# Hydrogen Induced Metallicity on the $\mathrm{ZnO}(10\bar{1}0)$ Surface

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(Received 24 August 2005; published 27 December 2005)

Exposure of the mixed-terminated $\mathrm{ZnO}(10\bar{1}0)$ surface to atomic hydrogen at room temperature is found to lead to drastic changes of the electrical properties. The insulator surface is found to become metallic. By employing several experimental techniques (electron energy loss spectroscopy, He-atom scattering, and scanning tunneling microscopy) together with *ab initio* electronic structure calculations we demonstrate that a low-temperature ($1 \times 1$) phase with two H atoms in the unit cell transforms upon heating to another ($1 \times 1$) phase with only one H atom per unit cell. The odd number of electrons added to the surface per unit cell gives rise to partially filled surface states and thus a metallization of the surface.

DOI: 10.1103/PhysRevLett.95.266104 PACS numbers: 68.49.−h, 68.37.Ef, 68.43.Bc, 82.65.+r

Understanding the interaction of hydrogen with zinc oxide is of fundamental interest in view of its widespread use in heterogeneous catalysis [1] and of promising applications in semiconductor devices [2]. Exposure to hydrogen strongly affects the electrical properties of ZnO and enhances its conductivity. In early molecular beam studies [3] ZnO single crystals were used as sensor material to determine the number of H atoms impinging on the surface by monitoring the electrical resistivity. By heating the ZnO substrate, hydrogen desorbs and the original (poor) conductivity is restored. Hydrogen treatment of undoped ZnO thin films has been shown to lead to well-conducting transparent electrodes which can be used in solar cells [4,5]. Furthermore, H impurities were identified recently as the main source of the commonly observed residual $n$-type conductivity in ZnO [6–8]. This is a rather unusual behavior since for most other semiconductor materials H atoms act as a passivating species and suppress the prevailing conductivity.

In order to elucidate how the initial adsorption of H atoms on the ZnO surfaces affects the bulk conductivity, we have carried out a detailed experimental and theoretical study, employing high resolution electron energy loss spectroscopy (HREELS), He-atom scattering (HAS), scanning tunneling microscopy (STM), and density-functional theory (DFT) calculations. We have focused on the mixed-terminated $\mathrm{ZnO}(10\bar{1}0)$ surface, which is the lowest-energy surface termination [9] and exhibits no electrostatic instability like the two polar surfaces of ZnO [10]. The $\mathrm{ZnO}(10\bar{1}0)$ surface consists of rows of ZnO dimers separated by trenches (see Fig. 1). In the bulk, the Zn and O atoms are fourfold coordinated. At the surface one of these nearest-neighbor bonds is broken. Upon hydrogen adsorption, one would expect that the two "dangling bonds" are saturated leading to a surface structure with two H atoms adsorbed per surface unit cell, one to an O and one to a Zn atom [in the following referred to as $\mathrm{ZnO}(10\bar{1}0)$—2H]. The result is an insulating surface with a similar band gap as for the clean surface. Figure 1(a) shows the fully relaxed atomic and the electronic structure for such a configuration obtained by DFT calculations [11]. A significant band gap is visible which is slightly larger than for the clean surface [9].

Exposing the $\mathrm{ZnO}(10\bar{1}0)$ surface to H atoms at low temperatures (200 K) yields a H-terminated surface which is fully consistent with this prediction. In Fig. 2(a) we present HREELS data [12] obtained for a clean (curve *A*) and a H-saturated $\mathrm{ZnO}(10\bar{1}0)$ surface at 200 K (curve *B*). The exposure to atomic hydrogen was carried out by backfilling the ultrahigh vacuum (UHV) chamber and by dissociating $H_2$ on a hot tungsten filament in line-of-sight from the substrate. In order to suppress the multiphonon losses, the HREELS data were recorded in 10° off-specular direction with an incidence angle of 55° with respect to the surface normal and a high primary electron energy of 10 eV [13,14]. In addition to the intense Fuchs-Kliewer modes, which dominate the spectrum [13], an OH band at 455 meV is observed and a weak loss at 200 meV appears

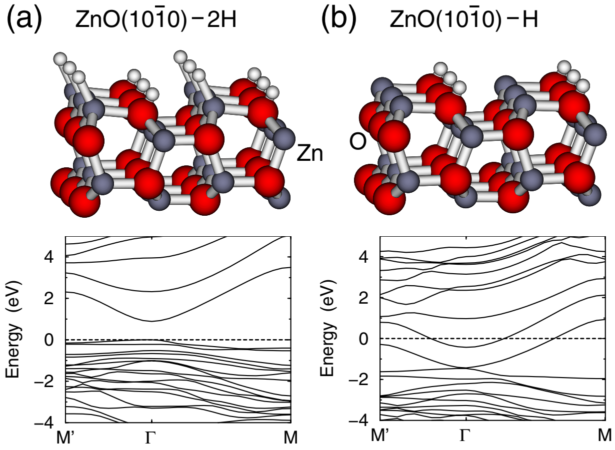

FIG. 1 (color online). Atomic and electronic structures of the $\mathrm{ZnO}(10\bar{1}0)$ surfaces with (a) two and (b) one adsorbed H atom per unit cell as obtained from DFT calculations. The energy of the highest occupied level is set to zero.

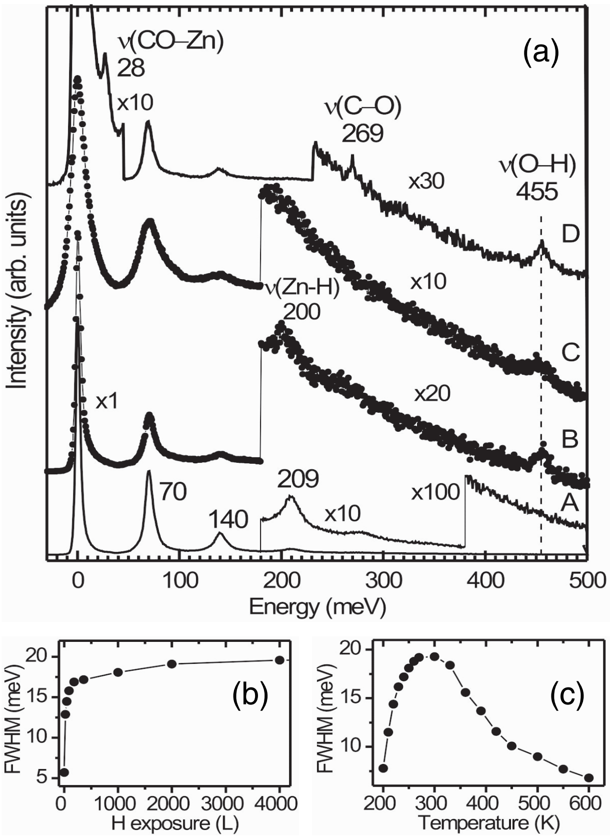

FIG. 2. (a) HREELS data recorded for the clean ZnO(10$\bar{1}$0) surface (curve *A*), after exposure to hydrogen at 200 K (curve *B*), after H saturation at room temperature (curve *C*), and after exposing the room temperature hydrogenated surface to 45 L of CO at 70 K (curve *D*). The spectra were taken at 300 K (curves *A* and *C*) and 70 K (curves *B* and *D*), respectively. The prominent losses at 70, 140, and 209 meV correspond to Fuchs-Kliewer phonons. The peaks at 455 meV are assigned to the OH stretch vibration. (b) FWHM of the quasielastic peak in the HREELS spectra as a function of H atom exposure at room temperature, and (c) as a function of temperature after exposing the ZnO(10$\bar{1}$0) surface to 2000 L hydrogen at 200 K.

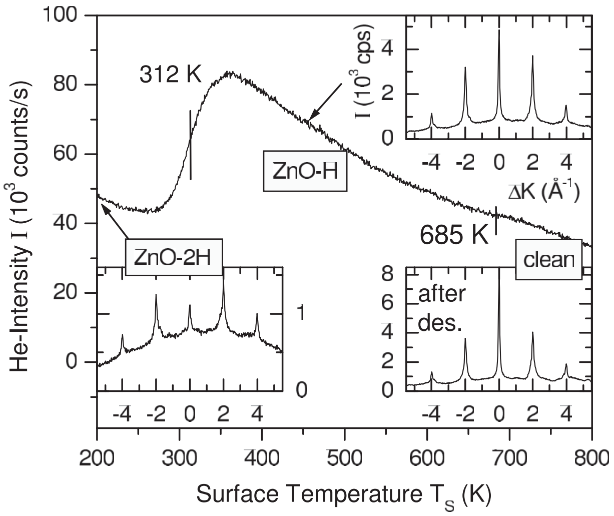

FIG. 3. He-atom specular signal of the ZnO(10$\bar{1}$0) surface saturated with hydrogen at 200 K recorded for a heating rate of 1 K/s (He-TDS). The He diffraction scans in the [1$\bar{2}$10] direction for the two hydrogen phases and the clean ZnO surface after hydrogen desorption (given in the insets) were measured by rotating the crystal around an axis perpendicular to the scattering plane. The angular distributions are converted to parallel momentum transfer $\Delta K$.

which is assigned to the ZnH stretching mode. For the clean surface the full width at half maximum (FWHM) of the diffuse elastic peak amounts to 5.7 meV, and the width does not change upon H adsorption.

The H atom adsorption was also monitored by HAS, a technique which has already been used successfully in a number of other studies of H atom adlayers on oxide surfaces (see Ref. [15], and references therein). The HAS studies were carried out under similar conditions as the HREELS measurements [12] but in a different apparatus. A nearly monoenergetic He beam is produced by a supersonic expansion. The scattered He atoms are detected at a fixed angle of 90.5° from the incident beam by a magnetic mass spectrometer. At 200 K the H atoms form an ordered adsorbate structure with a $(1 \times 1)$ periodicity (see "ZnO—2H" in Fig. 3). Monitoring the specular intensity as a function of surface temperature He thermal desorption spectroscopy (He-TDS) yielded a distinct feature at 312 K and a smaller increase at 685 K. Above 312 K a new phase appears in the He-atom diffraction pattern. Whereas the periodicity is the same as the low-temperature phase $(1 \times 1)$, the relative intensities of the diffraction peaks are significantly different from those seen for ZnO—2H and also from those seen for the clean surface (see "ZnO—H" and "clean" in Fig. 3). Only if the sample is heated to above 685 K, the same diffraction intensities as for the clean surface are restored.

When hydrogen is adsorbed above this transition temperature also the HREELS data reveal significant differences. After exposing the surface to 2000 L hydrogen, only one OH band at 455 meV is seen [curve *C* in Fig. 2(a)] but no ZnH band could be detected. Most interestingly, as shown in Fig. 2(b), the FWHM of the diffuse elastic peak now increases upon H adsorption from 5.7 meV for the clean surface to a value of about 19.5 meV at maximum H coverage. Annealing to above 600 K restores the width of this peak to its original value. Furthermore, the same state of the surface can be reached if the surface is exposed to H atoms at 200 K and then heated up as demonstrated by the data shown in Fig. 2(c).

The most straightforward explanation for the large width of the elastic peak in the HREELS data is that low-energy excitations are present on the room temperature H-saturated ZnO—H but not on the clean or the low-temperature ZnO—2H surface. Only a broadening but no individual features could be observed, therefore the fundamental energy of the excitation must be below 5 meV. Since the broadening was also observed for large $\Delta K$

values, the most likely assignment is that to low-energy electronic excitations [14]. If this assignment is correct, it directly implies the presence of metallic, i.e., partially filled electronic states on the surface formed upon H adsorption. On such a metallic surface the excitation of bulk and surface plasmons becomes possible, with an energy related to the charge density via $\omega_p^2 = ne^2/\varepsilon_0 m^*$ and $\omega_{sp} = \omega_p/\sqrt{2}$, respectively. From an energy of below 5 meV we obtain an upper limit for the carrier concentration of about $5 \times 10^{15}$ cm$^{-3}$, indicating that the metallicity must be restricted to the very surface region.

In Fig. 4 we show STM data recorded for a clean and a H-saturated (at 380 K) surface [16]. The STM topography for the H-covered surface is clearly different from that of the clean surface (which is very similar to that observed in previous work [17,18]). The corresponding $I(V)$ curves are also significantly different: whereas for the clean surface a gap is clearly visible, as expected for the semiconductor ZnO, for the H-saturated surface an approximately ohmic $I(V)$ characteristic for small voltages is seen, typical for a metal.

The ZnO(10$\bar{1}$0) system with adsorbed H at room temperature thus bears some similarity to the $\beta$-SiC(100)-(3 × 2) surface where recently also a metallization as a result of H atom exposure has been observed [19–21]. There the situation was explained by 3 H atoms being adsorbed at the surface per unit cell. Since each H atom adds one electron, an odd number immediately implies the presence of a half-filled electronic state. Since in the present case the HAS data shows a clear (1 × 1) periodicity and only an OH but no ZnH vibration is seen in the HREELS data we propose that exposure of the ZnO(10$\bar{1}$0) surface to H atoms at room temperature leads to the formation of surface hydroxyl groups but not to ZnH species. The geometric and electronic structure of such a (1 × 1) ZnO(10$\bar{1}$0)—H surface, as determined by DFT calculations [11], is shown in Fig. 1(b). The band structure clearly indicates the presence of partially filled electronic states, formed dominantly by Zn-4*s* states of the surface Zn atoms, rendering the surface metallic. Careful tests showed that this structure is stable toward symmetry-breaking distortions that might reintroduce a band gap.

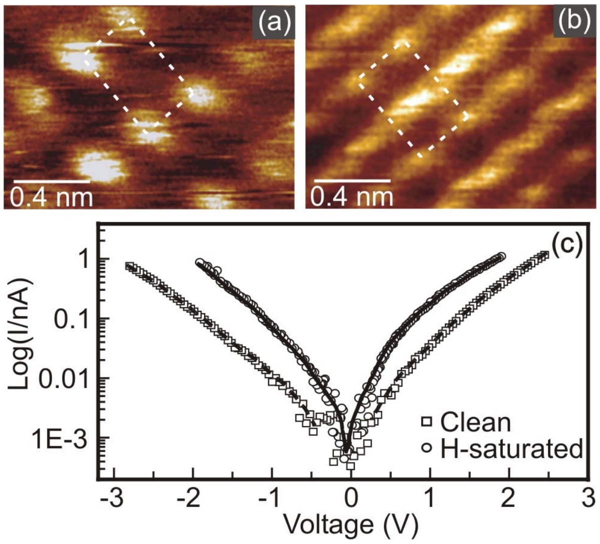

FIG. 4 (color online). STM images of (a) the clean and (b) the H-saturated ZnO(10$\bar{1}$0) surface recorded at 380 K. The (1 × 1) surface unit cell is indicated by dashed lines. (c) $I(V)$ curves for the two surfaces recorded at 300 K.

A sensitive test whether the surface Zn atoms are hydrogenated or not is to employ the chemical difference between ZnH and Zn species. In previous combined experimental and theoretical studies it was demonstrated that carbon monoxide, CO, chemisorbs on Zn atoms but not on ZnH groups and only physisorbs to OH surface species [10,22,23]. Thus probing the binding of CO to the H-saturated ZnO(10$\bar{1}$0) surfaces provides a direct way to test the structural models presented in Fig. 1. DFT calculations for the CO adsorption on the clean and H-saturated surface with one and 2 H atoms (summarized in Table I) confirm these expectations. The calculations furthermore predict that CO binds distinctly different to the Zn sites on the insulating clean and on the metallic ZnO(10$\bar{1}$0)—H surface. On the clean surface a weak Zn-CO bond and a blueshift of the CO stretching frequency are observed (which is typical for oxide surfaces), in full agreement with previous experimental results [24]. On the metallic ZnO(10$\bar{1}$0)—H surface, however, the theoretical results reveal a Blyholder-type CO adsorption characteristic for metal surfaces with a red shift of the CO vibration frequency [25] due to the now partial occupation of the Zn-4*s* states.

HREELS data recorded for the ZnO(10$\bar{1}$0)—2H phase exposed to CO at 70 K show no CO-related loss peaks, revealing that no CO is adsorbed at this temperature, thus confirming that the Zn sites are H capped. However, when the high-temperature ZnO(10$\bar{1}$0)—H phase is exposed to

TABLE I. Calculated CO binding energies $E_b$ (in eV) and vibration frequencies $\nu$(Zn—CO) and $\nu$(C—O) (in meV) for the clean ZnO(10$\bar{1}$0) surface and the two H-saturated surface models shown in Fig. 1. Only one stable CO adsorption site exists in all three cases. The vibration frequencies are calculated in harmonic approximation; the deviation to the calculated harmonic gas phase value of 265.6 meV is given in parenthesis.

| CO coverage | $E_b$ | $\nu$(Zn—CO) | $\nu$(C—O) |
|---|---|---|---|
| Clean ZnO(10$\bar{1}$0) surface: CO adsorbs at Zn sites | | | |
| 1/2 ML | 0.32 | 26.5 | 267.9(+2.3) |
| 1 ML | 0.24 | 28.0 | 265.8(+0.2) |
| ZnO(10$\bar{1}$0)—H surface: CO adsorbs at Zn sites | | | |
| 1/2 ML | 0.46 | 29.9 | 246.1(−19.5) |
| 1 ML | 0.37 | 32.4 | 246.5(−19.1) |
| ZnO(10$\bar{1}$0)—2H surface: CO adsorbs at OH sites | | | |
| 1/2 ML | 0.12 | 26.4 | 268.1(+2.5) |
| 1 ML | 0.08 | 25.9 | 268.3(+2.7) |

CO at 70 K, two new losses at 28 and 269 meV show up, which can be assigned to the $\nu$(Zn—CO) and $\nu$(C—O) vibration, respectively [see Fig. 2(a), curve *D*]. He-TDS measurements yield a CO binding energy of 320 meV, a value which is very similar as for CO adsorbed on the insulating clean ZnO$(10\bar{1}0)$ surface [26] and, in fact, is comparable to the CO binding energy of 279 meV observed for the polar Zn-terminated ZnO(0001) surface [10].

Altogether the CO adsorption studies very nicely corroborate the structural models shown in Fig. 1 and demonstrate that exposing the ZnO$(10\bar{1}0)$ surface to H atoms at room temperature only leads to the formation of hydroxyl species, whereas the Zn sites are unoccupied and available for CO adsorption. There is, however, an interesting difference to the theoretical prediction: the experimental CO binding energies for the clean and the ZnO—H surface are almost identical and the CO vibration frequency is only slightly redshifted from 272 meV for the clean surface [24] to 269 meV, whereas the DFT calculations predict much stronger changes. This might indicate that the extra charge added to the surface by hydroxylating the surface O atoms ($O^{2-} + H \rightarrow OH^{-} + e$) is mainly transferred to bulk defect states (which are not considered in the calculations) rather than to the surface Zn ions. We speculate that the H atoms adsorbed on the Zn sites at low temperatures diffuse into the bulk upon heating and create such defect sites [27], thereby actually causing the increase in bulk conductivity, which is the basic mechanism for using ZnO as a H atom sensor.

In conclusion, we have provided compelling experimental evidence that exposing the mixed-terminated ZnO$(10\bar{1}0)$ surface to H atoms at room temperature leads to the formation of a $(1 \times 1)$ overlayer with one H atom per unit cell. Theoretical results on the electronic structure demonstrate that for such a hydroxylated surface with an odd number of H atoms per unit cell the surface is metallic. Exposing the same surface to H atoms at a surface temperature of 200 K, on the other hand, leads to the formation of a hydrogen adatom overlayer containing two H atoms per unit cell, yielding one OH and one ZnH species, and no indications of metallicity are seen.

We thank Professor K. Jacobi for useful discussions. This work was supported in part by the DFG through SFB 558.

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[12] The HREELS experiments were performed in an UHV apparatus using a Delta 0.5 spectrometer (SPECS, Germany) with a straight-through energy resolution of 1 meV. The sample was cleaned by repeated cycles of sputtering (1 keV $Ar^{+}$, 30 min) and annealing in oxygen ($1 \times 10^{-6}$ mbar, 850 K, 2 min) and in UHV (850 K, 5 Min). Typically, two sputtering cycles with annealing in UHV were followed by one cycle with annealing in oxygen. The surface cleanness was checked by LEED and HREELS. Exposures are in Langmuir (L) ($1\ \mathrm{L} = 1.33 \times 10^{-6}$ mbar s).

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