedly large values of the sticking coefficient for molecular hydrogen have recently also been reported for the Zn-terminated polar ZnO-surface.¹⁴

We thus conclude that the O-terminated ZnO surface—in contrast to recently published experimental and theoretical work by Wander *et al.*⁴—does exhibit a (1×3) reconstruction. We speculate that the (1×1) surface reported in previous work actually does not correspond to the clean O-ZnO(0001) surface but to the corresponding hydrogen-saturated surface. The microscopic nature of the (1×3) reconstruction has not yet been unraveled, high-quality XPS data recorded at grazing take-off angles seems to point towards the presence of an ordered array of O-atom vacancies,¹⁸ as observed recently for the (1120) surface of Al_2O_3 .¹⁹

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