Low-energy-electron loss spectroscopy of ZnTe (110) and (111) surfaces.
I. Bulk and surface losses

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The present paper reports on electron-energy-loss spectroscopy of ZnTe (110) and (111) surfaces, cleaned by Ar^+ bombardment and annealed under ultrahigh-vacuum conditions, at primary electron energies from 75 to 250 eV. Several surface losses involving surface states have been measured in addition to bulk losses due to bulk interband transitions, bulk and surface plasmon excitations, and the core-level transitions from the Zn $3d$ and Te $4d$ levels to conduction-band states. The surface losses change in magnitude between the (110) and (111) surfaces, or change with primary-electron energies. They are sensitive to the state of the surface. On the basis of these observations we distinguish the surface losses from the bulk losses and try to identify the surface states involved in the surface losses. From the transition energy of the surface loss involving the Zn $3d$ core level, the empty Zn surface state is located at 2.2 eV above the valence-band maximum in the one-electron picture. The energy-loss spectrum of the clean and well-ordered surface shows that there are no surface states in the band-gap region. Upon oxidation or Ar^+ bombardment a surface state appears in the band-gap region, which is ascribed to the surface Te atoms.

I. INTRODUCTION

Electron-energy-loss spectroscopy (ELS) with primary-electron energies less than 1 keV has been used successfully to understand the electronic structure of surfaces as well as to determine energies of collective excitations in solids. In a previous paper,[1] we have reported on ELS studies of a ZnSe (111) surface. The loss spectrum of ZnSe exhibits surface losses involving an empty Zn-derived surface state and a filled Se-derived surface state. From the transition energy of the Zn-$3d$ core-level loss, the empty Zn surface state was located at ~5.1 eV above the bulk valence-band maximum on the ZnSe (111) surface. This result leads us to the conclusion that there are no empty surface states in the band-gap region on the ZnSe (111) surface.

This paper is concerned with ELS studies of ZnTe (110) and (111) surfaces. Zinc telluride is a more covalently bonded compound than ZnSe. Therefore, for the study of an ionic and covalent surface state, the results for ZnTe are of great importance. The (111) surface of ZnTe is of interest since the ELS data of this surface can be compared with those of the ZnSe (111) surface reported previously. The nonpolar (110) surface of ZnTe has been extensively studied in optical and electrical measurements. While gross features in the loss spectrum are similar for the (111) and (110) surfaces of ZnTe, the relative magnitude of the surface losses is different for each of them. We also investigate effects of oxygen contaminations on the surface losses in order to better understand the intrinsic surface states as well as to examine the oxidation of ZnTe. In this paper oxy-

gen effects on the intrinsic surface states are described. Detailed ELS results of oxidized surfaces will be presented in the following paper. A $(\overline{1}\overline{1}\overline{1})$ surface of ZnTe has been examined also, but no clear low-energy-electron-diffraction (LEED) patterns correlated with the $(\overline{1}\overline{1}\overline{1})$ plane have been observed: Heat treatments have developed $\{110\}$ and $\{331\}$ facets on the $(\overline{1}\overline{1}\overline{1})$ surface. Therefore, the ELS results for this surface are not included in the present paper.

II. EXPERIMENTAL

Undoped p-type crystals of ZnTe were grown from the melt. The (111) surfaces were cut from a boule with low resistivity (~10 Ω cm) and a boule with high resistivity (~10^7 Ω cm). The oriented (111) surface was chemically polished with a $K_2Cr_2O_7$-HNO_3 solution for 1 min, and was treated with a NaOH solution for 2 sec at room temperature just prior to introducing it into the chamber. The (110) surface was prepared by cleaving in air from a boule with resistivity of ~100 Ω cm just prior to introducing it into the chamber.

A stainless-steel Varian LEED/AES (Auger-electron spectroscopy) system was used. It was equipped with a 220-l/sec ion pump, a titanium sublimation pump, a single-pass cylindrical mirror analyzer (CMA) with a coaxial electron gun, four-grid LEED optics, an Ar^+ sputtering gun, a B-A gauge, and a quadrupole mass filter. The base pressure of the chamber was 1×10^{-10} Torr and the working pressure was 3×10^{-10} Torr. On exposing the crystal to oxygen, high-purity oxygen gases were introduced into the chamber

through a leak valve.

ELS and Auger-electron spectroscopy measurements were made with the CMA at primary-electron-beam normal incidence on the sample surface. The backscattered electrons were detected in a cone of 42° half aperture. The primary beam currents were set at less than 1 μA, in order to reduce electron-beam effects such as adsorption or desorption of oxygen as well as surface damages. ELS measurements were performed at primary electron energies E_p ranging from 75 to 250 eV. The second derivative d^2N/d^2E of the energy-distribution curve was recorded for ELS with modulation voltage ΔV of 0.5 V peak to peak at E_p below 150 eV and 0.2 V peak to peak above 150 eV. The zero of the loss energy E_L was determined from the zero of the first derivative of the elastically scattered electrons. In AES, the first derivative dN/dE was recorded with $E_p = 2$ KeV and ΔV of 1 V peak to peak for Auger-electron energies below 200 eV, and of 2 V peak to peak above 200 eV. The energy resolution in the loss spectrum was within 0.3 eV. To reduce the beam effects, the electron beam was irradiated on the surface only when the measurements were carried out. The recording time for an energy-loss or Auger spectrum was 5–7 min.

Clean surfaces were prepared by repeated cleanings consisting of Ar⁺ bombardment with 300–350-eV ions at 2 μA for 30 min and annealing at 300–400 °C for 10–30 min. Repeated heat treatment at 400–470 °C for 30 min per process gradually provided a clear LEED pattern. No residual impurities were detected by AES on the clean surfaces.

III. RESULTS

A. Clean surfaces

The (110) surface exhibits a 1×1 structure. The (111) surface displayed 1×1 and 2×2 structures. At initial stages of heat treatment rather diffuse 1×1 patterns appeared. Repeated heating provided a clear 2×2 pattern. Examples of the 1×1 pattern of the (110) surface and the 1×1 and 2×2 patterns of the (111) surface are presented in Fig. 1. A faceting pattern of the (1̄1̄1̄) surface is also included in the figure, indicating a formation of {110} and {331} facets superimposed on a 1×1 structure.

There are no essential differences in ELS between the (111) surfaces with low and high resistivities, except that charging effects prevent loss measurement at E_p below 100 eV for the high-resistivity sample. The ELS and AES results are reproducible from one cleaning to another. When no changes in loss spectrum were observed with further annealing, we assumed the surface to be
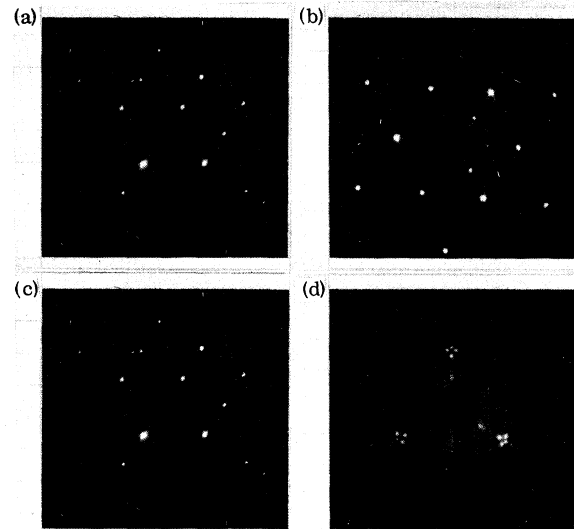

FIG. 1. Representative LEED patterns of ZnTe. (a) 1×1 pattern of the (110) surface with $E_p = 80$ eV. (b) 2×2 and (c) 1×1 patterns of the (111) surface with $E_p = 60$ eV. (d) Faceting pattern of a (1̄1̄1̄) surface with $E_p = 65$ eV, indicating formation of {110} and {331} facets on the (1̄1̄1̄) surface with a 1×1 structure.

well ordered.

Figure 2 shows a representative loss spectrum of ZnTe. Features labeled S_1, S_3, and S_4 are surface losses involving surface states, and $\hbar\omega_p$ corresponds to the bulk-plasmon loss. The S_4 loss is due to the transition between the Zn-$3d$ core level and the Zn surface state, as described in Sec. IV. Losses called Zn $3d$ and Te $4d$ are due to the transitions from the Zn $3d$ core level to a conduction-band state and from the Te $4d$ core level to a conduction-band state. The binding energy of the Zn $3d$ level is 9.8 and those of the Te $4d_{5/2}$ and $4d_{3/2}$ levels are 40.2 and 41.7 eV, respectively, with respect to the valence-band maximum, taken from the x-ray photoemission data of Ley et al.[2] A comparison of the loss spectra of the (110) 1×1 and (111) 2×2 surfaces is given in Fig. 3, with $E_p = 100$ eV. Bulk-interband losses, E, are identified in terms of a bulk-loss function, $-\text{Im}(1/\epsilon)$, calculated by Freeouf[3] and from ELS data of Hengehold and Pedrotti.[4] One can see in the figure that the S_4 peak is higher for the (111) surface than for the (110) surface, the S_3 peak is pronounced only for the (110) surface, and the S_1 peak is very weak for the (110) surface.

Figure 4 shows loss spectra of the (110) surface with different E_p's. The peak positions in the bulk-loss function of Freeouf[3] are shown by arrows in the figure, where the weak peaks are denoted by the label w. The enhancement of the S_2 peak is drastic at $E_p = 150$ eV, and the S_4 peak is signifi-
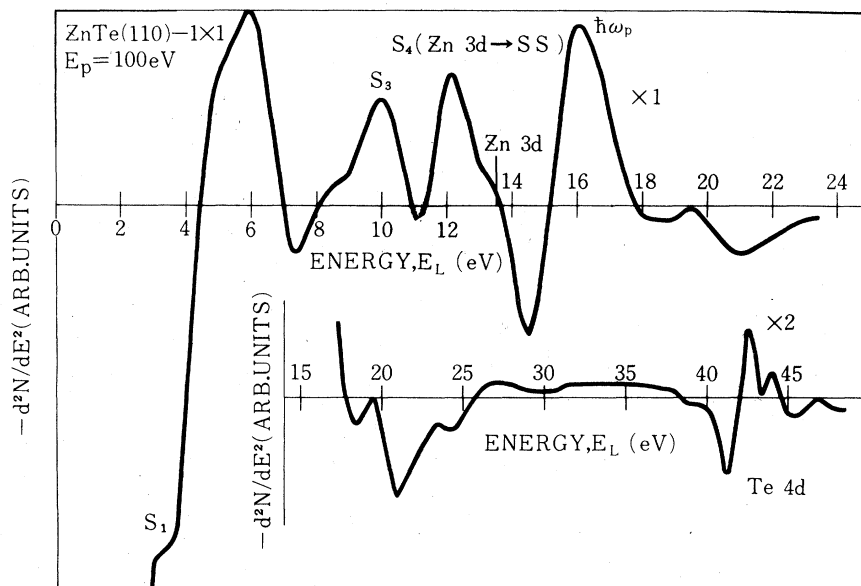
FIG. 2. Typical example of an electron-energy-loss spectrum of the ZnTe (110) 1×1 surface with $E_P = 100$ eV.

cant at $E_P \approx 100$ eV. The loss E_2 at 6.1 eV is dominant for all primary-electron energies. The E_3 loss at 8.5 eV is rather weak and observed only at lower and higher E_P's. It is noted that at lower or higher E_P the contribution of the bulk loss is expected to be more important than that of the surface loss because of the greater sampling depth. The features at 4.5 and 11.5 eV observed in the spectrum with $E_P \gtrsim 200$ eV are ascribed to bulk-interband transitions, called E_1 and E_4, respectively, from a comparison of their energy positions with the bulk loss function. A peak at 10.5 eV may be the surface-plasmon loss $\hbar \omega_s$.[4]

Figure 5 shows loss spectra for the (111) surface with different E_P's. Vertical lines in the

FIG. 3. Comparison of electron-energy-loss spectra of the (110) and (111) surfaces of ZnTe with $E_P = 100$ eV.

figure indicate the peak positions. The S_4 loss is substantial for E_P's from 75 to 150 eV. Because of the rather weak intensity of the S_3 loss at 10.0 eV, the surface-plasmon loss for this surface is significant at $E_P \gtrsim 150$ eV. A shoulder at 4.5 eV in the 120-eV spectrum can be ascribed to a surface loss S_2', from a consideration of oxygen effects; oxygen adsorption reduced the intensity of this peak drastically, as described in Sec. IV. The broad band appearing in the loss-energy region of 4–7 eV in the 75- and 100-eV spectra may consist of S_2' and E_2 losses.

The transition energies of the bulk-interband losses, the bulk- and surface-plasmon losses, and the Zn-3d and Te-4d core-level losses are summarized in Table I, together with the ELS results of Hengehold and Pedrotti[4] and the peak positions in the bulk-loss function of Freeouf.[3]
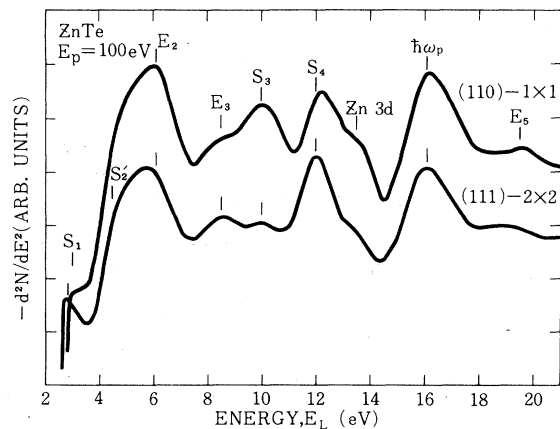
B. Effects of oxidation and disorder on surface losses

When the surface was exposed to molecular oxygen (the hot filament of the ion gauge was off), oxygen adsorption of about 0.5 monolayer coverage was observed for both the (110) and (111) surfaces at an exposure of 10^{13} L (1 langmuir = 10^{-6} Torr sec), the maximum exposure employed in this work. No indication of saturation in oxygen adsorption was observed. Electron-beam irradiation during ELS or AES measurements stimulates adsorption of oxygen. Even at a pressure of 4×10^{-10} Torr, beam irradiation gave rise to an adsorption of oxygen of about 3% of a monolayer coverage after an ELS measurement of the clean
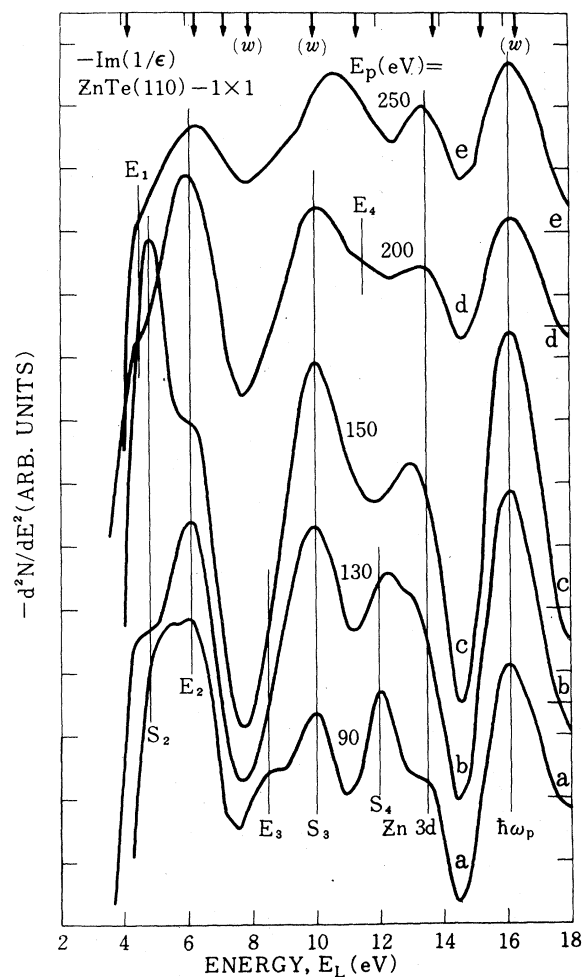
FIG. 4. Electron-energy-loss spectra of the ZnTe (110) surface with different primary electron energies; $E_P = 90$, 130, 150, 200, and 250 eV.
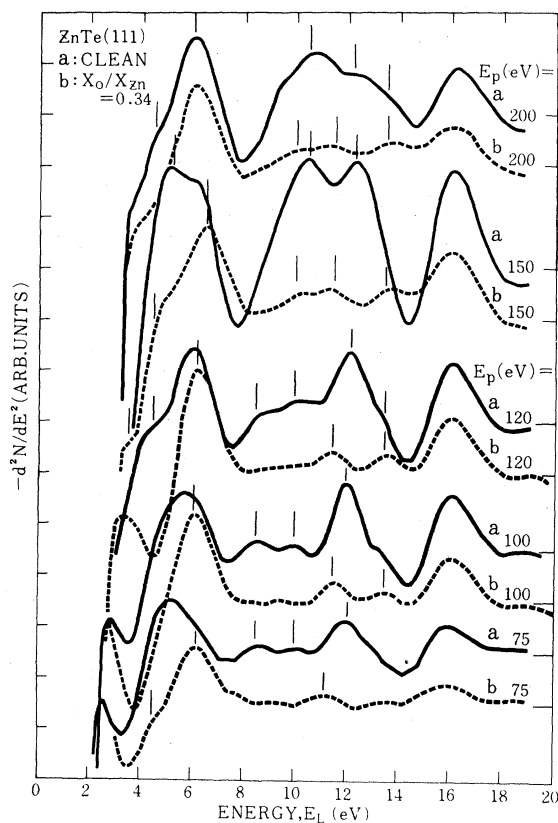

FIG. 5. Electron-energy-loss spectra of the ZnTe (111) surface with different primary electron energies; $E_P = 75$, 100, 120, 150, and 200 eV. The solid curves are obtained for a clean surface and the dashed curves for a surface with adsorbed oxygen with $X_O/X_{Zn} = 0.34$.

and well-ordered (110) surface for 120 min. After oxygen exposures greater than 10^{10} L, the pressure of the chamber rose to about 1×10^{-9} Torr, the beam effects became pronounced, and true bulk-like oxides were formed by beam irradiation for a long time.

The loss spectra of the (111) surface with adsorbed oxygen, with $X_O/X_{Zn} = 0.34$, are compared with those of the clean surface in Fig. 5, where X_O/X_{Zn} is a peak-to-peak-height ratio of the O Auger signal at 510 eV to the Zn signal at 990 eV. Upon oxidation the surface losses are diminished in magnitude except for the S_1 loss. One can also see in the figure that the E_4 loss at 11.4 eV becomes observable for all E_p's due to a removal of the S_4 loss at 12 eV. A low-lying broad band at 3–4 eV in the 120-eV spectrum may be composed of the S_1 loss and a new loss at 4 eV.

TABLE I. Transition energies for bulk interband losses (E_1-E_5), the bulk and surface plasmon losses $(\hbar\omega_s$ and $\hbar\omega_p)$, and the Zn-$3d$ and Te-$4d$ core-level losses (Zn $3d$ and Te $4d$). For a comparison the ELS result of Hengehold and Pedrotti (HP) and the peak positions in the bulk-loss function $[-\text{Im}(1/\epsilon)]$ of Freeouf are presented.

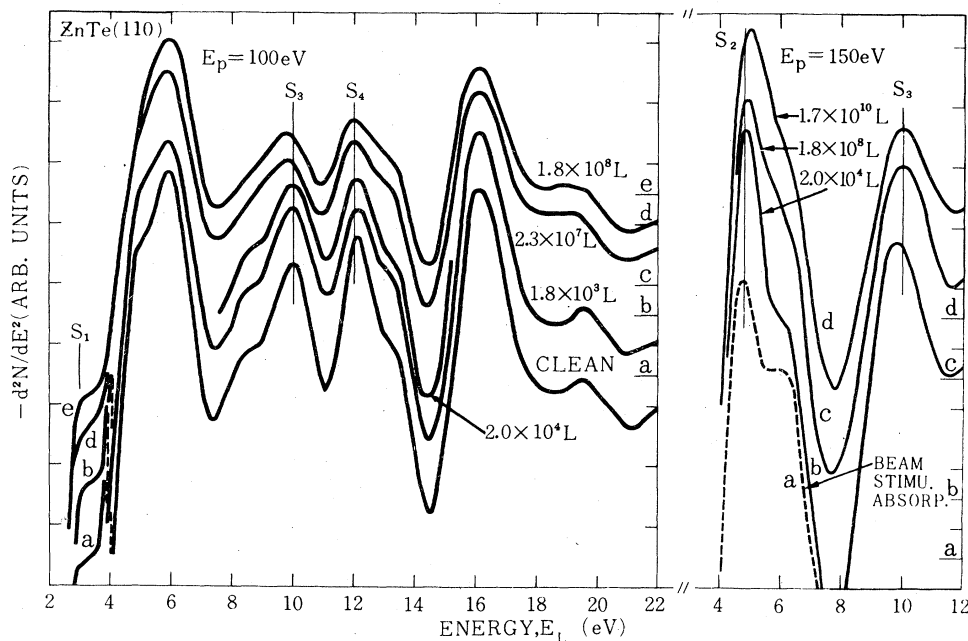| | Energy-loss spectrum | | |
	Present	HP [a]	$-\text{Im}(1/\epsilon)$ [b]
E_1	4.5	4.5	4.2
E_2	6.1	6.6	6.3
E_3	8.5		8.0
E_4	11.5		11.35
E_5	19.5		
$\hbar\omega_s$	10.6	10.4	
$\hbar\omega_p$	16.1	15.5	15.3
Zn $3d$	13.5	12.4	13.8
Te $4d_{5/2}$	42.5		
Te $4d_{3/2}$	44.0		
Te $4d$	46.8		

[a] Reference 4.
[b] Reference 3.

FIG. 6. Oxygen adsorption effects on surface losses for the ZnTe (110) surface with $E_P = 100$ and 120 eV.

Oxidation behaviors of the S_2 loss are somewhat different from those of the S_3 and S_4 losses, for the (110) surface. At the first $(1.8 \times 10^3$ L) and the second $(1.8 \times 10^4$ L) exposures the S_3 and S_4 losses diminished in magnitude; however, the S_2 loss remained unchanged. With successive exposures all these losses diminished. These observations are displayed in Fig. 6, where the loss spectra were taken from the areas which had not previously been irradiated by the electron beam. The Auger signal ratios X_O/X_{Zn} are less than 0.005 for exposures of 1.8×10^3 and 2.0 $\times 10^4$ L, and ~ 0.01, ~ 0.013, and 0.045 for exposures of 2.3×10^7, 1.8×10^8, and 1.7×10^{10} L, respectively. In the case of beam-stimulated oxidation, the S_2 loss as well as the S_3 and S_4 losses decrease in magnitude even at the first stage of oxidation, and particularly the S_2 loss tends to decrease rather drastically. The dashed curve in Fig. 6 is a loss spectrum of a beam-stimulated oxidized surface with $X_O/X_{Zn} \approx 0.015$. It is noted that no such differences in oxidation behavior were measured for the (111) surface. This fact may be due to the rather less pronounced magnitude of the S_2 loss for the (111) surface and/or the poorer qualities of the (111) surface.

Upon Ar^+ bombardment the surface losses were diminished in magnitude except for the S_1 loss. In addition, the extrinsic loss at 4.0 eV and another loss at 40.5 eV appear. The loss at 4 eV is seen most clearly in the 120-eV spectrum. The loss

spectra of the Ar^+-bombarded (111) surface are compared with those of the clean and oxygen-exposed surfaces with $E_P = 100$ and 120 eV in Fig. 7. The upward arrow in the figure indicates the loss which grows in magnitude and the downward arrow the loss which decreases in magnitude, upon Ar^+ bombardment or oxidation. From the figure one can see that the loss spectrum of the Ar^+-bombarded surface is somewhat similar to that of the lightly oxidized surface. The S_2' and S_4
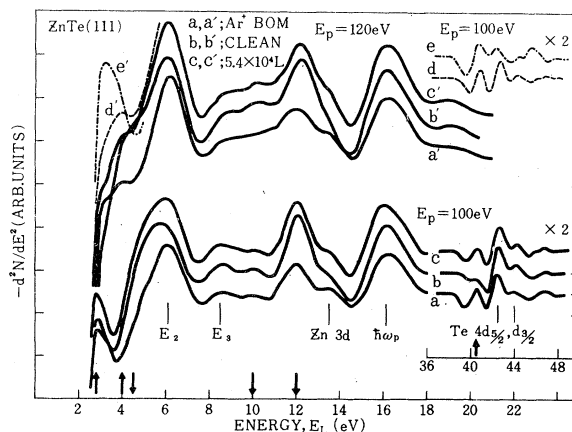

FIG. 7. Comparison of electron-energy-loss spectra of the Ar^+-bombarded (111) surface of ZnTe (curves a and a') with those of the clean (curves b and b') and oxidized (curves c, $c'-e$, e') (111) surfaces of ZnTe, with $E_P = 100$ and 120 eV.

losses are reduced in magnitude drastically on the Ar$^+$-bombarded surface. The peak at 4 eV is well resolved in the 120-eV spectrum of the Ar$^+$-bombarded surface.

The S_1 loss and the losses at 4.0 and 40.5 eV grow in magnitude with oxidation. Figure 7 shows loss spectra from surfaces with $X_O/X_{Zn} \approx 0.1$ (curves d and d') and 1.0 (curves e and e'). From the figure one can see that the pronounced broad loss at 3–4 eV in the 120-eV spectrum of the oxidized surface (see curves e' and b in Fig. 5) is composed of the S_1 and 4-eV losses, and the large dip at 4.5 eV in the same spectrum is caused by the removal of the S_2' loss and the appearance of the 4-eV loss.

The 40.5-eV loss can be ascribed to the transition from the Te $4d_{5/2}$ core level to the Te surface state, considering the energy difference. The transition from the Te $4d_{3/2}$ level to the Te surface state occurs at 42.0 eV, which overlaps with the transition at 42.5 eV, as the curves b, d, and e in Fig. 7 indicate. The weak losses at 44.0 and 45.5 eV in curve e in Fig. 7 are due to tellurium oxide, which probably is TeO$_2$, as described in the following paper.

For the Ar$^+$-bombarded (110) surface, no measurements were available at $E_p < 150$ eV, owing to charge effects. The loss spectrum of the Ar$^+$-bombarded (110) surface at 150 eV is rather similar to that of the ordered clean surface. However, it is a fact that the S_2 loss in the 150-eV spectrum decreases in magnitude and the dip at 18.5 eV disappears in the case of the Ar$^+$-bombarded surface. The disappearance of a dip at 18.5 eV is noted also in the case of the surface with adsorbed oxygen, as one can see in Fig. 6.

IV. DISCUSSION

The transition energies of the bulk interband losses, the Zn-3d core-level loss, and the bulk-plasmon loss are in good agreement with the peak positions in the bulk-loss function of Freeouf.[3] An agreement in loss energy between the present work and the previously reported results of Henghold and Pedrotti[4] is satisfactory. As to the Te-4d core level loss of the well-ordered clean surface, three peaks were measured at 42.5, 44.0, and 46.8 eV. They are rather insensitive to the state of the surface, indicating that they may be bulk losses. A spin-orbit splitting of the Te-$4d_{5/2}$ and $4d_{3/2}$ levels in ZnTe is 1.47 ± 0.02 eV, following Ley et $al.$[2] The energy difference between the 42.5- and 44.0-eV losses agrees with the spin-orbit splitting of the Te $4d$ level according to Ley et $al.$, and the peak height of the 42.5-eV loss is about two times as large as that of the 44.0-eV

loss. From these observations, we conclude that the losses at 42.5 and 44.0 eV are attributed to the transitions from the Te $4d_{5/2}$ and $4d_{3/2}$ levels to a conduction-band state, respectively. Owing to its rather weak intensity, no spin-orbit splitting was resolved for the 46.8-eV loss. This loss also may be due to transition from the Te $4d$ core level to a conduction-band state.

In ELS the transition from the cation core level to a conduction-band state or to the cation-derived surface state is now well-known.[1,5–8] In optical spectroscopy (reflectivity and electroreflectance), transitions between core levels and conduction-band states were reported for III-V compounds[9,10] and lead chalcogenides.[11] Table II summarizes the core-level losses for the clean and oxidized surfaces of ZnTe. Considering the energy difference, the final states of the Zn-3d losses at 12.0 and 13.5 eV are located at 2.2 and 3.7 eV, respectively, and those of the Te-4d losses at 42.5 and 46.8 eV are located at 2.3 and .6 eV, respectively, where the binding energies of Ley et $al.$[2] are used; Zn 3d lies at −9.8 and Te $4d_{5/2}$ at −40.2 eV, and Te $4d$ at −40.8 eV (weighted-mean value) for the Te-4d loss at 46.8 eV. Hereafter the energy reference is taken at the valence-band maximum. Among these losses the Te-4d loss at 40.5 eV which appears on the oxidized or Ar$^+$-bombarded surface, and the Zn-3d loss at 12.0 eV are the surface losses involving the Te- and Zn-derived surface states. The assignments of these surface losses and the other surface losses will be discussed later in this section.

The transition energy of 13.5 eV for the Zn-3d loss is in good agreement with the calculated peak position of 13.8 eV in the bulk-loss function.[3] For the Te-4d losses, the bulk-loss function can be evaluated to be $-\text{Im}(1/\epsilon) = -\text{Im}(1/\epsilon_1 + i\,\epsilon_2) \approx \epsilon_2$ ($\epsilon_1 \approx 1$ and $\epsilon_2 \ll 1$), following treatments by Rowe.[12] The loss spectrum in the Te-4d energy range might easily reproduce the conduction-band density of states in the dielectric model. Rowe has

TABLE II. Transition energies of the Zn-3d and Te-4d core-level losses and their one-electron final-state energies with respect to the valence-band maximum in ZnTe.

Transition energy (eV)	Initial state	One-electron final-state energy (eV)
12.0	Zn 3d	2.2
13.5	Zn 3d	3.7
40.5	Te $4d_{5/2}$	0.3
42.0	Te $4d_{3/2}$	0.3
42.5	Te $4d_{5/2}$	2.3
44.0	Te $4d_{3/2}$	2.3
46.8	Te $4d$	6.0

shown that the loss spectrum of the Ge-$3d$ loss in Ge reproduces the conduction-band density of states.[12] However, the observed final-state energy of 2.3 eV for the Te-$4d$ loss is too small to be interpreted in terms of the peak in the conduction-band density of states, because the conduction-band minimum occurs at 2.2 eV in ZnTe.[13]

There is now a general agreement that electron-hole interactions are significant in the core-level-to-surface-state loss in elemental and III-V semiconductors.[14,15] The bulk excitonic binding energy of II-VI compounds is, in general, larger than that of the elemental or III-V semiconductors, so the final-state energy derived from the difference between the observed loss energy and the core-level binding energy may be a lower limit. In optical spectroscopy, Thirly et al.[10] have reported that the one-electron picture free of excitonic effects cannot explain the transition between the core-level and conduction-band state, i.e., the one-electron final-state energy involved in the core-level transition cannot be explained by a calculated electronic structure based on the one-electron picture. In ELS electron-hole or hole-relaxation effects on the core-level-to-conduction-band transition have not been well understood. Thus, at present, the final-state energy, calculated by subtracting the Zn-$3d$ or Te-$4d$ core-level binding energy from the observed loss energy, should not be compared with the energy of the conduction-band density of state determined optically or calculated theoretically. Furthermore, in low-energy ELS it has not been established yet that either the dielectric model or any other model works well.[16]

For assignments of the surface losses, calculation of the surface electronic states is very useful. The electronic structure of the ZnSe (110) surface has been calculated by Chelikowsky and Cohen by a self-consistent pseudopotential method.[17] Unfortunately, there is no corresponding calculation for ZnTe. The electronic structures of (110) surfaces of II-VI compounds including ZnTe and ZnSe have been calculated by Calandra and Santoro with the tight-binding approximation.[18] The ZnSe {111} surfaces have been studied by Chadi and Cohen with the tight-binding approximation.[19] The ELS results for the ZnSe (111) surface yield the empty Zn surface state at 5.1 eV,[1] which is in good agreement with the calculated value of 5.25 eV.[17] The good agreement might be due to an accidental cancellation of an energy shift due to excitonic effects and a reconstruction of surface structure. It is noted that the calculations were carried out for the ideal structures, and Mark et al.[20] and Duke[21] have proposed a reconstructed structure for the ZnSe (110) surface as well as for the GaAs (110)

surface on the basis of the LEED intensity data. Very recently, Calandra et al.[22] have reported effects of surface reconstructions on the electronic states of the (110) surface of ZnSe. At present we assume that the nature of the surface states of ZnTe is somewhat similar to that of the ZnSe surface states except for shifts in the energy position of the surface state from ZnTe to ZnSe. In the light of the theoretical calculations of the surface states as well as the ELS results on ZnSe,[1] we will try to identify the surface states involved in the surface losses.

The S_4 loss is drastically reduced in magnitude by oxidation, indicating that the final state may be an empty Zn-derived surface state. From its large transition energy of 12.0 eV, the initial state is assigned as the Zn-$3d$ core level, on the basis of the bulk electronic structure of ZnTe.[13] Thus, the 12.0-eV loss is identified as the transition between the Zn $3d$ level and the Zn-derived surface state lying at 2.2 eV in the one-electron picture. In terms of the theoretical calculations, the empty Zn surface state can be specified as the Zn dangling-bond state. The high sensitivity of core-level losses to oxidation is now well known for the transition from the Ga $3d$ level to the Ga dangling-bond state of GaAs.[23,24] The S_4 loss is larger in magnitude for the (111) surface than for the (110) surface, indicating that the (111) surface has a higher density of Zn dangling-bond states than the (110) surface. If there is one-to-one correspondence between the density of the Zn dangling-bond states and that of the Zn surface atoms, the finding of the larger S_4 loss for the (111) surface is quite reasonable, because the AES data demonstrate that the (111) surface is richer in Zn surface atoms than the (111) surface is, as will be described in the following paper. The S_2' loss at 4.5 eV, which was measured most significantly for the 120-eV spectrum of the (111) surface, is very sensitive to oxidation. From this finding, we tentatively conclude that the S_2' loss can be identified as the transition from the valence band to the Zn dangling-bond state. In ZnSe the surface loss due to the transition from a valence-band state to the Zn dangling-bond state occurs at 5.7 eV.

The S_2 loss at 4.8 eV, which has somewhat bulk-like character, prefers the initial state to be lying near 2–3 eV below the valence-band maximum, to be a Zn-Te mixed state for the (110) surface or a Zn back-bond state for the (111) surface. The bulklike character means that the S_2 peak grows in magnitude with increasing E_p up to 150 eV and that it is insensitive to oxidation at the initial states of oxidation. Because of its large transition energy and very weak intensity for the (111) surface, the S_3 loss may be ascribed to the transi-

TABLE III. Transition energies of the surface losses of the (110) surface and their tentative assignments.

	Energy (eV)	Assignment
S_2	4.8	Zn-Te mixed state to CB[a]
S_3	10.0	Te-s-like state to CB[a]
S_4	12.0	Zn $3d$ to Zn dangling-bond state

[a] Conduction band.

TABLE IV. Transition energies of the surface losses of the (111) surface and their tentative assignments.

	Energy (eV)	Assignment
S'_2	4.5	VB[a] to Zn dangling-bond state
S_2	4.8	Zn back-bond state to CB[b]
S_3	10.0	Te back-bond state to CB[b]
S_4	12.0	Zn $3d$ to Zn dangling-bond state

[a] Valence band.
[b] Conduction band.

tion from a Te surface state, a Te s-like surface state for the (110) surface and a Te back-bond state for the (111) surface, on the basis of the energy position of the Se s-like state lying at -10 eV in ZnSe.[17] These tentative assignments of the intrinsic surface losses are presented in Tables III and IV.

The S_1 loss may be due to an extrinsic surface state. Both the S_1 and 40.5-eV losses increase in magnitude simultaneously with oxidation or appear upon Ar$^+$ bombardment, indicating that the surface state involved in the 40.5-eV loss may be responsible for the S_1 loss also. We have already described that the 40.5-eV loss is attributed to the transition between the Te $4d_{5/2}$ core level and the Te surface state. It is noted that the S_1 loss of somewhat large magnitude on the clean and or - dered (111) surface may be attributed to poorer qualities of the surface.

Very small oxygen exposures such as 10^4 L cause measurable decreases in magnitude of the S'_2 and S_4 losses involving the Zn dangling-bond state and the S_3 loss. Drastic changes in energy distribution curves of photoexcited electrons with small oxygen exposures such as 10 L (less than 10^5 times as small as that which is necessary to approach a half-monolayer coverage of oxygen) have been reported by Spicer et al.[25] for III-V compounds and also by Garner et al.[26] for IV semiconductors. It has been reported that the large changes in energy-distribution curves are caused by secondary effects of oxidation such as changes in arrangement of the atoms within the unit cell.[25,26] Recently Chey et al.[27] have proposed a model in order to interpret oxygen effects on the core-level loss in GaAs, in which extinction of excitons induced by the surface rearrangement due to oxygen adsorption is responsible for a disappearance of the core-level loss involving the surface state at very low oxygen coverage. The similarity in loss spectrum between the lightly oxidized surface and the Ar$^+$-bombarded surface suggests that adsorption of oxygen induces a rear-

rangement of the surface, which tends to disorder the surface.

While it seems quite probable that the Zn dangling-bond state of ZnTe is lower in energy than that of ZnSe, the energy difference of as much as 3 eV between them is too large to be interpreted by ionic and covalent considerations alone. Unidentified reconstructions in the surface structure and/or excitonic effects may be responsible for this large difference.

From the ELS results borne out of this work it is concluded that there are no surface states in the band-gap region for the clean and well-ordered surface of ZnTe. Upon oxidation of Ar$^+$ bombardment an extrinsic surface state appears within the band-gap reion, which may be responsible for pinning of the surface Fermi level in the band-gap region as in the case of the III-V compounds.[25] No empty surface states have been reported for both the clean and oxidized surfaces of ZnSe.[1] These results suggest that ZnTe may behave like a covalent compound in the formation of metal-semiconductor interfaces, whereas ZnSe may behave like an ionic compound. Pinning of the surface Fermi level has been reported for metal-ZnTe interfaces.[28]

In the course of preparation of this article we have met with a report by Ludeke on ELS of (100) surfaces of GaSb, InAs, and GaAs.[29] It reveals the presence of an empty Sb-derived surface state on the GaSb (100) surface, which lies close to the Ga-derived surface state near the bottom of the conduction band.

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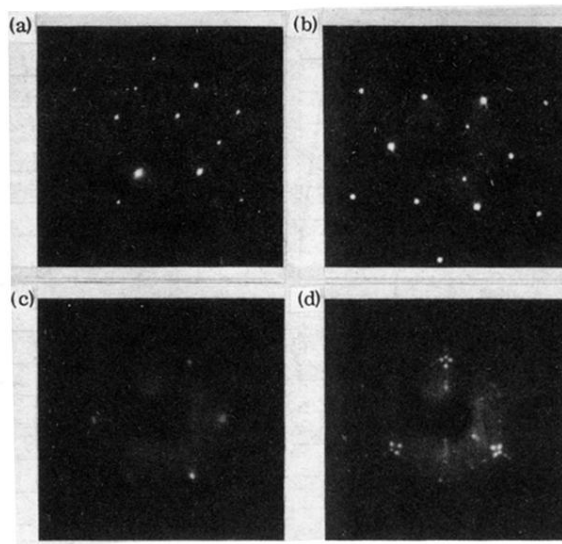
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FIG. 1. Representative LEED patterns of ZnTe. (a) 1×1 pattern of the (110) surface with $E_P = 80$ eV. (b) 2×2 and (c) 1×1 patterns of the (111) surface with $E_P = 60$ eV. (d) Faceting pattern of a $(\bar{1}\bar{1}\bar{1})$ surface with $E_P = 65$ eV, indicating formation of $\{110\}$ and $\{331\}$ facets on the $(\bar{1}\bar{1}\bar{1})$ surface with a 1×1 structure.