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Metallization of the ZnO Surface by Ethanethiol

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1 Introduction

ZnO is one of metal-oxide semiconductors which develop a two-dimensional electron gas (2DEG) at their surfaces [1]. The 2DEG formation results in the surfaces of metal oxides having a metallic conductivity. This property is crucial for realization of all-oxide electronics.

The single crystal surfaces of ZnO are known to be metallized by illumination of the ultraviolet light [2], hydrogen atom adsorption [1, 3], and methanol and water adsorption [4]. However, the metallic nature of these surfaces is easily removed when the surfaces are exposed to atmosphere. Thus, a more stable system is desired.

In the present study, surface electronic properties of Zn-terminated ZnO(0001) and O-terminated ZnO(000-1) surfaces modified by ethanethiol (C_2H_5SH) by angle-resolved photoelectron spectroscopy (ARPES) and X-ray photoelectron spectroscopy (XPS).

2 Experimental

The ARPES and XPS measurements were carried out at a beam line 13A of the Photon Factory [5]. The Zn- and O-terminated ZnO surfaces were cleaned in ultrahigh vacuum conditions (UHV) by cycles of Ar^+ sputtering and annealing at 1000 K in 1×10^{-4} Pa O_2. The clean surfaces were confirmed to be semiconductors in nature because of absence of a density of states at the Fermi level.

A vapor of ethanethiol was introduced to the loadlock chamber, in which the clean ZnO samples were stored and ethanethiol was allowed to be adsorbed on the surfaces. The adsorption temperature was 300 K.

3 Results and Discussion

The 2DEG at the oxide surfaces always accompanies a formation of a strong accumulation layer. Thus, a necessary factor for the metallic oxide surfaces is electron dopants on the surface. Hydrogen is known to be a very efficient dopants on the ZnO surfaces [1, 3]. Water and methanol also act as electron dopants [4]. These molecules adsorb dissociatively on the ZnO surfaces to give electron-donating hydrogen atoms. Ethanethiol is found in the present XPS study to dissociate into ethanethiolate (C_2H_5S) and H on both Zn- and O-terminated ZnO surfaces at room temperature. Thus, the H adatoms are expected to donate the electrons to ZnO. This is true on the O-terminated surface but is not on the Zn-terminated surface. Upon adsorption of the saturation amount of ethanethiol on the O-terminated surface, the energy levels of ZnO shift by 0.85 eV to a high binding energy side. A sufficient number of the electrons are transferred from adsorbates to the substrate. On the other hand, an adsorption-induced shift is negligible on the Zn-terminated surface. Thus, dissociated H is not so effective to donate electrons on the Zn-terminated surface.

Fig. 1 shows an ARPES intensity plot of the ethanethiol-saturated O-terminated ZnO surface. A slightly bright region is seen at just below the Fermi level around the center of the surface Brillouin zone (a wave number of 0 nm^{-1}). This proves the metallic nature of this surface. On the other hand, no such state is observed on the Zn-terminated surface after ethanethiol adsorption. Thus, ethanethiol is effective for metallization of the O-terminated ZnO surface. This result may pave the way for thiolate-protected ZnO-based optoelectric devices whose thioate-ZnO interface is metallic in nature.

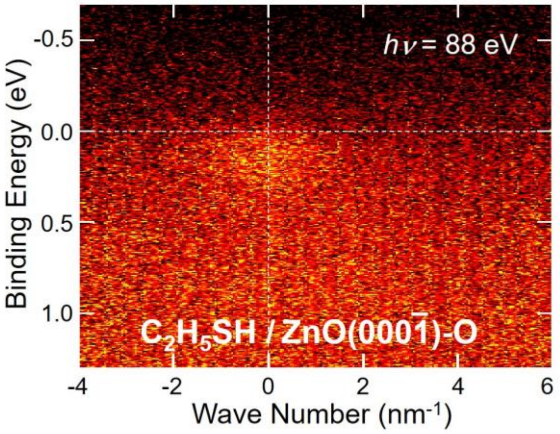

Fig. 1 ARPES intensity map of the ethanethiol-saturated O-terminated ZnO surface.

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