Two-dimensional Electron Gas at Thiol/ZnO Interface

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Electronic modification of O-terminated ZnO(0001) and Zn-terminated ZnO(0001) by ethanethiol (C₂H₅SH) adsorption was investigated by angle-resolved photoelectron spectroscopy (ARPES) and X-ray photoelectron spectroscopy (XPS). Ethanethiol dissociates on both surfaces at room temperature to form C₂H₅S and H. The saturation coverage of ethanethiol is nearly three times larger on ZnO(0001) than on ZnO(0001). This suggests that Zn atoms exposed to the surface should act as adsorption and dissociation sites. Adsorption on the (0001) surface induces large downward band bending and accompanies a Zn 4s-derived metallic state at the center of the surface Brillouin zone. This proves that ethanethiol is a good electron donor on ZnO(0001). Contrastingly, ethanethiol on ZnO(0001) hardly affects the energetic position of the ZnO band so that surface metallization is not brought about.

Keywords 2DEG; ARPES; ZnO; Thiol; Organic/oxide interface

I. INTRODUCTION

Zinc oxide (ZnO) belongs to a class of metal-oxide semiconductors which host a two-dimensional electron gas or liquid (2DEG/L) on their surfaces [1−5] or at interfaces with other materials [6−9]. The 2DEG/L brings the surfaces or interfaces of metal oxides having a metallic conductivity. Therefore, the technology that controls the 2DEG/L shall pave the way for all-oxide electronics.

It has been known that the 2DEG/L is a consequence of an accumulation-layer formation on the surfaces or at the interfaces of oxides. Regarding the ZnO surfaces, illumination of an ultraviolet light [10, 11] or adsorption of atomic hydrogen [10−15] induces the accumulation layer. Goldstein, Many, and their coworkers [10, 11] examined the electrons confined in the accumulation layer formed on the O-terminated ZnO(0001) surfaces by electron energy loss spectroscopy (EELS) and observed two-dimensional plasmons, which are regarded as indirect evidence for the 2DEG. More recently, Wang et al. demonstrated by using high-resolution EELS and scanning tunneling spectroscopy [12] that, although the ZnO(1010) surface remained semiconducting when both unsaturated surface Zn and O atoms were terminated by H atoms, it turned to be metallic when the H atoms were bonded only to the surface O atoms. The metallization mechanism proposed by Wang et al. is somewhat different from the metallization by the accumulation-layer formation. Thus, Ref. 12 has triggered a renewed interest in the metallization mechanism of the ZnO surfaces.

The first study which experimentally verified a metallic band formed on the ZnO surface was reported in 2010 [13]. A free-electron like band was specified by angle-resolved photoelectron spectroscopy (ARPES) measurements at the center of the surface Brillouin zone (SBZ) on ZnO(0001) [13]. The authors of Ref. 13 speculated that the surface, which was cleaned in an ultrahigh vacuum, was unintentionally covered with H so that the accumulation layer was formed in the surface region. Ozawa and Mase, then, carried out a systematic ARPES study [14], in which the clean ZnO surfaces with (1010), (0001), and (0001) orientation were exposed to the H atoms at room temperature. Although H adsorption pushed down the surface valence states of ZnO to form accumulation layers on all three surfaces, the 2DEG was observed only on ZnO(1010) and (0001). Absence of
the 2DEG on the Zn-terminated ZnO(0001) surface is considered to be due to surface roughness as a result of H etching [14]. However, a recent ARPES study reported a 2DEG on ZnO(0001), which was again unintentionally covered with H [15]. Our study [14] as well as the study of Ref. 15 suggest that both of the formation of the accumulation layer and the smooth surface atomic structure are necessary conditions for the 2DEG on the ZnO surfaces.

Adsorbed H atoms on the ZnO surfaces behave as strong electron donors and induce large downward band bending. Though not as strong as H, water and methanol also exhibit an electron donating character so that the ZnO(1010) surface is metallized by adsorption of these molecules [16]. Judging from the size of the electron pocket by the metallic band, the donating ability is larger for methanol than water [16]. These molecules dissociate into H and CH₃O (in the case of methanol) and into H and OH (water) on ZnO(1010). Thus, the different electron donating ability of the molecules may arise from a different electron withdrawal ability between CH₃O and OH [16].

Although the ZnO surfaces are rather easily metallized by adsorption of electron donating species (H, methanol, and water), the metallized surfaces are fragile against gas absorption [10]. Thus, a more stable system is desired for practical applications of ZnO to optoelectric devices. A thiol/ZnO system is one of such candidates because thiol/ZnO interface properties are expected to be self-protected by alkyl chains of the thiol molecules. Thus, it is desired to clarify, as a first step, how the electronic structure of the ZnO surface is modified by thiol adsorption.

In the present study, we examined the interface electronic structure between ZnO and ethanethiol (C₂H₅SH) by ARPES and X-ray photoelectron spectroscopy (XPS). Zn-terminated ZnO(0001) remains semiconducting after the saturation amount of ethanethiol is accommodated. On the other hand, ethanethiol exhibits a sufficient electron donating ability on O-terminated ZnO(0001) so that the thiol/ZnO interface turns to be metallic in nature.

II. EXPERIMENTAL

The ARPES and XPS measurements were carried out at a beam line 13A of the Photon Factory, High Energy Accelerator Research Organization (KEK) [17], utilizing a p-polarized synchrotron radiation light as an excitation source. Photoelectron spectra were acquired by a hemispherical electron energy analyzer (Gamma Data/Scienta SES200) with an overall energy resolution of 70 meV, 150 meV, and 200 meV at photon energies (hν) of 65 eV, 350 eV, and 600 eV, respectively. The measurements were made at the ZnO sample temperature of 300 K. The binding energy of the spectra refers to the Fermi level (E_F) of a Mo sample holder which was electrically in contact with the ZnO samples.

ZnO single crystals with (0001) and (0001) orientation (10 mm × 10 mm × 0.5 mm) were purchased from Goodwill, Russia. The surfaces were cleaned in an ultrahigh vacuum chamber by cycles of Ar⁺ sputtering (2 kV, 3.5 μA, 20 min) and annealing at 1000 K in O₂ atmosphere (1 × 10⁻⁴ Pa) for 10−20 min until no carbon contaminant was detected by XPS. The clean surfaces showed sharp (1 × 1) low-energy electron diffraction patterns. The sample cleaning was done in a preparation chamber, which was directly attached to a measurement chamber. On the other hand, molecular adsorption was carried out in a sample loadlock chamber, whose base pressure was better than 2 × 10⁻⁷ Pa. Ethanethiol...
was dosed onto the clean ZnO surfaces at room temperature by backfilling the loadlock chamber with a vapor of the molecule \( (1.33 \times 10^{-2} \text{ Pa}) \). The amount of the coverage was controlled by an exposure time. The ethanethiol-adsorbed samples were transferred to the measurement chamber via the preparation chamber without exposing them to air.

For comparison, we also examined the methanol adsorbed ZnO(0001) and (0001) surfaces. Preparation of the methanol/ZnO systems was the same as the preparation procedure of the ethanethiol/ZnO system.

### III. RESULTS AND DISCUSSION

#### A. Evidence of surface metallization

The clean ZnO(0001) and (0001) surfaces prepared in the present study were semiconducting in nature because no state was observed at \( E_F \). Figure 1(a) shows spectra in the band gap region of the clean and C\(_2\)H\(_5\)SH-dosed ZnO(0001) surfaces acquired at \( h\nu = 65 \text{ eV} \). Although no structure is observed in the spectrum of the clean surface, a weak but definite hump is seen at just below \( E_F \) on the ethanethiol-dosed surface. This hints a metallization of the ZnO surface. Inset panels in Figure 1(a) show the two-dimensional APRES intensity maps on these surfaces. A structure associated with the metallic state is not obvious. However, when the photon energy is tuned from 65 eV to 88 eV, a bright structure is emerged at the center of the SBZ at just below \( E_F \) [Figure 1(b)]. As indicated in the inset of Figure 1(b), an integrated spectrum bears a peak which is characteristic of a metallic state. The intensity enhancement at \( h\nu = 88 \text{ eV} \) is due to a resonance emission involving an interference between a Zn 4s photoemission and a Zn 4s emission induced by an Auger decay after the Zn 3p →4s photoexcitation. The Zn 3p →4s excitation is rationalized by the fact that the Zn 3p core level of ZnO is located at ~90 eV [18]. This enhancement mechanism suggests that the Zn 4s orbital should be a dominant component of the metallic state.

Another possible explanation for the intensity enhancement is that, on the surfaces of n-type semiconductors such as ZnO [13, 16], Cd\(_{1-x}\)Zn\(_x\)O [19], InN [20], etc., the metallic state is intensified when the center of the bulk Brillouin zone (the \( \Gamma \) point), where the bottom of the conduction band is located, is probed. In the present case of the ethanethiol/ZnO(0001) surface, the excitation light at \( h\nu = 88 \text{ eV} \) can probe the state at \( k_z = 50 \text{ nm}^{-1} \) in the normal emission geometry, which is closer to the \( \Gamma \) point \( (k_z = 48.3 \text{ nm}^{-1}) \) than \( k_z = 44 \text{ nm}^{-1} \) by \( h\nu = 65 \text{ eV} \), as shown in Figure 1(c). Thus, the intensity enhancement is expected at \( h\nu = 88 \text{ eV} \).

To understand the origin of the metallic state on the ethanethiol/ZnO(0001) surface, valence electronic structures of both clean and ethanethiol-dosed ZnO(0001) surfaces were examined and the result is shown in Figure 2. On the clean surface, the O 2p-dominant valence states are observed between 2 eV and 9 eV, and an intense peak at ~10 eV is attributed to the Zn 3d state. The valence band maximum (VBM) is determined to be 2.2 eV. Taking the ZnO band gap energy of 3.37 eV [21] into account, the conduction band minimum (CBM) should be at 1.2 eV above \( E_F \) at the \( \Gamma \) point of the bulk Brillouin zone. Since the CBM in the bulk of intrinsically n-type ZnO is expected at 0.2–0.3 eV above \( E_F \) [14], a strong depletion layer must be formed on clean ZnO(0001), as schematically drawn in a left panel in the inset of Figure 2.

As the surface is being covered with ethanethiol, the valence states of ZnO move towards the higher binding energy side by 0.85 eV. The shift is caused by downward band bending because the O 2p-dominant valence states and the Zn 3d state are rigidly shifted by the same amount. Adsorption-induced downward bending means an electron donation from ethanethiol to ZnO. The donated electrons should occupy the ZnO conduction band, whose energy minimum coincides with the center of the SBZ [22]. Thus, the observed metallic state in Figure 1 can be associated with the CBM. This assignment is further supported by the fact that the metallic state is derived from the Zn 4s state, which is a main component of the lower conduction band [22].

A right panel in the inset of Figure 2 shows an energy level diagram of ethanethiol-dosed ZnO(0001), which is derived from the VBM position of 3.05 eV and the band gap of 3.37 eV. Strangely, the CBM of ZnO does not reach \( E_F \) at the surface. This contradicts the observation of the Zn 4s-derived CBM (Figure 1). A possible explanation to resolve this inconsistency is that the band gap of ZnO may be diminished at the electron-doped surface by band renormalization [4, 23]. If the ZnO band gap is supposed to be di-
also examined the effect of methanol on the surface electronic structures of the ZnO surfaces, and the results are shown in Figure 3. Methanol adsorption on ZnO(0001) induces the shift of the ZnO band by 0.90 eV, which is larger than the ethanethiol-induced shift of 0.85 eV [Figure 3(a)]. Large downward band bending results in the metallization of ZnO(0001), as proved by the inset in Figure 3(a).

Methanol-induced metallization is also observed on Zn-terminated ZnO(0001). Figure 3(b) shows that methanol adsorption induces downward band bending as well as a metallic state in the band gap region. This is the first observation of the metallization of the ZnO(0001) surface by species other than hydrogen [15]. Actually, the ZnO(0001) surface is more difficult to be metallized than the ZnO(0001) and (1010) surfaces. Thus, methanol is a good electron donor for the ZnO(0001) surface.

Regarding the ethanethiol–ZnO(0001) interaction, ethanethiol hardly affects the VBM position, though the Zn 3p peak is slightly shifted by 0.17 eV towards the higher binding energy side [Figure 3(b)]. This means that the amount of transferred charge is very small or almost negligible at the ethanethiol/ZnO(0001) interface. As shown below, absence of the O 1s core-level shift upon ethanethiol adsorption also supports the negligible charge transfer. Thus, the electron donating ability of ethanethiol is not enough to bring the ZnO(0001) surface to be metallized.

### B. Adsorption state of ethanethiol

Chemical modification of the ZnO surfaces by ethanethiol is found to depend on the surface orientation; the ZnO(0001) surface is metallized while the ZnO(0001) surface is not. From the practical point of view, therefore, the (0001) plane of the ZnO crystal is more useful to fabricate, for example, a switching devise or a chemical sensor because its electronic property is more sensitive to the surrounding environment than that on the (0001) plane. This advantage is further emphasized by the fact that a small amount of ethanethiol is required for surface metallization on ZnO(0001), as reported below.

In Figure 4, core-level spectra of ethanethiol-saturated ZnO surfaces are compared between the (0001) and (0001) surfaces. It is apparent that the peak intensities of the C 1s and S 2p spectra of adsorbed ethanethiol are smaller on ZnO(0001) than ZnO(0001). Peak intensity ratios \( I_{ZX}/I_{XO} \), where \( I_{ZX} \) and \( I_{XO} \) are the integrated intensities of the photoemission peaks on the (0001) and (0001) surfaces, respectively, are 2.1 for the C 1s peaks and 3.5 for the S 2p peaks. An average of these values is 2.8, and this value reminds us that the surface Zn density should be three times larger on ZnO(0001) \((8.2 \times 10^{-14} \text{ cm}^2)\) than ZnO(0001) \((2.7 \times 10^{-14} \text{ cm}^2)\) [24], both of which undergo reconstruction to compensate for the surface polarity. Thus, the active site for ethanethiol adsorption must be the surface Zn atoms though no spectroscopic evidence is provided by the present XPS data. A saturation coverage of ethanethiol on ZnO(0001), estimated from the intensities of the O 1s and C 1s spectra acquired with \( h \nu = 600 \text{ eV} \), is approximately \( 3 \times 10^{-14} \text{ cm}^{-2} \), suggesting that nearly all Zn atoms exposed to the surface are bonded to ethanethiol.

The C 1s peaks on ZnO(0001) and ZnO(0001) are reproduced by single Voigt functions with their peak maxima at 285.8 eV and 285.6 eV, respectively [Figure 4(b)]. On the other hand, curve-fitting of the S 2p spectrum requires a spin-orbit doublet with a splitting energy of 1.2 eV and an

![Figure 3](image-url)
The intensity ratio of 2:1 for the 2p\(_{3/2}\) and 2p\(_{1/2}\) states [24]. However, the overall S 2p spectral shape cannot be reproduced by a single spin-orbit doublet component, and an additional component is required at the lower binding energy side of the main component, as shown in Figure 4(c). This indicates that there are at least two sulfur species on the ZnO surfaces.

Adsorption and reaction of methanethiol (CH\(_3\)SH) and ethanethiol on metal and semiconductor surfaces have been studies by XPS and other techniques [25−29]. These molecules adsorb both molecularly and dissociatively, depending on the surface reactivity, at room temperature. Dissociative adsorption results in thiolate and H by S−H bond cleavage, while C−S bond breaking is known to occur at temperatures higher than 400 K on Cu(111) [26], 500 K on the surfaces of Si [27] and GaAs [28], and 460 K on ZnO(0001) [29]. The XPS studies [25−28] have revealed that S in adsorbed thiolate gives an S 2p\(_{3/2}\) peak at ~163 eV (±1 eV), while a peak from undissociated thiol appears at 164−165 eV. In the present study, the S 2p\(_{3/2}\) peak of the main doublet component [red lines in Figure 4(c)] is observed at 163.1 ± 0.1 eV on both ZnO(0001) and (0001). Thus, a majority of ethanethiol adsorbs in the form of thiolate on the ZnO surfaces. This observation contradicts the earlier report [29], in which the authors concluded from the thermal desorption study that, although ethanethiol dissociated on ZnO(0001), it adsorbed molecularly on ZnO(0001) at room temperature. Dissociative adsorption of ethanethiol on ZnO(0001) can be understood because this ZnO surface undergoes reconstruction to form hexagonal terraces or saw-teeth shaped steps [30, 31], whose edges should be truncated by coordinatively unsaturated Zn atoms. These Zn atoms are chemically active to induce S−H cleavage upon thiol adsorption.

The low binding energy components of the S 2p spectra are located at 161.9 eV and 162.2 eV (the S 2p\(_{3/2}\) level) on ZnO(0001) and (0001), respectively [Figure 4(c)]. They are well associated with atomic S [25−28]. There are two possible origins; one is that there is a certain amount of especially highly active sites at which C−S bond cleavage is facilitated, and the other is photodamage of adsorbed ethanethiolate by an intense synchrotron radiation. Atomic S is always observed on the thiol adsorption systems at room temperature irrespective of the surface [25−28]. More studies are required to specify the mechanism to form atomic S on the ZnO surface.

Formation of thiolate upon ethanethiol adsorption results in dissociated H. These H atoms should be bonded to the surface O atoms to form hydroxyl (OH) groups on the ZnO surfaces. An adsorption-induced component at the higher binding energy side of the main component in the O 1s spectrum, indicated by a red line in each panel of Figure 4(a), should originate from the surface OH groups. Densities of the OH groups on ZnO(0001) and (0001) are estimated from the peak intensities to be 5 × 10\(^{14}\) cm\(^{-2}\) and 3.5 × 10\(^{14}\) cm\(^{-2}\), respectively. Considering that the saturation coverages of ethanethiol, deduced from the C 1s and S 2p peak intensities as mentioned above, are ~9 × 10\(^{14}\) cm\(^{-2}\) and ~3 × 10\(^{14}\) cm\(^{-2}\) on ZnO(0001) and (0001), respectively, all dissociated H atoms are bonded to the surface O atoms on ZnO(0001), but only a fraction of dissociated H remains on ZnO(0001) and the rest may desorb as H\(_2\) (though no evidence is obtained in the present study). Figure 5 summarizes the adsorption structure of ethanethiol on the ZnO(0001) and (0001) surfaces.

H on the ZnO surfaces is known to behave as an efficient electron donor and makes the surfaces be metallic in nature [1, 10−15]. Surface metallization on the ZnO(10\(^{10}\)) surface by methanol and water is also considered to arise from an adsorption-induced transition in the density of states of ZnO.
electron donation from adsorbed H that is provided by dissociative adsorption of the molecules [16]. Regarding the ethanethiol adsorption systems, the XPS study proved dissociative adsorption into ethanethiolate and H on both ZnO(0001) and ZnO(0001). Thus, dissociated H should donate its electron to the substrate and cause downward bending of the ZnO band. Ethanethiolate is, on the other hand, expected to withdraw some charge from the ZnO surface, as judged from the results of the theoretical investigation for the methanethiolate/ZnO(0001) system [25]. Nevertheless, the amount of charge donated by H must surpass the amount of withdrawn charge by thiolate to realize net downward bending. Essentially the same mechanism should be operative for adsorption-induced metallization of both ZnO(0001) and (0001) surfaces by methanol adsorption; namely, dissociated H donates a sufficient amount of charge, a part of which is withdrawn by the methoxy moiety. Although not conclusive, the charge withdrawal ability of methoxy may be smaller than that of ethanethiolate because of a stronger overall electron donating ability of methanol than ethanethiol, as indicated in Figures 2 and 3.

IV. CONCLUSIONS

ARPES and XPS were utilized to elucidate the electronic modification of the O-terminated and Zn-terminated ZnO (0001) and (0001) surfaces, respectively, by ethanethiol (C₂H₅SH) and its adsorption characteristics on the surfaces. Ethanol dissociates on both ZnO(0001) and (0001) surfaces at room temperature to form ethanethiolate (C₂H₅S) and H. The active site for adsorption should be the surface Zn atoms because the ethanethiol coverages reflect the surface Zn densities on the surfaces. On the ZnO(0001) surface, ethanethiol hardly affects the energetic positions of the ZnO band so that the surface remains semiconductor after adsorption. Contrastingly, large downward band bending and resultant formation of a metallic state are induced at the ethanethiol/ZnO(0001) interface. This surface dependence should reflect the balance between the amounts of the electron donor (adsorbed H) and the electron acceptor (ethanethiolate); namely, the amounts of H and ethanethiolate are comparable on ZnO(0001), whereas the amount of ethanethiolate is ~1.8 times larger than that of H on ZnO(0001). Thus, adsorbed ethanethiol is as a whole a good electron donor on the (0001) surface while it is not on the (0001) surface.

The metallic state on the (0001) surface exhibits the Zn 4s character and is observed at the center of the SBZ. These features reflect the properties of the ZnO conduction band. This fact, together with large downward bending, is suggestive of the formation of the 2DEG at the thiol/ZnO(0001) interface.

Thiol is one of the molecules that are used to functionalize solid surfaces. For this purpose, thiol molecules with a longer alkyl chain is more suitable than, for example, methanethiol and ethanethiol. Regarding the thiol/ZnO adsorption systems, octanethiol [32] and dodecanethiol [33] have been investigated so far. Although these preceding studies did not pay attention to the thiol/ZnO interface electronic structure, there is a possibility of an interface metallization if the molecules dissociatively adsorb to give thiolate and H. This will be a key factor for practical applications of the thiol/ZnO system to electronic devices.

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