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Electronic surface and bulk transitions on clean ZnO surfaces studied by electron energy-loss spectroscopy*

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Clean cleaved $(1\bar{1}00)$, (0001), and $(000\bar{1})$ surfaces of ZnO have been studied by electron energy-loss spectroscopy with primary energies E_0 between 35 and 100 eV. Differences between the nonpolar $(1\bar{1}00)$ and the polar (0001) surfaces can be explained by the optical anisotropy of ZnO. The different chemical composition of the two polar surfaces studied simultaneously by Auger-electron spectroscopy explains the different loss spectra on these faces. A strong increase of surface sensitivity for $E_0 \leq 40$ eV allows the observation of surface excitations near 7.5 and 11 eV. The interpretation of the 7.5-eV transition as due to oxygen and zinc "dangling-bond" surface states is supported by uv photoemission measurements on the clean and oxygen-covered polar (0001) Zn face.

I. INTRODUCTION

In recent years several authors[1,2] have studied electronic bulk and surface transitions by electron energy-loss spectroscopy in the low-primary-energy range ($E_0 \leq 100$ eV). Besides experimental convenience the use of a cylindrical mirror energy analyzer (CMA) allows simultaneous measurements of Auger-electron distributions which is particularly helpful in the case of adsorption studies or with compound semiconductors, where the chemical surface composition may play an important role.

One of the problems with the use of a standard CMA is the complex scattering geometry which makes it difficult to estimate the experimental surface sensitivity for different primary energies from theoretical considerations. In the present work it is shown that for anisotropic materials this problem can be solved by an analysis of the different anisotropy effects for bulk and surface scattering, respectively. Conclusions drawn from this analysis are in accord with adsorption studies at different primary energies and with the energy dependence of surface losses.

Most of the previous work has been done on the elemental semiconductors Si and Ge and on some III–V compounds because of their importance for electronic solid-state technology. Another class of materials, namely, the metal oxides may become more important with regard to heterogeneous catalysis. ZnO is known to be a good catalyst for some important reactions (oxidation of CO, synthesis of methanol, decomposition of formic acid[3]). Another interesting feature of this material is the possibility of preparing three different types of surfaces by cleavage. These surfaces (nonpolar and polar) are different with respect to their chemical composition. Additionally the composition can be varied by annealing at moderate temperatures ($T_a < 1000$ K). We therefore think that ZnO is particularly favorable for investigations of surface states related to different surface atoms or vacancies which may influence the catalytic activity of the material.

II. EXPERIMENTAL

The ZnO single crystals were cut from hexagonal prisms that had been grown from the vapor phase in this laboratory. During the growing process the crystals were slightly copper doped giving rise to a bulk conductivity of about 10^{-3} $(\Omega\,\text{cm})^{-1}$. Etch patterns on the different surfaces were used to determine the direction of the crystallographic c axis[4] prior to mounting the crystal on the holder. The samples studied had a length of 13 mm and a thickness of about 3 mm.

Using the double-wedge technique nonpolar $(1\bar{1}00)$ surfaces with a mirrorlike finish were obtained by cleavage parallel to the c axis. Polar oxygen $(000\bar{1})$ and zinc (0001) faces were obtained by cleavage normal to the c axis. For this purpose the sample had been clamped to the holder at one end and was cleaved by pressing the free end against an edge of the sample holder. Surfaces prepared in that way are usually slightly convex with a high density of atomic steps.[5] In some experiments the freshly cleaved Zn face could be brought in a position just opposite the oxygen face at a distance of about 0.5 mm. By heating the Zn face it was possible to deposit Zn atoms onto the opposite O face.[6] Leads for resistive heating (Au) and for the thermocouple (Au-Constantan) were attached to the crystals by pressure bonding. The sample holder could take two samples simultaneously and could be cooled down to about 80 K by liquid nitrogen.

The ultra-high-vacuum system was a standard stainless steel chamber which could be separated from the ion pump (200 liter/sec) by means of a gate valve. The operating pressure was $\leq 1 \times 10^{-10}$ Torr. The sample could be positioned in front of a four-grid low-energy electron-diffraction optics (PHY), a quadrupole mass spectrometer (Riber), and a single-pass cylindrical mirror energy analyzer (Varian) with integral electron gun. The acceptance angle of the analyzer was $42° \pm 6°$.

With a primary voltage of 2000 V and a beam current of 8.5×10^{-6} A first-derivative Auger-electron spectra (AES) were obtained by recording the collector current of the CMA multiplier at the fundamental frequency (17 kHz) of the modulation voltage (5 V). The energetic resolution was about 0.4%. The time necessary for a spectrum between 20 and 1300 eV was about 5 min.

Second-derivative electron energy-loss spectra (ELS) at low primary energies ($E_0 \leq 100$ eV) were recorded in an analogous manner at the first harmonic of the modulation voltage (1 V). The energetic resolution given by the full width at half-maximum of the elastically scattered electrons was about 0.8 eV. The energetic position of spectral structures could be read with an accuracy of ±0.2 eV. The recording time for one spectrum was typically 5 min.

Ultraviolet photoemission spectroscopy (UPS) was performed by means of the same CMA with lock-in detection. The differentiated spectra were integrated by computer to yield the distribution $N(E)$ of photoemitted electrons. The energetic resolution is therefore limited by the differentiation process (modulation voltage 1 V) to about 0.7 eV. As light source for 21.2 eV photons a differentially pumped He resonance lamp was used.

III. RESULTS

For experimental convenience (compromise between energetic resolution and time necessary for one spectrum) most of the loss spectra were taken with $E_0 = 80$ eV. At this primary energy the loss structures of the polar surfaces and the nonpolar surface, respectively, differ considerably below 25 eV loss energy (Fig. 1). On the zinc face loss peaks are found at 4.3, 7.6, 9.1, 11.8, 15.3, 19.0, 23.6, and 26.8 eV. Additional losses appear on the nonpolar face at 12.6, 17.3, and 21.6 eV whereas the peak at 11.8 cannot be observed. If cleaved at 300 K, the oxygen face exhibits the same spectrum as the zinc face except for two losses at 11.4 and 12.9 eV instead of the 11.8 eV peak on the Zn face (Fig. 2). The energetic positions of all losses are summarized in Table I.

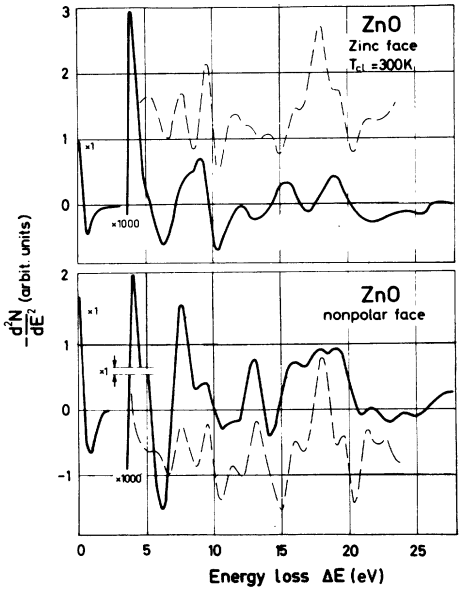

FIG. 1. Curves in full line: Doubly differentiated loss spectra measured with a primary energy $E_0 = 80$ eV on clean cleaved Zn (0001) and nonpolar (1$\bar{1}$00) surfaces, respectively (T_{cl} is the cleavage temperature). Curves in dashed-dotted line: Doubly differentiated loss functions calculated from optical data (Ref. 12) (zero line arbitrary).

In order to get more information about the difference between the loss spectra of the Zn and O face we changed the chemical composition and/or the geometrical arrangement of atoms on the polar surfaces by: (a) variation of the cleavage temperature, (b) annealing for 10 min at different temperatures, and (c) deposition of Zn on the oxygen face by heating the Zn face in front of the O face.[6]

At higher cleavage temperatures, 370 and 450 K, the loss spectrum of the O face [Fig. 3(a)] shows only one peak at about 11.8 eV like the Zn

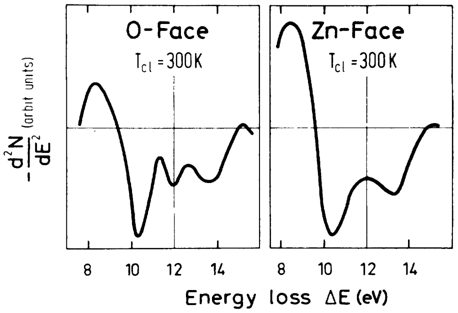

FIG. 2. Comparison of the loss spectra of clean polar O (000$\bar{1}$) and Zn (0001) surfaces in the spectral range $8 < \Delta E < 16$ eV (T_{cl} is the cleavage temperature).

TABLE I. Summary of energetic positions of all losses.

Energy losses (eV) ($E_0 = 80$ eV)			Surface energy losses (eV) ($E_0 = 35$ eV)			
Nonpolar face (1$\bar{1}$00)	Zinc face (0001)	Oxygen face (000$\bar{1}$)	Nonpolar face (1$\bar{1}$00)	Zinc face (0001)	Oxygen face (000$\bar{1}$)	Zinc face after O_2 adsorption (0001)+O_2
4.3	4.3	4.2				
7.8	7.6	7.8	7.4			7.0
9.1	9.1	9.0				
		11.4	10.9	10.7	11.2	
	11.8					
12.6		12.9				11.7
15.8	15.3	15.5				
17.3						
18.9	19.0	19.0				
21.6						
23.9	23.6	23.6				
27.1	26.8	26.8				

face cleaved at 300 K (Fig. 2). Upon annealing this peak disappears and the two losses typical for an O face cleaved at 300 K reappear [Fig. 3(b)]. Cleavage at lower temperatures has no effect on the loss spectra of O and Zn faces, respectively. The spectral structure of the Zn face does not change at higher cleavage temperatures or upon annealing. Deposition of Zn on the O face cleaved at 300 K produces one broad maximum at about 11.8 eV instead of the two peaks at 11.4 and 12.9 eV (Fig. 4).

All these different treatments of the polar surfaces of ZnO have been studied by AES simultaneously. The AES peak ratios Zn(994 eV)/O(510 eV) are shown in Fig. 5 in dependence on annealing temperature T_a. For cleavages at 300 K there is a difference of about 15% between Zn and O faces, respectively. Upon annealing the peak ratio of the O face decreases monotonically whereas this ratio exhibits a small minimum at about 780 K for the Zn face. For cleavage at higher temperatures the AES peak ratio on the oxygen face increases considerably and decreases again upon annealing to temperatures higher than 600 K. For ratios below 0.8 the two maxima at 11.4 and 12.9 eV typical for the loss spectrum of an O face cleaved at

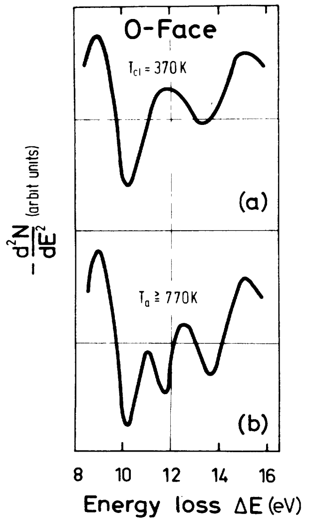

FIG. 3. Room-temperature loss spectrum of a clean polar O (000$\bar{1}$) face (a) after cleavage at 370 K (T_{cl}) and (b) after annealing at about 770 K (T_a).

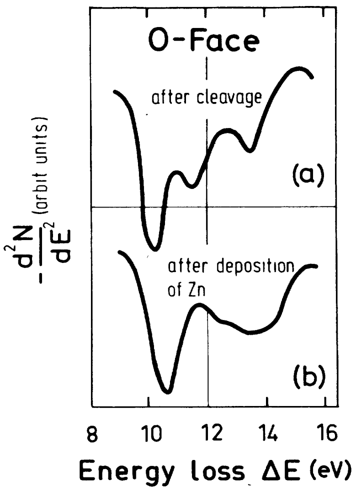

FIG. 4. Loss spectrum of a polar O (000$\bar{1}$) face (a) after cleavage at room temperature and (b) after deposition of Zn atoms from the opposite Zn face being annealed in front of the O face.

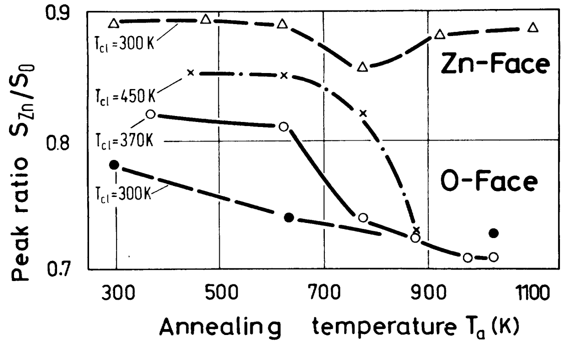

FIG. 5. Effect of annealing on the peak height of the zinc (994 eV) and the oxygen (510 eV) Auger signal S for the two polar surfaces (T_{cl} are cleavage temperatures).

300 K reappear. The peak ratio of the zinc to the oxygen Auger signal, $S_{\mathrm{Zn}}/S_{\mathrm{O}}$, of the O face is enhanced upon deposition of Zn by about 10%. The latter measurement was performed using a different sample holder so that the sample analyzer distance was not exactly the same as with the annealed surfaces. Since the AES peak ratio proved to be extremely sensitive to this distance, the absolute values obtained with different holders cannot be compared.

In the loss energy range $5 < \Delta E < 15$ eV the detailed features of the loss spectra of all the faces studied change drastically by going to primary energies lower than 60 eV. On the *nonpolar face* (Fig. 6) the loss at 7.8 eV increases strongly with decreasing primary energy simultaneously shifting to lower energies. At $E_0 = 35$ eV its energetic position is 7.4 eV. At the same time a new peak appears at 10.9 eV.

On both *polar faces* (Zn and O) only a shoulder is seen at about 7.8 eV loss energy (Fig. 6). With decreasing E_0 this shoulder grows but always stays smaller than the peak at 9.1 eV. Its energetic position at $E_0 = 35$ eV is about 7.5 eV. Near 11 eV on both polar surfaces a loss is growing with decreasing primary energy.

On both the polar and the nonpolar faces the relative heights of the losses at about 15.3 and 19.0 eV change. At $E_0 = 80$ eV the 19.0 eV peak is slightly larger, whereas at $E_0 = 35$ eV the 15.3 eV loss is more prominent. In all spectra measured a small peak at about 2.5 eV whose maximum does not reach the zero line can be seen. For reasons to be discussed later (Sec. IV D), this peak has been omitted in the diagrams.

In addition to the data for clean surfaces a loss spectrum of the Zn face after an exposure to 10^4 langmuir ($1\mathrm{L} = 10^{-6}$ Torr sec) oxygen at 300 K has been measured with $E_0 = 35$ eV and $E_0 = 80$ eV (Fig. 7). In comparison with the clean surface two new

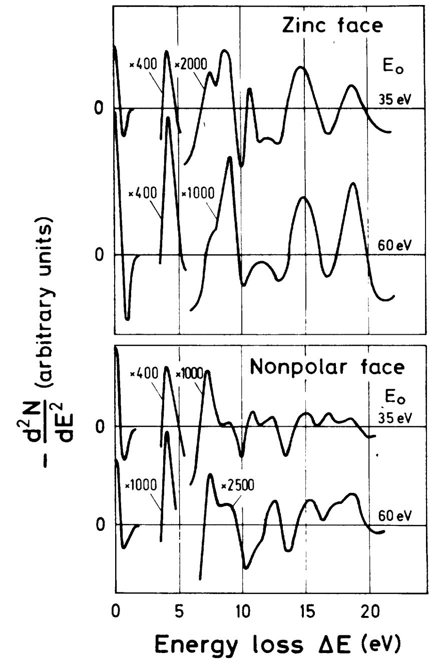

FIG. 6. Doubly differentiated loss spectra of the clean polar Zn (0001) and the nonpolar (1$\bar{1}$00) surface for two different primary energies E_0 (amplification factors given with each spectrum are with respect to the primary peak height).

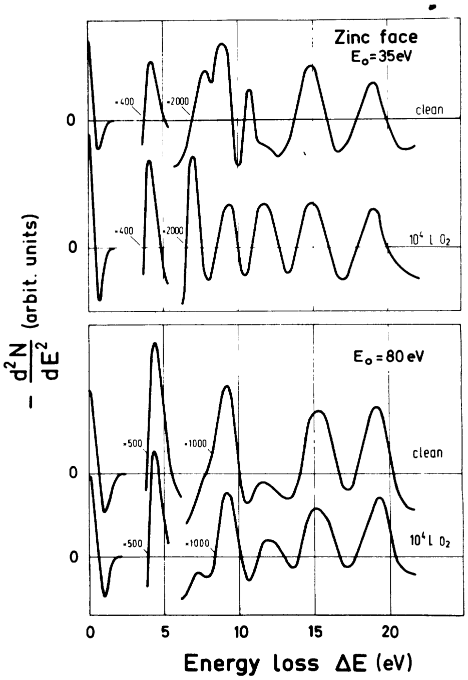

FIG. 7. Loss spectra of the polar Zn (0001) surface after cleavage (clean) and after exposure to 10^4-L oxygen: Upper part: measured with a primary energy of 35 eV; lower part: measured with a primary energy of 80 eV.

losses are found at 7.0 and 11.7 eV with $E_0 = 35$ eV. These transitions are obviously characteristic for the adsorbed oxygen. At $E_0 = 80$ eV only a small change of the spectral structure can be seen after oxygen adsorption. The same oxygen characteristic changes ($E_0 = 35$ eV) are observed on a clean Zn face which has been annealed to about 500 °C after cleavage.

To get more insight into the oxygen adsorption process UPS spectra have been measured on the clean annealed ($T_a \approx 500$ °C) and oxygen covered polar Zn surface (Fig. 8): electron binding energies in Fig. 8 are referred to a zero at the vacuum level for the oxygen-exposed spectrum and the clean surface spectrum is slightly shifted to align the valence-band maxima E_v of both curves to account for the 0.2 eV upwards (depletion) band-bending change caused by the adsorbed oxygen. The 10^5-L oxygen exposure furthermore increases the work function slightly from 7 to 7.1 eV. Beside the true secondary structure the spectrum of the clean surface exhibits as prominent bands the emission due to the ZnO valence band between 7 and 13 eV and the Zn $3d$-level structure near 15 eV binding energy. The spectral changes due to adsorbed oxygen were completely reproducible, i.e., repeated heat cleaning and exposure produces one or the other type of spectra in Fig. 8. At least two new emission bands at 10.1- and 14.5-eV binding energy are induced by the adsorbed oxygen as can be seen from the difference curve $\Delta N(E)$ in Fig. 8. The structure near 17.5 eV which is not reproducible is probably due to a deformation of the true secondary peak.

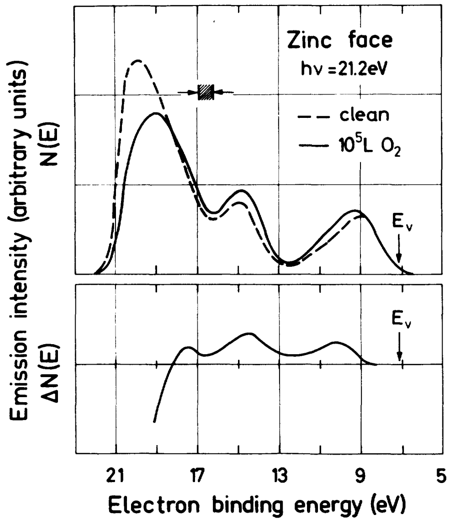

FIG. 8. Upper part: UPS spectra of the annealed clean polar Zn (0001) surface and after 10^5 L($1\mathrm{L} = 10^{-6}$ Torr sec) exposure to oxygen (E_v, valence-band maximum). The spectrum of the clean surface has been shifted to lower binding energies by 0.2 eV to account for the upwards band bending change due to the adsorbed oxygen. Lower part: Difference spectrum (exposed minus clean). Electron binding energies are referred to a zero at the vacuum level for the spectrum after oxygen adsorption.

IV. DISCUSSION

A. Optical anisotropy of ZnO and surface sensitivity

According to the "dielectric theory" (for a review see Ref. 7) the probability for an electron to lose a discrete amount of energy $\Delta E = \hbar\omega$ in a scattering event is given by the loss functions $-\mathrm{Im}[\epsilon(\omega)]^{-1}$ and $-\mathrm{Im}[\epsilon(\omega)+1]^{-1}$ for bulk and surface scattering, respectively. Since this theory has been applied successfully also to the interpretation of low-energy ELS ($E_0 \le 100$ eV),[1,8] the discussion of the present results is also based on the dielectric theory even though its validity for the low-energy regime has not been proved on a theoretical basis.

In electron reflection experiments one has to distinguish between four possible scattering processes according to Evans and Mills[9,10]: (i) large-angle inelastic scattering; (ii) multiple scattering; (iii) large-angle diffraction followed by small-angle inelastic scattering; (iv) small-angle inelastic scattering followed by large-angle diffraction. The scattering probability for bulk scattering is given by (see Ref. 11):

$$P(\Delta E, \vartheta)\, d(\Delta E)\, d\Omega \sim -\mathrm{Im}\epsilon^{-1}\, (\vartheta^2 + \vartheta_{\Delta E}^2)^{-1}\, d(\Delta E)\, d\Omega\,, \tag{1}$$

with ϑ the scattering angle and $\vartheta_{\Delta E}$ the angle at half of the maximum. The angle dependence [Eq. (1)] of the scattering probability shows that large-angle scattering can be neglected if small-angle scattering is possible, i.e., if low-energy-electron diffraction spots lie in the acceptance angle of the analyzer. For the nonpolar face of ZnO this is the case for all primary energies used, whereas for the polar surfaces this situation is given for primary energies lower than 60 eV. Multiple scattering has been neglected, too, because no applicable theory is known to the authors. For anisotropic materials like ZnO an "effective" dielectric function ϵ_{eff} enters the scattering probability for bulk scattering [Eq. (1)]. Depending on the scattering geometry ϵ_{eff} has to be calculated[11] by

$$\epsilon_{\mathrm{eff}} = \epsilon_{\perp}(\omega)\sin^2\theta + \epsilon_{\parallel}(\omega)\cos^2\theta\,, \tag{2}$$

where $\epsilon_{\perp}$ and $\epsilon_{\parallel}$ are the components of the dielectric tensor perpendicular and parallel to the hexagonal c axis, θ is the angle between c axis and the wave vector of the polarization wave excited by the scattered electron. For an approximate calculation of ϵ_{eff} the following assumptions have been made: (a) Loss-diffraction and diffraction-loss processes, respectively, occur with the same probability; (b) $\vartheta \leq \vartheta_{\Delta E}$. This is a reasonable assumption because with $E_0 = 80$ eV, $\vartheta_{\Delta E}$ for a typical energy loss $\Delta E = 16$ eV coincides with the maximum allowed deviation of 6° from the ideal acceptance angle 42° of the analyzer. Electrons scattered with larger ϑ out of the diffracted beam cannot pass the analyzer.

Using the angle dependence [Eq. (1)] for bulk scattering an averaged dielectric function $\hat{\epsilon}$ has been calculated from the "effective" dielectric functions [Eq. (2)] of all scattering processes allowed by the experimental geometry:
polar face,

$$\hat{\epsilon}(\omega) = 0.6\epsilon_{\parallel}(\omega) + 0.4\epsilon_{\perp}(\omega), \tag{3a}$$

nonpolar face,

$$\hat{\epsilon}(\omega) = 0.9\epsilon_{\perp}(\omega) + 0.1\epsilon_{\parallel}(\omega). \tag{3b}$$

In Fig. 1 the experimental spectra of the nonpolar face and the polar Zn face are compared with the bulk loss function calculated from optical data after Klucker *et al.*[12] by means of the averaged dielectric constants $\hat{\epsilon}$ [Eqs. 3(a) and 3(b)]. The first energy loss is to be seen at about 4.3 eV on both faces. According to Froitzheim and Ibach[8] the direct band gap of 3.4 eV cannot be observed because of its excitonic nature. From theoretical arguments Hopfield and Thomas[13] postulated a 50 Å thick exciton free layer for ZnO. In the region $\Delta E \geq 15$ eV the loss functions do not differ considerably. The difference between the maxima of the loss functions at about 18.2 eV and the observed losses at about 19.0 eV might be explained by errors in the Kramers-Kronig analysis necessary for the calculation of the loss function from reflectivity data.

The anisotropy of ZnO manifests itself strongly in the region $5 < \Delta E < 15$ eV. Corresponding to the different loss functions, peaks are observed at 12.6 eV on the nonpolar face and at 11.8 eV on the Zn face. Also the relative heights of the 7.6 and 9.1 eV losses are found, as one would expect from the calculation, though the 7.6 eV loss on the nonpolar face seems to be too large (see Sec. IV C). The good agreement between theoretical and experimental curves again justifies the use of the bulk scattering formula. Even though bulk scattering has been shown to be the dominating process at $E_0 \geq 60$ eV, surface scattering cannot be neglected as the observed excitation of the surface plasmon shows.

Measuring at lower primary energies ($E_0 = 35$ eV) the loss structures of both the nonpolar face and the polar surfaces change considerably (Fig. 6). Part of this change can be explained by the assumption that at $E_0 = 35$ eV surface scattering is the dominating process. This would result in a change of the anisotropy effects.

Surface waves excited in surface scattering processes are accompanied by electric field vectors with components parallel and perpendicular to their wave vector, i.e., parallel and perpendicular to the surface.[8,14] In a first approximation both components are assumed to have equal absolute values. For the experimental geometry used waves are excited with equal probability for all directions in the surface. With the above assumption the averaged dielectric constants for the different surfaces in the case of surface scattering are then given approximately by:
polar,

$$\hat{\epsilon}(\omega) = 0.5\epsilon_{\parallel}(\omega) + 0.5\epsilon_{\perp}(\omega), \tag{4a}$$

nonpolar,

$$\hat{\epsilon}(\omega) = 0.75\epsilon_{\perp}(\omega) + 0.25\epsilon_{\parallel}(\omega). \tag{4b}$$

In the region $5 < \Delta E < 15$ eV where the anisotropy could best be observed at $E_0 \geq 60$ eV, this change of the "effective" dielectric function should lead to an increase of the 7.6 eV loss on the polar surfaces and to a decrease of the 7.6 and 12.6 eV losses on the nonpolar face. Moreover, a 12.6 eV loss might appear on the polar faces. With decreasing primary energy, on both polar faces the 7.6 eV loss increases in relative height, as is expected from the change in the type of scattering (Fig. 6). On the Zn face the 12.6 eV loss does not occur. The nonpolar face shows the expected decrease of the 12.6 eV loss but in contrast to the discussion above the relative height of the 7.6 eV loss increases strongly. This unexpected increase of the 7.6 eV loss on the nonpolar face as well as the increase of the loss at about 11 eV on all faces cannot be explained by a change of the type of scattering. The energy dependence of the latter transitions, therefore, suggests an interpretation in terms of surface-state transitions (see Sec. IV C).

In accordance with the increase of the peak heights of surface transitions for $E_0 < 60$ eV on the clean surfaces, adsorption of oxygen on the Zn face gives rise to two large characteristic losses for E_0 as low as 35 eV, whereas only very small spectral changes can be seen with a primary energy of 80 eV (Fig. 7).

The change of anisotropy effects with primary energy, the energy dependence of surface transitions on the clean surfaces and the adsorption studies of oxygen show a surprisingly sharp increase of surface sensitivity for E_0 between 40 and 60 eV. This increase cannot be explained in terms of the energy dependence of the escape depth as in ultraviolet and x-ray photoemission spectroscopy.[15] Surface sensitivity in ELS might be dependent on the excitation process itself as can be seen from the strong energetic correlation between surface scattering and the appearance of surface-state excitations.

Most of the observed bulk transitions have been discussed in the literature.[12,16] Figure 9 shows some of these transitions in relation to the bulk density of states of ZnO. Some of the observed transitions have been attributed to points of high density of states by Bloom and Ortenburger[16] who calculated the density of states of the conduction and valence band. The energetic position[17] and the qualitative shape of the Zn-3*d* and the O-2*s* levels are taken from the literature.[18]

B. Effect of surface composition on the loss spectra of the polar surfaces

From the viewpoint of optical anisotropy one would expect the same loss spectra for both polar surfaces. The different features of the Zn face (11.8 eV loss) and the O face (11.4 and 12.9 eV losses) in Figs. 2–4, therefore, must be attributed to surface characteristic properties of these surfaces. Different treatments of the polar surfaces in combination with AES measurements show that the single loss observed on the Zn face can also be seen on an O face enriched with Zn atoms. We, therefore, conclude that the 11.8 eV transition is connected with Zn surface atoms. From uv photoemission measurements Lüth *et al.*[3] and Ranke[17] obtain the energetic position of the Zn-3*d* core level at 7.8 eV below the valence-band edge (Fig. 8). As Fig. 9 shows, the 11.8 eV loss characteristic for Zn atoms on the surface, therefore, is most probably due to an excitation from the Zn-3*d* level into a point of high density of states in the conduction band. This explains why this loss is strongly suppressed on the O face cleaved at room temperature where preferentially oxygen atoms form the uppermost layer.

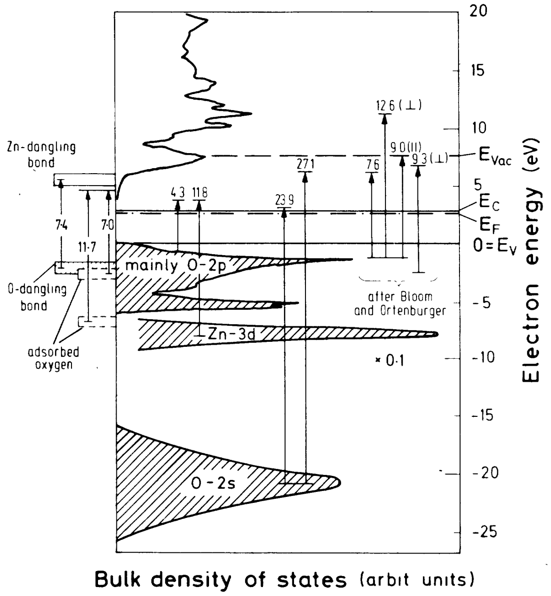

FIG. 9. Interpretation of some electronic transitions observed in ELS in terms of the density of states. Surface-state levels and surface transitions (except back-bond states) are given qualitatively on the left side. Transition energies are given in eV (near the final states for bulk transitions). (∥ and ⊥ mean light polarization parallel and normal to the *c* axis, E_v valence-band edge, E_c conduction-band edge, E_F Fermi energy, E_{vac} vacuum level obtained from Ref. 26). The distribution of empty conduction-band and occupied valence-band states is taken from a calculation of Bloom and Ortenburger (Ref. 16). The energetic position and qualitative shape of the Zn-3*d* and the O-2*s* levels is derived from Refs. 17 and 18, respectively.

C. Surface-state transitions

The existence of surface-state bands has firmly been established both experimentally and theoretically for the elemental semiconductors Si and Ge.[1,19,20] On the clean cleaved (111) surface the so-called dangling bond surface states are located close to the Fermi level reaching far into the forbidden band. According to recent investigations[21,22] these dangling bond surface states lie in the energy range of the bulk valence and conduction bands, respectively, on the clean cleaved GaAs (110) surface.

For III-V and for II-VI compound semiconductors theoretical considerations[23,24] and experimental results[2] suggest that the upper empty band of surface states is mainly cation derived whereas the lower occupied branch is built up from anion "dangling-bonds."

Transitions between filled and empty dangling bonds have been observed on Si and Ge.[1,19] On ZnO this type of transition should only be observed on the nonpolar face which contains both Zn and O dangling bonds. The loss spectra of the clean surfaces show two types of surface losses. One present on all faces at about 11 eV and one present only on the nonpolar face at about 7.5 eV. The discussion above suggests an interpretation of the latter loss in terms of a transition between filled O and empty Zn dangling bonds. The energetic position of both surface states cannot be derived from ELS data alone. From theoretical consideration[23] the O dangling bond should lie in the energetic range of the bulk valence band which is mainly O-2*p* (Ref. 17) derived. After Bloom and

Ortenburger[16] the initial level of the 7.6 eV bulk transition lies about 1.5 eV below the maximum of the valence band. After oxygen adsorption on the Zn face (Fig. 7) two characteristic losses are observed at 7.0 and 11.7 eV.

Their corresponding initial states are given by the present UPS data near 3.0 and 7.4 eV below the maximum of the valence band, respectively (Fig. 8). A reasonable assumption, therefore, is that the O dangling bond states energetically lie between the bulk state at 1.5 eV and the highest filled level of adsorbed oxygen near 2 eV below the maximum of the valence band. Accordingly, the position of the Zn dangling bond is at about 2 eV above the minimum of the conduction band (Fig. 9). Final states for the oxygen characteristic transitions on the Zn face (1 eV above the conduction-band edge) might be bulk conduction-band states or the empty Zn dangling-bond states discussed above (Fig. 9).

Besides the "dangling bonds" a second type of surface states ("back-bonds") is frequently discussed in the literature. The origin of these surface states can be seen in the change of bonding strength between the topmost and the second atomic layer. From the geometrical similarity of the "back bonds" on the different types of ZnO surfaces one might expect similar energetic positions of these "back-bond" states on all surfaces. We therefore, attribute the 11 eV loss to a surface transition arising from "back-bond" initial states. Assuming as final states the lower part of the conduction band the lowest possible energetic position of these "back bond" states is about 7.5 eV below the upper valence-band edge. Most of the observed transitions (except "back-bond") are shown together with the bulk density of states of ZnO in Fig. 9.

The two emission bands of oxygen adsorbed on the Zn polar face observed in UPS near 10.1 and 14.5 eV binding energy (Fig. 8) explain the oxygen characteristic losses at 7 and 11.7 eV (Fig. 7, Table I). Without further investigations of the oxygen adsorption itself, however, detailed conclusions about the type of oxygen bonding should not be drawn. An oxygen bond continuing the ZnO lattice does not seem unreasonable.

D. Simulated loss structures in second-derivative ELS

In most of the ELS spectra of the clean surfaces a peak was found near 2.5 eV which has been omitted from further consideration because of the following reasons: The double differentiation technique transforms a single peak of the nondifferentiated spectrum into a structure consisting of a maximum above and two minima on both sides of the maximum below the zero line. Two neighboring peaks of equal size are well resolved as long as their maxima do not mix. Things are more difficult if one of the peaks is much larger than the other, as e.g., in the case of the primary peak and a neighboring loss peak. The minimum of the loss peak located in the flank of the primary peak simulates a maximum. By means of a calculation we could simulate a maximum near 2.8 eV by superposition of two Gaussian shaped peaks using energetic position and halfwidth of the primary and the first real loss peak at $\Delta E = 4.3$ eV. We, therefore, think that the observed structure at $\Delta E = 2.5$ eV (omitted from the diagrams) is simulated by the double differentiation process. This is in agreement with results of Froitzheim and Ibach,[8] who did not observe any transition below 4 eV in high-resolution ELS. Similar structures on the steep flank of the primary peak found on other materials[25] might also be simulated.

V. SUMMARY AND CONCLUSIONS

The most interesting results of the present work shall be summarized as follows.

(i) With the assumption of prevailing bulk scattering for primary energies higher than 60 eV the differences between the ELS spectra of the nonpolar and the polar faces can be understood in terms of the optical anisotropy of ZnO on the basis of the dielectric theory. Differences between the ELS spectra of the Zn and O polar surfaces are explained by the different chemical composition of the uppermost layers of these surfaces.

(ii) The sensitivity of ELS (at least for ZnO) to surface excitations has been shown to increase rapidly with primary energies decreasing below 60 eV. This behavior is of central interest for the application of ELS to adsorption studies.

(iii) On the clean nonpolar surfaces, surface-state transitions are found which are most probably due to filled oxygen dangling bonds within the energy range of the bulk valence band and empty zinc dangling bonds in the conduction-band range.

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