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ELECTRONIC STRUCTURE OF A VACUUM CLEAVED ZnTe (110) SURFACE STUDIED BY ELECTRON SPECTROSCOPY

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The vacuum cleaved ZnTe (110) surface before and after oxygen exposures was examined by electron-energy-loss spectroscopy, 21-eV photoemission spectroscopy, and LEED I-V profiles. At early stages of exposures, the oxygen combines with surface Te atoms, leading to changes in valence-band states. Besides this, a very oxidizable state, probably, due to excess Zn atoms appears occationally after cleaving. The surface reconstruction tends to be removed for the surface with $\theta \approx 1$.

I. Introduction

This work has been done in the course of our studies of surface properties of 2-6 compounds. In our previous work [1], we used a technique of electron-energy-loss spectroscopy (ELS) together with Auger-electron spectroscopy and low-energy-electron diffraction (LEED). The ELS technique presented features due to transitions involving surface states, but there were some complications in analysis of the result. In order to obtain further insight in the surface electronic structure, we have made 21-eV photoemission (UPS) experiments, in combination with ELS and LEED, in the present work. In UPS, the energy distribution curve (EDC) presents information on the occupied state. This information may complement the data from ELS.

II. Experimental

The ELS experiments were performed with a base pressure less than 1×10^{-10} Torr. The loss and Auger spectra were measured by a single-pass CMA with a coaxial electron gun. The LEED intensities were obtained using a Varian 4-grid LEED system and a Hamamatsu TV vidicon, C1000-12, combined with a Hewlett-Packard 9835 A computer. A separate setup was used for UPS experiments. The base pressure was 5×10^{-10} Torr, but it rose to 5×10^{-9} Torr on operation of a He-discharge lamp. The EDC was detected with a spherical can 50 mm in diameter, which served as a retarding-field energy analyzer. Single crystals of ZnTe grown from the melt were cleaved in vacuum. No impurities were detected on the cleaved surface. At the instant of cleaving, the pressure rose to about 2×10^{-9} Torr. The cleaved surface was stable for the contamination with oxygen; even after electron-beam irradiation of 120 min, no oxygen signal was detected. However, sometimes a very oxidizable state appeared when the pressure rose to about 1×10^{-7} Torr upon cleaving. This unstable state disappeared after holding the surface in vacuum for about 3 h.

III. Results

We show in Fig. (1) the ELS spectra from the cleaved surface before (curve a) and after (curves b-e) oxygen exposures. Peaks at 5, 10.2, and 12.2 eV are surface losses, called S_2, S_3, and S_4, respectively [1]. The S_4 loss is due to the transition from the Zn 3d core level to a Zn-derived surface state. The Zn 3d (bulk) loss is seen at 13.5 eV as a shoulder of the S_4 loss. The doublet at 42.5 and 44.0 eV is the Te 4d loss.

At initial stages of oxygen uptakes, the S_2 - S_4 losses reduce in magnitude, whereas the 6.3-eV loss increases (see curve b). The increased loss is called A_1. With increasing exposures, the S_4 loss decreases further and becomes a shoulder, but the S_3 loss remains nearly unchanged (called A_2). In the Te 4d region, a new loss appears at 40.6 eV at an oxygen coverage, θ , of ≈ 0.3. The spectrum from the surface with θ =0.5 differs significantly from that of the clean surface; peaks occur newly at 3.5, 6.6, 11.5, 14.3, and 45.5 eV and almost all the features due to ZnTe disappear.

Figure (2) shows the photoemitted EDC's from the cleaved surface

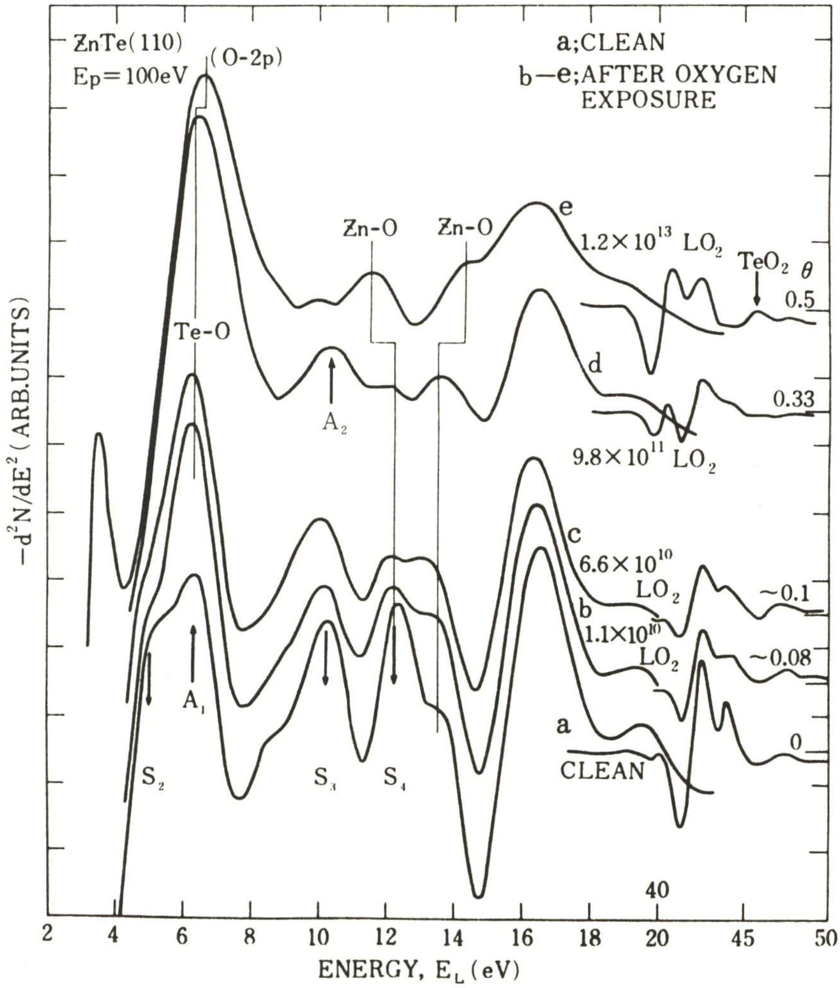

Fig. 1 ELS spectra from the cleaved ZnTe (110) before (curve a) and after (curves b-e) oxygen exposures, at E_p=100 eV

before (curve a) and after oxygen exposures at $4.0\text{x}10^{10}$, $4.4\text{x}10^{11}$, and $4.4\text{x}10^{12}$ L (curves b-d). The difference curves were obtained by subtracting curve a from curves b and c. For a comparison, the spectrum from a cleaved ZnO $(10\bar{1}0)$ is also given in this figure, where the energy scale has been shifted to that the O-2p resonance peak at 1.65 eV in ZnO is coincided to a peak at 4.3 eV in ZnTe with $\theta \geq 0.27$. The Zn-3d core level of the clean surface lies at 9.65±0.15 eV below the valence band maximum (VBM). The pronounced peak at 4.3 eV appearing for $\theta \geq 0.27$ is due to the O-2p resonance peak. At $\theta \leq 0.20$, the Zn-3d level exhibits no changes in both peak position and line shape, whereas the valence-band states show some changes in structure, as we can clearly see in curves a-c or in the difference curves. At $\theta = 0.27$, we detected a broadening in structure on the higher energy side for the Zn-3d state. It is noted that electron-beam irradiation on the surface exposed highly oxygen ($\gtrsim 10^{13}$ L) greatly enhanced oxidation, leading to a formation of ZnO overlayers [1].

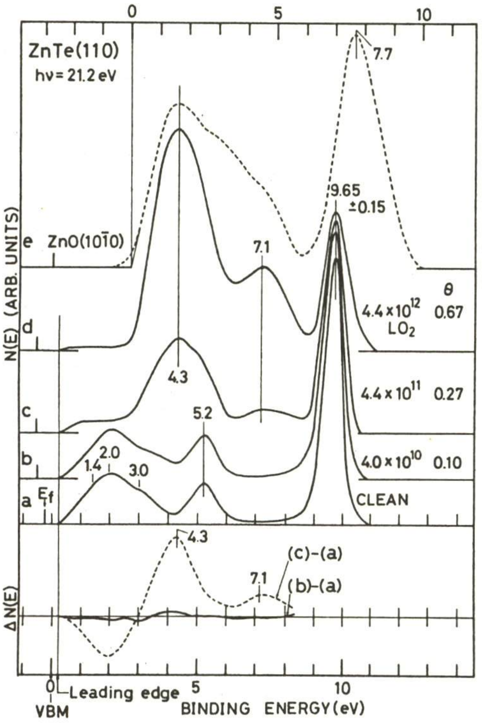

Fig. 2 Photoemitted EDC's from the cleaved surface before (curve a) and after (curves b-d) oxygen exposures, and difference curves: For a comparison, an EDC of ZnO is also shown (curve e)

LEED I-V profiles from the cleaved surface before oxygen exposures agree fairly well with data reported by Duke et al. [2], indicating a reconstructed structure. With oxygen uptakes, the diffraction intensity decreases considerably and the background intensity increases, as shown in Fig. (3). However, the spot size remains unchanged, as we can see from the extended intensity profiles from the $(0\bar{1})$ beam. The I-V profile exhibits no shift in energy scale nor braodening in structure with oxygen uptakes. However after the exposure at $1.1\text{x}10^{13}$ L, we detected significant changes in intensity; for the $(0\bar{1})$ beam a peak at 90 eV decreased dractically as compared with a peak at 150 eV, and for the (11) beam a peak at 120 eV reduced in magnitude more greatly than that at 70 eV.

The unstable surface appearing after cleaving is very easily oxidized on electron-beam irradiation during the course of AES and ELS measurements. After beam irradiation for only 20 min, we detected an oxygen uptake of $\theta = 0.1$ and the 40.6-eV loss. However, the intensity of the S_4 loss tends to remain unchanged. This result indicates that at the initial stages of the oxidation ($\theta \lesssim 0.1$) the oxygen state may be different between the unstable and stable surfaces. It is emphasized that the Auger ratio of the Te signal at 30 eV to the Zn signal at 55 eV is 0.56 for the unstable surface, which is compared with a value of 0.65 of the stable surface.

IV. Discussion

The peaks at 4.3 and 7.1 eV in the difference curve or curves c and d in Fig. (2) may be responsible for the A_1 and A_2 losses, respectively. The appearences of the 11.5- and 14.3-eV losses and the broadened Zn-3d state in EDC indicate the formation of Zn-O bonding.

The oxidizable state appearing after cleaving may be correlated to deficients in surface Te atoms. The Te defects lead to excess in surface Zn atoms with double-dangling bond, as proposed by Mele and Joannopoulos [3]. With such cation defects the oxygen may combine fast. Very recently, Su et al. [4] have reported bonding of the oxygen to the surface Ga atoms at the very initial stages of oxygen exposures of the cleaved GaAs(110). In our case, the excess Zn atom may have an occupied dangling bond, and it can be an electron donor to the oxygen and thus binds to the oxygen very fast, because the heat of formation of ZnO is larger than that of TeO_2 [1]. This oxide may be an origin of the 40.6-eV loss of the unstable surface.

The change in I-V profile detected after the 10^{13}-L exposure seems to be interpreted by a change in surface structure. A dynamical calculation of I-V profiles based on a computer program developed by Van Hove and Tong [5] suggests a removal of the reconstruction. Some details in atomic structure of the ZnTe(110) will be reported elsewhere. We note that in the case of the GaAs(110) a comparison of experimental and theoretical I-V profiles indicates a release of the reconstruction with adatoms [6,7].

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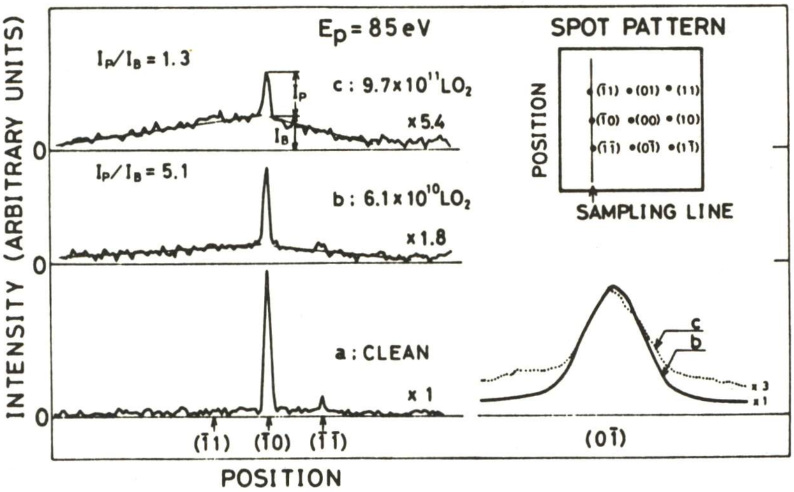

Fig. 3 LEED intensity profiles of the cleaved ZnTe (110) before (curve a) and after (curves b,c) oxygen exposures, at Ep=85 eV