Experimental surface electronic band structure of the $(10\bar{1}0)$ surfaces of CdS and CdSe

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The band structure of surface electronic states on the $(10\bar{1}0)$ cleavage surfaces of the wurtzite II-VI semiconductors CdS and CdSe has been studied experimentally. With the use of synchrotron radiation excited angle-resolved ultraviolet photoelectron spectroscopy, the surface electronic band structures have been investigated along the high-symmetry directions in the surface Brillouin zone (BZ). Through the observation of structures with two-dimensional dependence on the wave vector $\mathbf{k}$, i.e., showing no dispersion with the perpendicular component of $\mathbf{k}$ within a direct transition model, two surface resonances on each of the studied surfaces have been identified. Their energy dispersions along the boundary of the respective surface BZ and the polarization dependence of the uppermost resonances, S_1 and S'_1 , are presented. By comparing the results with a recent calculation for ZnS by Wang and Duke, conclusions about the relaxation of the surfaces are made.

INTRODUCTION

The understanding of the electronic structure of the cleavage surfaces of tetrahedrally coordinated semiconductors is an area in which there is considerable interest. With the development of new materials based on II-VI semiconductors where *in situ* growing techniques are applied, the investigation of the electronic structure of the surfaces used as substrates, as well as of the surfaces to be grown, is a matter of great scientific and technological interest. This is a subject of its own, besides the fundamental problem of finding the correct theoretical description of the electronic and geometric structure of these surfaces. The two compounds CdS and CdSe, both crystallizing in the wurtzite phase, have previously been investigated experimentally using low-energy electron diffraction (LEED) (Refs. 1 and 2) where the geometrical structure of the surfaces was studied, while studies of the electronic structure of the cleavage surfaces using angle-

resolved ultraviolet photoelectron spectroscopy (ARUPS) are very sparse. The work by Magnusson *et al.* on CdS (Ref. 3) is the only paper so far. The work presented in the present paper is a continuation of this earlier work, extending the examination of the CdS surface and including a similar study of the equivalent surface of CdSe. From the comparison of these results with the results of calculations, conclusions can be made about the relaxation model most appropriate for these surfaces.

EXPERIMENTAL DETAILS

Single-crystal bars, $5 \times 5 \times 25$ mm³, of low-resistivity CdS ($\rho \sim 10$ Ω cm) and CdSe ($\rho \sim 5$ Ω cm) were held in a sample holder with five degrees of freedom and cleaved *in situ* at a pressure of 5×10^{-10} Torr. The crystals of wurtzite structure were oriented such that cleaving produced 5×5 mm² well-ordered unreconstructed $(10\bar{1}0)$ surfaces, as checked with LEED. Figure 1(a) shows the geometri-

FIG. 1. (a) The surface geometrical structure of the $(10\bar{1}0)$ surface of the wurtzite crystals CdS and CdSe. (b) The experimental geometry and the surface Brillouin zone. The surface normal is $\mathbf{n}$, α is the angle of incidence, β is the azimuthal angle with respect to the $[0001]$ direction, and (θ, θ') are the spherical angles of emission.

cal structure of the ideally terminated $(10\bar{1}0)$ surface. Note that we are using the standard, crystallographic notation of the wurtzite structure, as opposed to Ref. 3.

Electron-energy distribution curves (EDC's) were recorded using an electron-energy analyzer, mounted on a two-axis goniometer, and a multichannel analyzer with the count rate in each channel normalized to the photon flux. Figure 1(b) shows the experimental setup, defining the angles of incidence (α) and emission (θ, θ') used and relates the azimuthal angle (β) to the crystal directions. Photons were supplied from the storage ring Doppel-Ring Speicherring (DORIS II) at Hamburger Synchrotronstrahlungslabor (HASYLAB), DESY in Hamburg, the Federal Republic of Germany, via the Seya-Namioka beam line.⁴ The total resolution, determined by the monochromator slit widths and the pass energy of the analyzer, was always better than 0.20 eV.

The crystals were electrically connected to the sample holder through a GaAl alloy and the Fermi energy of the system, used as energy reference, was found by recording the Fermi edge of Au, evaporated *in situ* on the sample holder. In the case of CdS the reference energy was chosen as the Cd $4d$ level, the binding energy of which is known from previous experiments.

RESULTS AND DISCUSSION

From Fig. 1(a) one may note that the plane spanned by the surface normal and the c axis is a mirror plane of the crystal structure and of the unreconstructed (1×1) (Refs. 1 and 2) surface. Light polarization selection rules are expected to follow from this and have been observed in previous ARUPS experiments,^{3,5,6} measuring in this mirror plane. LEED studies and theoretical calculations have presented a relaxation model for this surface of other wurtzite semiconductors⁷⁻⁹ in which the metallic cation relaxes into the surface while the anion, holding most of the bonding charge before cleaving, relaxes out of the surface, with a subsequent surface-bond and back-bond tilt and change of length, quite similar to proposed models for the (110) surface of zinc-blende structure semiconductors.¹⁰

CdS($10\bar{1}0$)

In Fig. 2 are presented EDC's recorded with 20 eV photon energy, angle of incidence 15° , and the polarization vector perpendicular to the c axis. The upper panel shows spectra for emission angles θ' along the $(000\bar{1})$ azimuth. Three structures in the spectra have been marked and labeled C, A, and S_1 in order to follow their energy dispersions. In this series, states are probed on the $\bar{\Gamma}-\bar{X}'$ line in the surface BZ. The panels at the bottom of Fig. 2 show spectra recorded close to the $\bar{X}$ and $\bar{M}$ points in the surface Brillouin zone (BZ) for the structure S_1 .

The analyses of the data are made within the model of momentum-conserving direct transitions and assuming the loss of the wave vector perpendicular to the surface, $k_\perp$, as a good quantum number upon the crossing of this. This model yields that bulk electronic states, being three-dimensional in $\mathbf{k}$ will show energy dispersion with a change in photon energy, if the final-state band in the

direct transition remains the same. Surface states, whether or not they are resonant in energy with bulk states, will show the same energy dispersion with respect to the wave vector parallel to the surface, $k_\parallel$, independent of the photon energy used. To see this, note that when $k_\parallel$ has been uniquely determined from the kinetic energy and the angle of emission, a difference in initial-state energy at the same $k_\parallel$ at two photon energies can only be due to a relation between the initial-state energy and $k_\perp$. This is a

FIG. 2. EDC's recorded at 20 eV photon energy and with the polarization perpendicular to the c axis of the CdS($10\bar{1}0$) surface at a light incidence angle of 15° , $\beta=0^\circ$, and for various angles of emission θ' , probing states along $\bar{\Gamma}-\bar{X}'$ ($\theta=0^\circ$) (upper panel), and the $\bar{M}$ ($\theta=30^\circ$, $\theta'=31^\circ$) and $\bar{X}$ ($\theta=30^\circ$, $\theta'=15.5^\circ$) points for the structure S_1 (lower panels).

zero relation for any surface feature. In a previous paper,³ the structure labeled S_1 was shown to be of surface origin, through the observation of nearly identical dispersions along $\bar{\Gamma}-\bar{X}'$ for three different photon energies. This structure has also been found to be stationary in initial-state energy in normal emission, $k_{\parallel}=0$, at photon energies from 18 to 25 eV, in a recent study.⁶ From this recent study it is further obvious that structures A and C are due to direct transitions from the two odd-symmetry upper valence bands. In the present study the surface resonance S_1 has been studied along the rest of the boundary of the surface BZ. The emission from S_1 is weak in the normal direction and is most clearly resolved in the second surface BZ. Although we have no explanation of this behavior, we have used this observation and the ability of the electron analyzer to be moved independently in the two angles of a spherical coordinate system to investigate this resonance in the second surface BZ. During these measurements a second structure was observed along the $\bar{X}'-\bar{M}$ line, dispersing downwards, which we have labeled S_2 . We suggest this to be the emission from a surface state or resonance on the $(10\bar{1}0)$ surface of CdS, located in, or close to, the open lens in the projected bulk band structure. The assignment of this state is based on the discovery of a similar structure on the CdSe $(10\bar{1}0)$ surface, to be discussed later in this paper, which has been thoroughly investigated and found to be of surface origin.

In Fig. 3 the S_1 surface resonance can be studied under different excitation geometries, displaying its dependence on polarization with respect to the mirror plane, with respect to the surface normal, i.e., p_z dependence, and the

FIG. 3. EDC's recorded from the CdS $(10\bar{1}0)$ surface, probing the same $k_{\parallel}$ point for the structure S_1 under various excitation conditions. The angle of incidence α is 15° , the emission angle θ' is 30° in the direction of the sulfur broken bond ($\beta=0^\circ$), and the polarization perpendicular to the c axis, unless otherwise stated. In (a) the polarization is parallel to the c axis ($\beta=90^\circ$, $\theta=30^\circ$), in (b) the azimuth is in the direction opposite the sulfur broken bond ($\beta=180^\circ$), and in (d) the angle of incidence (α) is 45° .

intensity variation of the emission from this state on opposite sides of the surface normal but within the mirror plane. Notable is that S_1 is only clearly observed in Fig. 3(c), which is in the direction of the sulfur broken bond, and not in Fig. 3(b), which is in the opposite direction. In Fig. 3(a), where the polarization of the radiation is parallel to the mirror plane, bulk states of opposite symmetry as compared with Fig. 3(c) are being excited, and it is evident that S_1 has largely the same symmetry as the bulk states excited in Fig. 3(c), i.e., odd with respect to the mirror plane. Concerning the p_z dependence, the spectrum shown in Fig. 3(d) is recorded with an angle of incidence $\alpha=45^\circ$ while Fig. 3(c) is recorded with $\alpha=15^\circ$. This changes the component of the polarization vector in the z direction (surface normal) but at the same time mixes the two types of mirror symmetry states mentioned above. The resulting spectrum must thus be compared with a sum of the spectra shown in Figs. 3(a) and 3(c) and this makes it difficult to determine the precise p_z dependence of S_1 . One may, however, note the absence of the large increase in emission intensity upon an increase in p_z excitation, which would be indicative of a strong p_z character of this state.

The results of this experimental investigation of CdS $(10\bar{1}0)$ are summarized in Fig. 4 where the measured surface electronic band structure is plotted along the symmetry directions of the surface BZ. The position of the valence-band maximum with respect to the Fermi energy E_F , 2.4 eV, in agreement with Ref. 11, has been deduced from measured binding energy of the Cd $4d$ states within the two reference systems.

CdSe $(10\bar{1}0)$

Figures 5 and 6 present EDC's recorded at 15° angle of incidence and for various angles of emission, θ' , at photon energies 20 and 24 eV, probing points in the surface BZ of CdSe $(10\bar{1}0)$. The polarization was held perpendicular

FIG. 4. The experimental surface electronic structure of CdS $(10\bar{1}0)$ found in this study, mapped along the high-symmetry lines of the surface Brillouin zone.

FIG. 5. EDC's recorded at (a) 20 eV and (b) 24 eV photon energy, angle of incidence 15° , and with the polarization perpendicular to the c axis of the CdSe(10 $\bar{1}$ 0) surface for various angles of emission θ' ($\theta=0^\circ$), probing states along $\bar{\Gamma}-\bar{X}'$ in the surface Brillouin zone, at $\beta=0^\circ$.

ular to the c axis. Figure 5 focuses on the S'_1 structure along the $\bar{\Gamma}-\bar{X}'$ line and suggests this state to be of surface origin by the observation of its close to identical energy dispersion at these two different photon energies. Figure 6 shows the dispersion along $\bar{X}'-\bar{M}$ of the structure S'_2 , the equivalent of S_2 observed on the CdS(10 $\bar{1}$ 0) surface, at 20 eV photon energy. This structure has also been found to have the same dispersion independent of photon energy, thus suggesting it to be of surface origin. The structure labeled Y is also found to be a structure stationary with respect to photon energy, but since it only has a minute energy dispersion with respect to $k_{||}$, we believe further tests of the origin of this structure are needed before drawing any conclusion. In the two lower panels the $\bar{X}'$ point for S'_2 on the other side of the surface normal, showing the emission intensity to be strongest in the direction opposite the selenium broken bond, and the $\bar{X}$ point for S'_1 , are shown.

A characterization of the S'_1 structure is presented in Fig. 7. The conclusions to be made from this are ap-

FIG. 6. EDC's recorded at 20 eV photon energy, angle of incidence 15° , and with the polarization perpendicular to the c axis of the CdSe(10 $\bar{1}$ 0) surface for various angles of emission, probing states along $\bar{X}'-\bar{M}$ ($\beta=180^\circ$, $\theta'=14^\circ$) (upper panel), the $\bar{X}'$ point in the direction of the selenium broken bond for the structure S'_2 ($\beta=0^\circ$, $\theta'=14^\circ$), and the $\bar{X}$ point for the structure S'_1 ($\beta=180^\circ$, $\theta=27.5^\circ$, $\theta'=29^\circ$) (lower panels).

FIG. 7. EDC's recorded from the CdSe(10 $\bar{1}$ 0) surface, probing the same $k_{\parallel}$ point for the structure S'_1 under various excitation conditions. The angle of incidence α is 15°, the emission angle θ' is 32.5° in the direction of the selenium broken bond ($\beta=0^\circ$), and the polarization perpendicular to the c axis, unless otherwise states. In (a) the polarization is parallel to the c axis ($\beta=90^\circ$, $\theta=32.5^\circ$), in (b) the azimuth is in the direction opposite the selenium broken bond ($\beta=180^\circ$, and in (d) the angle of incidence (α) is 45°.

parently similar to those concerning the S_1 structure on CdS(10 $\bar{1}$ 0), indicating a close relationship between the two structures.

The above-described results of this investigation of the (10 $\bar{1}$ 0) surface of CdSe are summarized in Fig. 8 where the experimental surface electronic band structure is plotted along the symmetry directions of the surface BZ. The position of the valence-band maximum with respect to E_F , 1.4 eV, has been deduced from measured binding energies of the Cd 4*d* states within the two reference systems. The value is in fair agreement with Ref. 11; the difference is probably due to the differing surface quality.

SUMMARY AND CONCLUSIONS

The electronic structures of the two cleaved semiconductor surfaces studied in this work show large similarities, with differences mainly in absolute energy positions. Both of the surface features S_1 and S'_1 found close to the projected valence-band edge are shown to be surface resonances with energy positions at $\bar{\Gamma}$ of -0.20 eV for CdS and -0.35 eV for CdSe, energies referenced to the valence-band maximum, VBM. Further energy values for S_1 are -0.6 eV at $\bar{X}'$ and -1.3 eV at $\bar{M}$, while S'_1 is found at -0.85 eV at $\bar{X}'$. The structures S_2 and S'_2 may be surface states (as opposed to resonances), i.e., may have their energies within the open lens known to exist in the projected valence-band structure. Since no projected valence-band structure for CdS or CdSe has been reported, the distinction between surface state and resonance must be deferred. The observed energy position for S_2 is

FIG. 8. The experimental surface electronic structure of CdSe(10 $\bar{1}$ 0) found in this study, mapped along the high-symmetry lines of the surface Brillouin zone.

-2.85 eV at $\bar{X}'$ and for S'_2 -3.2 eV at $\bar{X}'$, -4.8 eV at $\bar{M}$, and -4.1 eV at $\bar{X}$, all energies referenced to the VBM.

There exist no theoretical predictions of the electronic structure of any of these two surfaces, so comparisons must be made with results from systems believed to be electronically similar. Ivanov and Pollman have calculated the surface electronic structure of wurtzite ZnO (Ref. 8) and recently Wang and Duke have done a similar tight-binding calculation for wurtzite ZnS.⁹ The results have some parallels but we choose the calculation for ZnS as a model surface with which to compare our results. In the comparison with this calculation one may associate the experimentally observed surface resonances S_1 and S'_1 with the predicted surface state s_1 (lower case letters are used for the predicted states) which in analogy with the results for ZnS should be due to the broken bond on the surface anion. According to Wang and Duke⁹ the charge in the broken bond redistributes upon relaxation and the charge transfer is mainly to the back bonding between the p_z component of the top layer S or Se atoms and the p_z (or p_x) component of the second-layer Cd atoms. The observed surface features S_2 and S'_2 are associated with the predicted surface state s_4 which is situated in the lower part of the open lens in the projected bulk band structure. The s_4 state is identified by Wang and Duke as due to the backbonding between the s component of the first-layer cation, which in our study is Cd, and the p_x component of the second-layer anion.

The calculation⁹ is obviously not yielding a dispersion for the topmost surface feature in good agreement with our measurement. In the calculation s_1 evolves from a surface resonance to a surface state by having an upward dispersion going from $\bar{\Gamma}$ to $\bar{X}'$. On the other hand, the s_4 state shows a dispersion quite similar to the measured dispersion. A prediction of the character of s_1 and s_4 and an explanation for the appearance of S'_2 only in the direction opposite the anion broken bond would be of great

value in a further identification of the observed surface structures.

In summary, the experimentally determined surface electronic band structure of the (10 $\bar{1}$ 0) surfaces of CdS and CdSe are very similar, suggesting a close relationship between the relaxation of the cleaved surfaces. The relaxation model proposed by Wang and Duke for ZnS (Ref. 9) is largely in line with the results of this paper. A construction of a similar model for CdS and CdSe would be of great benefit to the further description of the surface

electronic structure of these wurtzite II-VI semiconductors.

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