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Hydrogen and oxygen adsorption on ZnO nanowires: A first-principles study

Hu Xu,[1,2] Wei Fan,[1,2] A. L. Rosa,[3,*] R. Q. Zhang,[1,4,†] and Th. Frauenheim[3]
[1]*Nano-organic Photoelectronic Laboratory, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China*
[2]*Graduate University of Chinese Academy of Sciences, Beijing 10080, China*
[3]*BCCMS, Universität Bremen, FB1/NW1, 28359 Bremen, Germany*
[4]*Center of Super-Diamond and Advanced Films (COSDAF) and Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, China*

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We employ first-principles calculations to investigate the structural stability and electronic properties of zinc oxide (ZnO) nanowires adsorbed with different chemical functional groups. The nanowires with one hydrogen monolayer on the surfaces adsorbed with both O and Zn atoms maintain their bulklike geometries, whereas the surface relaxation is found to be significant for the bare and partially adsorbed nanowires. While a half monolayer coverage of hydrogen on an oxygen-adsorbed surface induces metallic behavior, the adsorption of a full monolayer removes the states from the band gap to render a system with a well-defined band gap, revising previous theoretical predictions of metallicity in the latter. On the other hand, when all surface atoms are saturated, either with hydrogen atoms only or with both OH and H groups, the semiconducting behavior is recovered. Our results open up the possibility of tailoring the electronic properties by controlling the surface adsorption sites.

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Zinc oxide (ZnO) nanostructures have attracted considerable attention in the past few years due to their promising electrical, piezoelectric, and optical properties.[1–5] ZnO materials are especially useful for optical applications, owing to their wide direct band gaps and large exciton binding energies. Recent investigations on ZnO nanowires have been motivated by the possibility of fabrications of nanosensors for optical, chemical, biological detection, and optoelectronic nanodevices. The interaction of chemical species with nanowire surfaces is currently being actively studied for the development of hydrogen sensors for leak detection in hydrogen fuel storage systems and fuel cells.[6] Experimentally, ZnO nanorods grown by site-selective molecular-beam epitaxy show current-voltage characteristics that are sensitive to the presence of hydrogen or ozone for temperatures as low as 385 K.[7] Resistance changes of more than 4 or 2 orders of magnitude were observed when the ZnO nanowire or nanorod devices were exposed to a moisture pulse of 97% relative humidity.[8]

Furthermore, hydrogen is a common impurity during the preparation process of ZnO nanowires. Moreover, recent first-principles calculations suggest that the electronic behavior of ZnO nanowires with $(2\bar{1}\bar{1}0)$ surfaces can be tuned by hydrogen adsorption.[9] Therefore, gaining a deep understanding of the interaction of ZnO surfaces with their environment is important. In this work, we employ first-principles calculations to investigate the adsorption of hydrogen and water on **c**-oriented ZnO nanowires. We show that the structures with full passivation are energetically stable. Besides, we suggest that water molecules are likely to dissociate on the ZnO nanowire surfaces. Furthermore we suggest that the electronic structure of these wires can be tuned by exposing the ZnO wires to different ambient environments.

Our calculations have been performed using density-functional theory within the generalized gradient approximation (GGA) as implemented in the Vienna *ab initio* simulation package (VASP).[10] The Perdew and Wang (PW91) form[11] of the GGA with the projected augmented wave (PAW) (Ref. 12) potentials was adopted. The Zn 3*d* electrons were treated as valence electrons. A cutoff energy of 500 eV was used throughout the calculations. The nanowires were separated by a vacuum region of 15 Å. We used a $(1\times1\times8)$ *k*-point Monkhorst-Pack mesh for all nanowires. The atomic coordinates within the supercell were fully optimized. All atoms were allowed to relax until the forces were smaller than 0.001 eV/Å.

In order to mimic hydrogen and water exposure to the ZnO wires, we have considered the following configurations: (i) bare nanowire, as shown in Fig. 1(a); (ii) 1/2 H-O—a half monolayer (ML) of surface oxygen atoms is adsorbed with H atoms, as shown in Fig. 1(b); (iii) 1 ML H-O—all the surface oxygen atoms are adsorbed with H atoms, as shown in Fig. 1(c); (iv) 1 ML H-ZnO—all the surface Zn and O atoms are adsorbed with H atoms, as shown in Fig. 1(d); (v) 1 ML OH-Zn+1 ML H-O—one monolayer of OH groups on Zn atoms and one monolayer of hydrogen atoms on O, as shown in Fig. 1(e); (vi) 1 ML H_2O-Zn—all Zn atoms are adsorbed with H_2O molecules, as shown in Fig. 1(f); and (vii) 1/2 ML H_2O-Zn—1/2 ML water molecules dissociated on the surface and 1/2 ML adsorbs as molecular water, as shown in Fig. 1(g).

We start our discussion with the hydrogenated nanowires shown in Figs. 1(a)–1(d). The formation energies for the hydrogenated wires are calculated as follows:

$$E_f = E_{\text{tot}}^{\text{wire}} - E_{\text{bare}}^{\text{wire}} - n_{\text{H}}\mu_{\text{H}}, \qquad (1)$$

where $E_{\text{tot}}^{\text{wire}}$ is the total energy of the hydrogenated wire, $E_{\text{bare}}^{\text{wire}}$ is the total energy of the bare nanowire, and μ_{H} is the chemical potentials of H. For gaseous species, the temperature and pressure dependences of the chemical potential are particu-

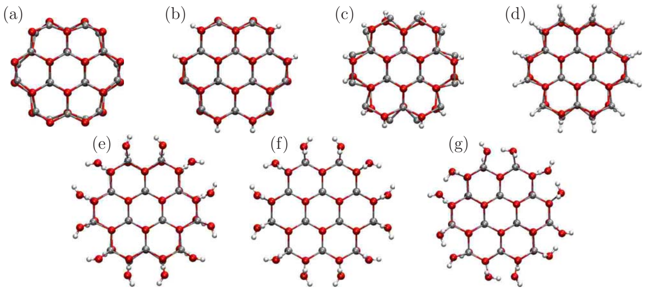

FIG. 1. (Color online) Top view of the relaxed structures of the ZnO nanowires. (a) Bare: bare nanowire; (b) 1/2 ML H-O: half monolayer hydrogen adsorbed on surface oxygens; (c) 1 ML H-O: one monolayer of hydrogen adsorbed on all surface oxygens; (d) 1 ML H-ZnO: one monolayer of hydrogen adsorbed on all surface Zn and O atoms; (e) 1 ML OH-Zn+1 ML H-O: one monolayer of water adsorbed as OH groups on Zn and hydrogens on O atoms; (f) 1 ML H_2O-Zn: one monolayer of water molecules adsorbed on Zn sites; and (g) 1/2 ML H_2O-Zn: one monolayer of water adsorbed as half monolayer dissociated on the wire and the other half adsorbs on Zn sites. Zn, O, and H atoms are represented by gray, red, and white spheres.

larly important. So we include the temperature and pressure dependences of the hydrogen reservoir following Van de Walle and Neugebauer,[13]

$$2\mu_{\mathrm{H}} = E_{\mathrm{H}_2} + kT\left[\ln\left(\frac{pV_Q}{kT}\right) - \ln Z_{\mathrm{rot}} - \ln Z_{\mathrm{vib}}\right], \qquad (2)$$

where E_{H_2} is the energy of a H_2 molecule, p is the pressure, k is the Boltzmann constant, T is the temperature, and $V_Q = (h^2/2\pi mkT)^{3/2}$ is the quantum volume. Z_{rot} and Z_{vib} are the rotational and vibrational partition functions.

The hydrogen chemical potential was allowed to be in the range of the formation energy of the H_2 molecule. The catalyst-assisted vapor-liquid-solid growth of ZnO nanowires usually takes place at temperatures around 1200–1300 K. In metal-organic chemical vapor deposition (MOCVD) techniques, the temperature needed to grow well-aligned wires is somewhat lower, ranging from 800 to 1000 K. Table I shows the formation energies for the structures (i)–(iv) calculated at a typical growth temperature of 1300 K ($p=1$ atm) and can be considered as an upper bound. It is worth mentioning that at 1300 K the hydrogen chemical potential is around 1 eV lower than that at $T=0$ K. Under hydrogen-rich conditions, all nanowires have lower formation energies than the bare wire (indicated by the negative sign of the formation energies). We find that a structure containing a full monolayer of hydrogen adsorbed on both O and Zn surface atoms (1 ML H-ZnO) is energetically stable under H-rich conditions. As the hydrogen chemical potential decreases, structures with more hydrogen on the nanowire surface become energetically unstable with respect to the bare wire.

TABLE I. Formation energies (in eV) for ZnO nanowires adsorbed with hydrogen for the structures shown in Fig. 1.

Structure	H rich	H poor
1/2 ML H-O	−1.65	1.42
1 ML H-O	−1.82	1.26
1 ML H-ZnO	−2.35	0.72

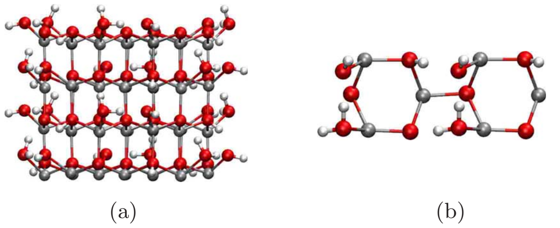

FIG. 2. (Color online) (a) Side view of the 1/2 ML H_2O-Zn wire where half monolayer of water is dissociated on a ZnO nanowire $(10\bar{1}0)$ facet, and (b) the $(10\bar{1}0)$ facet of the 1/2 ML H_2O-Zn wire.

Next we explore the possibility of water dissociation on the ZnO nanowire surfaces. We have considered 1 ML water coverage on several adsorption sites. The most stable configurations are shown in Figs. 1(e)–1(g) and Figs. 2(a)–2(b). The calculated adsorption energies per H_2O molecule as a function of the water chemical potentials are shown in Fig. 3. The zero of the water chemical potential is set at the total energy of a single water molecule in gas phase. We can see that the structure where half of the water molecules dissociate on the surface is the most stable one.

The calculated adsorption energies per H_2O molecule using water in the gas phase as reservoirs of H and O are 0.87 eV for a full water monolayer adsorbed on the Zn sites, 0.94 eV for the structures with dissociated water, and 1.13 eV for the 1/2 ML H_2O-Zn nanowire with half-dissociated water (Fig. 3). Thus, our study indicates that half water molecules are likely to dissociate upon adsorption on ZnO nanowire surfaces. We should point out that in our calculations we have only considered coverages with one monolayer of wa-

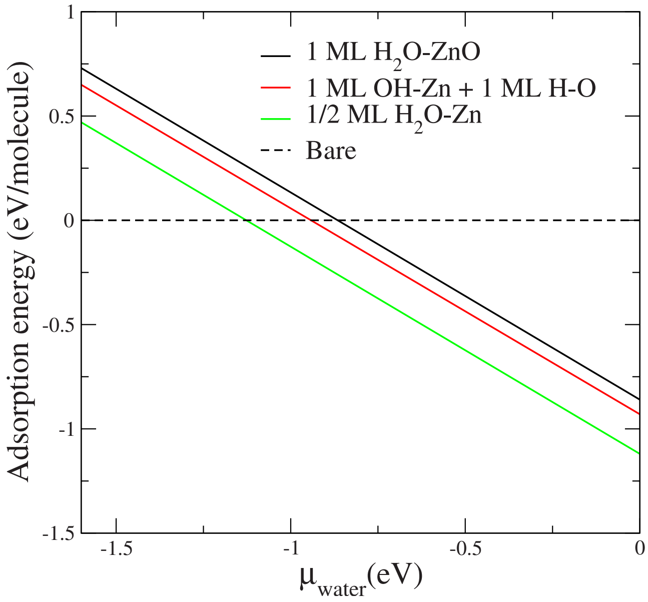

FIG. 3. (Color online) Adsorption energies for 1 ML of water adsorbed on ZnO nanowires. The zero of the water chemical potential is set at the total energy of a water molecule in gas phase.

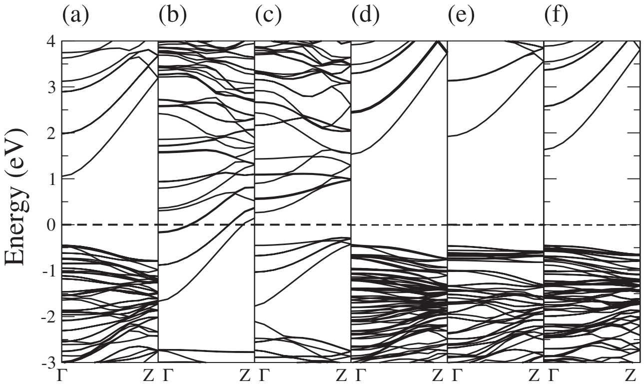

FIG. 4. Electronic band structure of ZnO nanowires along the [0001] direction. (a) Bare nanowire; (b) 1/2 ML H-O: half monolayer of surface oxygens adsorbed with H atoms; (c) 1 ML H-O: all the surface oxygens are adsorbed with H atoms; (d) 1/2 ML H_2O-Zn; (e) 1 ML H-ZnO: all the surface Zn and O atoms are adsorbed with H atoms; and (f) 1 ML OH-Zn+1 ML H-O: OH groups on Zn and hydrogen atoms on O atoms. All the Fermi levels are shifted to zero.

ter. A more detailed investigation on the water coverage dependence is on the way and will be published elsewhere. The fact that OH and H groups on the ZnO nanowire surfaces are stable might have important consequences for exposure of ZnO wires to water, suggesting that water molecules are likely to dissociate on the surface. Previous first-principles calculations predicted that H_2O molecules on the ZnO$(10\bar{1}0)$ surfaces dissociate upon adsorption.[14–16] Indeed, it has been observed that the H_2O molecules adsorbed on the ZnO surface can have a fast dynamics with water molecules undergoing repeated associations/dissociations.[15]

Now we turn our attention to the electronic properties of the investigated wires. The electronic band structure along the growth direction of the nanowires is shown in Fig. 4. The bare wire shown in Fig. 4(a) has a semiconducting behavior with a direct band gap of 1.50 eV, which is much larger than that of bulk ZnO, indicating strong quantum confinement effects, as reported in our previous work.[17] Adsorbing 1/2 ML of hydrogen on the surface oxygen atoms induces metallicity with bands crossing the Fermi level, as shown in Fig. 4(b). Since each H atom provides one electron to the ZnO wire, the excess electron can partially occupy the 4*s* states of surface Zn atoms, inducing metallic behavior. Additional 1/2 ML hydrogen on the other hand [as shown in Fig. 4(c)] recovers the semiconducting behavior. The distance of the surface Zn atoms is 2.65 Å, which is very close to the value for hexagonal bulk Zn (2.66 Å).[18] The newly formed surface Zn-Zn bonds can drastically affect the electronic structures of nanowires, as the excess electrons donated by hydrogen atoms are mainly located at the Zn-Zn surface bonds. We find that this wire has an indirect band gap of 0.54 eV, which is contrary to previous first-principles calculations.[19,20] We believe that this discrepancy comes from the fact that in Ref. 19, no reconstruction of the Zn-Zn bonds is found, while in our case, a strong relaxation of the surface atoms was seen, inducing semiconducting behavior. We should mention that for the unrelaxed structure (no atomic relaxation is allowed), we also find a metallic behavior with the states crossing the Fermi level as shown in Fig. 5, in agreement with Refs. 19 and 20.

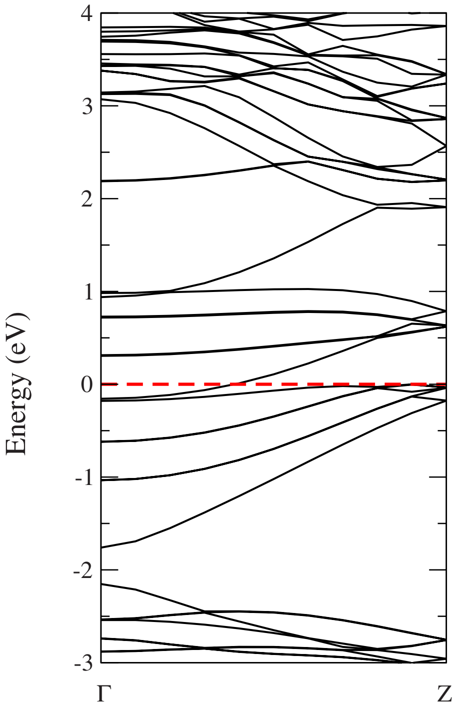

FIG. 5. (Color online) Electronic band structure of the unrelaxed ZnO nanowire where all the surface oxygens are adsorbed with H atoms. The red dashed line is the Fermi level and it is set to zero. This ZnO nanowire has a metallic behavior with the states crossing the Fermi level.

The structures of 1 ML H-ZnO, 1/2 ML H_2O-Zn, and 1 ML OH-Zn+1 ML H-O have defined band gaps of 2.00, 2.38, and 2.06 eV, respectively. The nanowires recover their semiconducting behavior, and this also suggests that the band gaps can be tuned by hydrogen and water adsorption (which will eventually dissociate upon adsorption). Recent investigations on OH groups adsorbed on InP nanowires[21] have led to similar conclusions.

In summary, we have employed first-principles density-functional calculations to investigate the structural stability and electronic properties of ZnO nanowires with different surface adsorptions. The nanowires with one hydrogen monolayer on both O and Zn atoms keep their bulklike geometries, whereas surface relaxation is found to be significant for the bare and partially adsorbed nanowires. While the adsorption with half a monolayer of hydrogen on an oxygen surface induces metallic behavior, the adsorption with a full monolayer removes states from the band gap to render a system with a well-defined band gap. Our results revise previous theoretical predictions of metallicity in this kind of wire. On the other hand, when all surface atoms are saturated, either with hydrogen atoms only or with both OH and H groups, the semiconducting behavior is recovered. We conjecture that the ZnO nanowires with surface Zn atoms saturated by -NH_2 and -Cl groups will exhibit a similar metallic behavior. Our results open up the possibility of tailoring the electronic properties by controlling the surface adsorption sites and should motivate further investigations to better understand the effects of surface reconstruction and hydrogen species on ZnO nanowires.

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*darosa@bccms.uni-bremen.de

†aprqz@cityu.edu.hk

[1] X. Y. Kong, Y. Ding, R. Yang, and Z. L. Wang, Science **303**, 1348 (2004).

[2] W. Z. Wang, B. Q. Zeng, J. Yang, B. Poudel, J. Y. Huang, M. J. Naughton, and Z. F. Ren, Adv. Mater. (Weinheim, Ger.) **18**, 3275 (2006).

[3] M. H. Zhao, Z. L. Wang, and S. X. Mao, Nano Lett. **4**, 587 (2004).

[4] J. F. Conley, L. Stecker, and Y. Ono, Appl. Phys. Lett. **87**, 223114 (2005).

[5] C. H. Liu, W. C. Yiu, F. C. K. Au, J. X. Ding, C. S. Lee, and S. T. Lee, Appl. Phys. Lett. **83**, 3168 (2003).

[6] H. T. Wang, B. S. Kang, F. Ren, L. C. Tien, P. W. Sadik, D. P. Norton, S. J. Pearton, and J. Lin, Appl. Phys. Lett. **86**, 243503 (2005).

[7] B. S. Kang, Y. W. Heo, L. C. Tien, D. P. Norton, F. Ren, B. P. Gila, and S. J. Pearton, Appl. Phys. A: Mater. Sci. Process. **80**, 1029 (2005).

[8] Y. S. Zhang, K. Yu, D. S. Jiang, Z. Q. Zhu, H. R. Geng, and L. Q. Luo, Appl. Surf. Sci. **242**, 212 (2005).

[9] C. Wang, G. Zhou, J. Li, B. Yan, and W. H. Duan, Phys. Rev. B **77**, 245303 (2008).

[10] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[11] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[12] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[13] C. G. Van de Walle and J. Neugebauer, Phys. Rev. Lett. **88**, 066103 (2002).

[14] B. Meyer, D. Mark, O. Dulub, U. Diebold, M. Kunat, D. Lanenberg, and C. Wöll, Angew. Chem., Int. Ed. **43**, 6641 (2004).

[15] O. Dulub, B. Meyer, and U. Diebold, Phys. Rev. Lett. **95**, 136101 (2005).

[16] Y. F. Yan and M. M. Al-Jassim, Phys. Rev. B **72**, 235406 (2005).

[17] W. Fan, H. Xu, A. L. Rosa, Th. Frauenheim, and R. Q. Zhang, Phys. Rev. B **76**, 073302 (2007).

[18] E. R. Jette and F. Foote, J. Chem. Phys. **3**, 605 (1935).

[19] J. M. Jia, D. N. Shi, J. J. Zhao, and B. L. Wang, Nanotechnology **18**, 455708 (2007).

[20] W. Fan, A. L. Rosa, Th. Frauenheim, and R. Q. Zhang, Solid State Commun. **148**, 101 (2008).

[21] M. D. Moreira, P. Venezuela, and T. M. Schmidt, Nanotechnology **19**, 065203 (2008).