

Metallization of ZnO(10 $\bar{1}$ 0) Surface Induced by Adsorption of Hydrogen, Methanol and Water

Angle-resolved photoelectron spectroscopy (ARPES) was utilized to investigate the electronic structure of the nonpolar ZnO(10 $\bar{1}$ 0) surface and its modification by adsorption of hydrogen, methanol and water. All of these species act as electron donors and induce downward band bending. Donated electrons are transferred to and accumulated in the potential wells at the surfaces. Surface metallicity originates from the charge accumulation layers, in which the electrons behave as free-electron gases along the surface parallel, but exhibit quantized features in the surface perpendicular direction.

Owing to its unique optical and electrical properties, characterized by a wide band gap (3.37 eV) and strong n-type conductivity as well as relatively easy control of the carrier density by doping, ZnO is a potential candidate for a transparent conductive oxide. Hydrogen (H) is known to be a good electron donor in ZnO [1]. It is experimentally demonstrated that, when the ZnO(10 $\bar{1}$ 0) surface is covered with H, substantial electron donation from H to the ZnO substrate occurs and the surface exhibits metallic properties [2]. Interestingly, both density functional theory (DFT) calculations and scanning tunneling spectroscopy (STS) measurements imply a gap-less band structure for the metallized surface [2]. However, considering the large band-gap energy of ZnO, such a H-induced change in the band structure is unexpectedly drastic. Thus, understanding the metallization mechanism is important from scientific and technological viewpoints. In the present study [3], we examined the electronic structure of ZnO(10 $\bar{1}$ 0) and its modification by adsorption of atomic H, a strong electron donor, and as a comparison, methanol and water, weak donors, by ARPES. The ZnO(10 $\bar{1}$ 0) surface has a

unique atomic structure, consisting of Zn-O dimer rows [Fig. 1(a)]. Reflecting the different bonding strength, H interacts mainly with surface O at around room temperature [2]. Molecularly-adsorbed methanol and water are, on the other hand, expected to occupy the Zn site.

The ARPES measurements were carried out at beam line 11D using an SES-200 electron-energy analyzer (VG Scienta) with an overall energy resolution of 50 meV. Atomic H and methanol and water molecules were dosed on the surface at room temperature. The spectra were acquired also at room temperature.

Figure 1(b) shows valence-band spectra of a clean and an adsorbate-covered ZnO(10 $\bar{1}$ 0) surfaces. At a glance, adsorption of foreign species hardly affects the spectral lineshape. However, a close examination reveals faint peaks in the band-gap region (see the inset of Fig. 1(b)). These gap states exhibit the same photon-energy dependent change in the emission intensity [Fig. 1(c)]. This implies that the gap states should be associated with ZnO-derived states rather than adsorbate-related states.

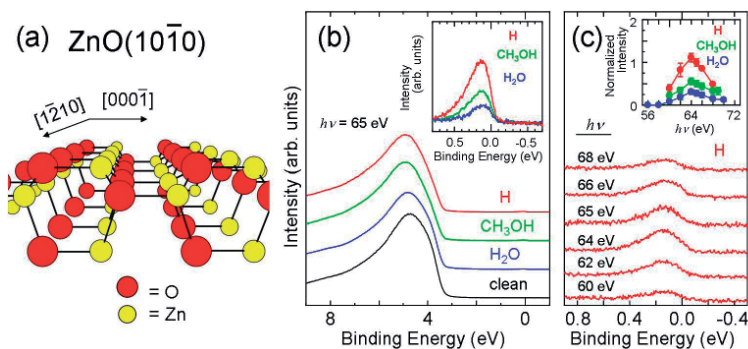


Figure 1 (a) Schematic of the atomic structure of ZnO(10 $\bar{1}$ 0). (b) Angle-integrated valence-band spectra of clean, H-, methanol- and water-covered ZnO(10 $\bar{1}$ 0). The adsorbates form overlayers without any ordered structures. Coverages are 0.40 for H, and 0.15 for both methanol and water, where 1.0 corresponds to the density of the surface Zn or O atoms; $5.9 \times 10^{14} \text{ cm}^{-2}$. The inset shows the results of detailed measurements of the adsorbate-induced band-gap states. The photon energy was 65 eV. (c) The photon-energy dependence of the H-induced gap states. Similar results were obtained for the methanol- and water-induced states. The inset shows the plots of the integrated intensities of the gap states.

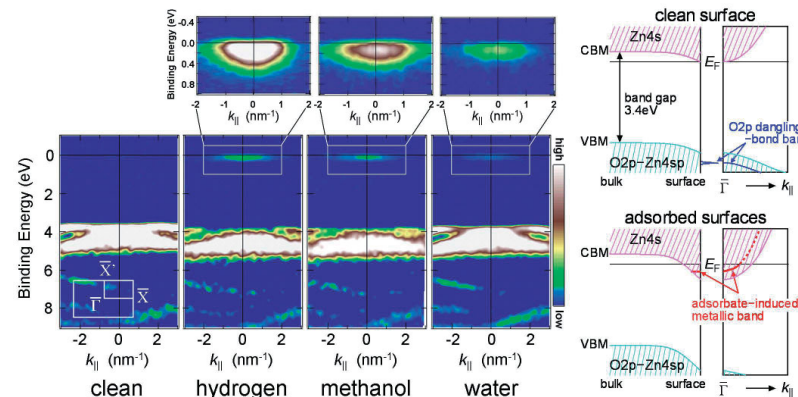


Figure 2 (left) Intensity plots of the second derivatives of the ARPES spectra. The spectra were recorded with the photon energy of 65 eV. The results of detailed measurements of the gap states are shown in the upper panels. (right) Schematic of the energy band structures of the clean and adsorbate-covered ZnO(10 $\bar{1}$ 0) surfaces.

Further information on the gap states is obtained from ARPES intensity plots. The left-half panels of Fig. 2 are the intensity plots of the clean and the adsorbate-covered surfaces, where the ZnO valence bands are observed in the binding-energy region larger than 3 eV. The plots clearly indicate that the gap states are formed at ca. 3 eV above the ZnO valence bands. This proves the absence of the adsorption-induced band-gap closure. The DFT and STS results [2] apparently overestimated the H-induced change in the surface electronic structure. The magnified views of the gap states reveal that each gap state forms a partially occupied band with parabolic energy dispersion. Observation of the metallic band is the first direct evidence for metallization of the ZnO(10 $\bar{1}$ 0) surface by adsorption of not only atomic H but also methanol and water, both of which are considered very weak electron donors.

The emission intensity of the gap state is the highest for the H adsorption system and decreases in order of methanol and water. This trend is related to the magnitude of downward band bending (0.40, 0.19 and 0.15 eV for H, methanol and water, respectively). From this fact, together with the photon-energy dependence of the metallic state [Fig. 1(c)], we propose a mechanism for surface metallization as follows: The adsorbates donate a fraction of valence electrons to ZnO and induce downward bending of the ZnO band. As a result, a potential

well is formed between the conduction-band edge and the surface/vacuum interface. Donated electrons are accumulated in this potential well and behave as a two-dimensional electron gas, whose density depends on the depth of the potential well, i.e., the magnitude of induced band bending. The right part of Fig. 2 shows schematically the metallization mechanism. The fact that the potential well depth depends on the adsorbates means that we can control the density of metallic charge by selection of adsorbates with appropriate charge donating ability.

In summary, we have successfully identified the metallic bands on the ZnO (10 $\bar{1}$ 0) surfaces formed by adsorption of H, methanol and water and have clarified the mechanism of metallization.

REFERENCES

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