

Metallization of ZnO(10-10) by Hydrogen Adsorption: Angle-Resolved Photoelectron Spectroscopy

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Introduction

Hydrogenation is a commonly employed technique to passivate semiconductor surfaces like silicon surfaces. Inertness of hydrogenated semiconductor surfaces originates from quenching of chemically-active surface dangling bonds. From the electronic structure point of view, hydrogen adsorption eliminates band-gap states so that the surface turns to be more insulator-like. However, hydrogenation induces metallization of some semiconductor surfaces [1,2]. A recent high-resolution electron energy loss spectroscopy and scanning tunneling microscopy study combined with density functional theory calculations [2] has indicated the H-induced metallization of ZnO(10-10). An interesting result is that H adsorption may induce significant lowering of the conduction bands and the resultant band-gap closure. Such a modification of the surface electronic structure is surprising since ZnO is a wide band-gap material with the gap energy of 3.4 eV. In the present study, the valence electronic structure of the H/ZnO(10-10) surface is examined by angle-resolved photoelectron spectroscopy (ARPES) in order to elucidate the mechanism of the H-induced metallization [3].

Experimental

The ARPES measurements were carried out at beam line 11D of the Photon Factory, KEK. A ZnO single crystal with (10-10) orientation was cleaned in the ultrahigh vacuum chamber by cycles of Ar⁺ sputtering and annealing. The clean surface was exposed to H₂ gas while a hot tungsten filament, which was heated between 2100-2200 K, was placed at a distance of ca. 15 cm away from the sample surface. The sample temperature during H exposure was between 300 and 350 K, and the ARPES spectra were measured at room temperature.

Results and Discussion

Fig. 1 shows normal emission valence-band spectra at various H₂ exposures. H adsorption induces downward bending of the ZnO band by 0.40 eV. The work function of the ZnO(10-10) surface is decreased by H adsorption. Both indicate the donor character of adsorbed H on the surface. Also induced by H adsorption is a state just below the Fermi level. It forms a band with a free-

electron-like dispersion at around the surface Brillouin zone (SBZ) (see the inset of Fig.1). The origin of the surface metallization is the formation of this metallic band. The metallic state exhibits a faint photoemission intensity. This fact together with an isotropic band structure along the high symmetry axis of the SBZ and a small effective mass ($0.16m_e$) of the electron, a contribution of the Zn 4s orbital is evident. Moreover, absence of the band-gap closure is clarified. Therefore, metallicity of the H-adsorbed ZnO(10-10) surface results from H-induced downward bending of the ZnO band and the resultant partial filling of the Zn 4s conduction band.

References

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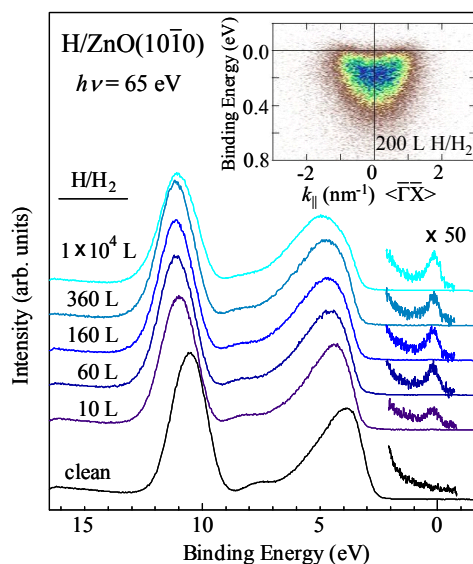


Fig. 1. Normal emission spectra of ZnO(10-10) at various H₂ exposure. The inset shows the ARPES-intensity plot of the H-induced band along one of the high symmetry axes.

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