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Test of band offset commutativity by photoemission from an *in situ* grown ZnTe/CdS/ZnTe quantum well

W. G. Wilke, Ch. Maierhofer, and K. Horn

Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-1000 Berlin 33, West Germany

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We have characterized the ZnTe–CdS heterojunction by valence and core level photoemission with synchrotron radiation, using quantum wells grown *in situ* on ZnTe(110) substrates. The valence band offset of $\sim \Delta E_v = 0.9$ eV shows that this heterojunction is of the staggered type (type II), rarely encountered in experimental studies. We find evidence for chemical reaction involving Te at the interface. The band offsets at both sides of the CdS quantum well exhibit small differences on the order of 0.1 eV, which are also reflected in the dipole contribution at the interfaces. This study, while reporting only small deviations from commutativity, suggests that dipole contributions of varying magnitude, caused by interface reactions, influence the magnitude of the band offset.

I. INTRODUCTION

The experimental study of semiconductor heterojunctions by photoelectron spectroscopy has greatly extended our knowledge of the physical and chemical characteristics of these systems, and the determination of valence band offsets ΔE_v by this technique has yielded a reliable data base for a comparison with band offsets calculated using different approaches.^{1,2} Considerable progress has also been achieved in the theoretical description of factors influencing band offsets. Several models predict the band offset on the basis of a characteristic bulk midgap energy level, which serves as the band lineup reference level; this reference level is often invoked in a heuristic way. An alternative way, conceptually more appealing, has been to carry out band structure calculations for a slab consisting of two different semiconductor layers in a supercell geometry, using modern band structure calculational schemes;³ these calculations take into account charge transfer at the interface and, therefore, are likely to correctly estimate the interface dipole. However, midgap energy models continue to be important for those systems that are more difficult to treat by supercell calculations, for example, because of a large lattice mismatch at the interface, and for a physical insight into the trends observed in band offsets for different semiconductor combinations.

At present, all "general-purpose" theories based on specific bulk properties have one feature in common: they predict a linear dependence of the band offset on these properties.⁴ A direct consequence of linearity is the concept of commutativity, i.e.,

$$\Delta E_v^{(A-B)} = \Delta E_v^{(B-A)}. \quad (1)$$

In practical terms, this means that two different interface preparations (A grown on B, and B grown on A, respectively), should give identical band offsets. Unfortunately, experimental tests of band offset commutativity have been inconclusive so far. Katnani and Margaritondo,⁵ in their study of a large number of heterojunctions involving Si and Ge, arrived at the conclusion that, on average, deviations from linearity (here derived from the concept of transitivity) were < 0.03 eV per interface. Waldrop *et al.*, on the other hand, found a difference of 0.27 and 0.23 eV for different

growth sequences of AlAs–GaAs(110) and ZnSe(110)–Ge;⁶ however, Katnani and Bauer, in a later study, found a negligible deviation from commutativity for GaAs–AlAs(100).⁷ In order to provide a wider experimental basis for a discussion whether commutativity is fulfilled, we have studied band offsets between ZnTe and CdS by photoemission, using ZnTe/CdS/ZnTe quantum wells grown *in situ*, thus removing the influence of changes in the experimental parameters. Our results also extend the data base for heterojunctions between II–VI semiconductors, for which fewer reports are available than for the widely studied III–V junctions. Apart from an earlier study of ZnSe–MnSe,⁸ this is the only *in situ* photoemission study of band offsets in a single quantum well.

II. EXPERIMENTAL

The experiments were carried out in a commercial angle-resolving photoelectron spectrometer (ARIES HA 50 by VSW Ltd.), with an angular resolution of $\sim 2^\circ$ half-angle; the chamber also contained a crystal holder with heating facility, a low-energy electron diffraction (LEED) optics, and a cleavage device. Photoemission experiments were carried out at the BESSY (Berliner Speicherring-Gesellschaft für Synchrotronstrahlung mbH) storage ring on the toroidal grating monochromator TGM 4. The photon energy range from 40 to 70 eV was used, yielding an overall resolution of ~ 0.1 eV. The chamber had base pressures of 3 to 6×10^{-11} mbar.

The ZnTe(110) surfaces were prepared by cleaving of undoped ZnTe crystals (provided by G. Lamprecht, West Germany) *in vacuo*. CdS and ZnTe layers were deposited from CdS and ZnTe powder in two Knudsen cells of our own design,⁹ as described previously.^{10,11} Layer thicknesses and growth rates were determined from the intensities of the substrate and overlayer core level photoemission as a function of deposition; due to the fact that the Cd 4*d* level overlaps with the Zn 3*d* level, this procedure is liable to a fairly large error for CdS. However, we were able to estimate growth rates from our previous work with ZnTe overlayers on GaSb(110).¹⁰ The evaporation rates for CdS, evaluated

from the Te 4d level intensities by this procedure, agreed well with rate determinations from the Cd and S₂ vapor pressures resulting from the congruent evaporation at the cell temperatures that were used. Substrate temperatures were measured by a chromel–alumel thermocouple mounted between the crystal holder and the sample, thus being liable to a certain error; they ranged from room temperature to 200 °C. Five different quantum wells were grown in this way, with well thicknesses in the range from 8 to 50 Å.

In order to determine the energies of the core level lines and the valence band maximum with respect to the Fermi energy E_F , spectra were recorded from a gold plate mounted in electrical contact with the substrate crystal. The absolute value for the photon energy was determined using light from the second order of the diffraction grating. The work function change during CdS deposition was measured by recording the low-energy cutoff in the photoelectron spectrum with a negative potential of 10 eV applied to the crystal.

III. RESULTS AND DISCUSSION

The growth of the CdS quantum well on the ZnTe(110) substrate may be readily followed by the intensities of substrate and overlayer core level photoemission lines as shown in Fig. 1. The data were recorded using a photon energy of 70 eV, in electron emission normal to the surface, and an angle of incidence of the light of 50°; they were normalized with respect to the photon flux using the signal from the monochromator refocusing mirror, the gold-coated surface of which was used as a monitoring diode. The bottom spectrum shows the emission from the clean ZnTe(110) surface, displaying the well-resolved Te 4d doublet and the Zn 3d line which, due to its band character, exhibits a main line and a smaller peak at lower binding energy; their relative intensi-

ties and exact positions depend on photon energy and emission direction, indicative of the contribution of direct (i.e., k conserving) transitions from the Zn 3d initial states.¹² Upon deposition of small amounts of CdS, the Te 4d intensity decreases, and a shoulder at higher binding energy grows on the Zn 3d peak. Subsequent depositions enhance this trend, until, at a thickness of 8 Å, the signal from Cd 4d dominates, and the Te 4d level is strongly suppressed. In the particular experiment from which the data shown in Fig. 1 were taken, a subsequent layer of ZnTe was grown on the CdS film. The corresponding spectra are shown; apart from the expected increase in Te 4d and Zn 3d intensity, note that the Te 4d doublet is less well-resolved than in the spectra from the clean surface.

Previous experiments have shown that a sizeable interface reaction can occur in heterojunctions between III–V and II–VI compound semiconductors;^{10,11} they are also likely to occur in the present case of a II–VI/II–VI junction. This aspect of interface formation is particularly important in the present study, since a varying extent of the reaction may contribute to a growth sequence dependence of the valence band discontinuity. Information on such a reaction was therefore derived from high-resolution core level spectra, which have been shown to be invaluable for the analysis of interface elemental and chemical composition. The data for the Te 4d core level are shown in Fig. 2. The bottom spectrum shows the clean ZnTe(110) Te 4d core level. Apart from the data points we also show a fit curve (line), based on one Lorentzian line representing intrinsic linewidth, convoluted by a Gaussian to take into account monochromator

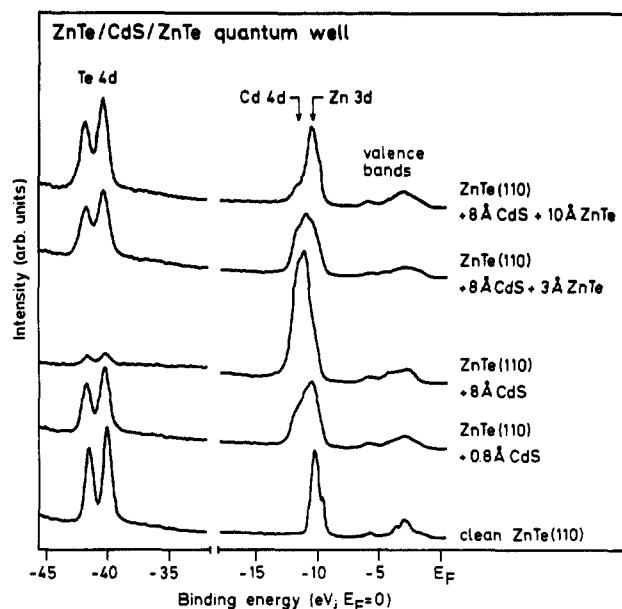


FIG. 1. Photoelectron spectra of the core and valence band region of ZnTe(110), covered with different amounts of CdS and ZnTe as indicated. Photon energy 70 eV, normal electron emission. Note the coverage-dependent changes in the Te 4d intensity and the shape of the Zn 3d/Cd 4d region.

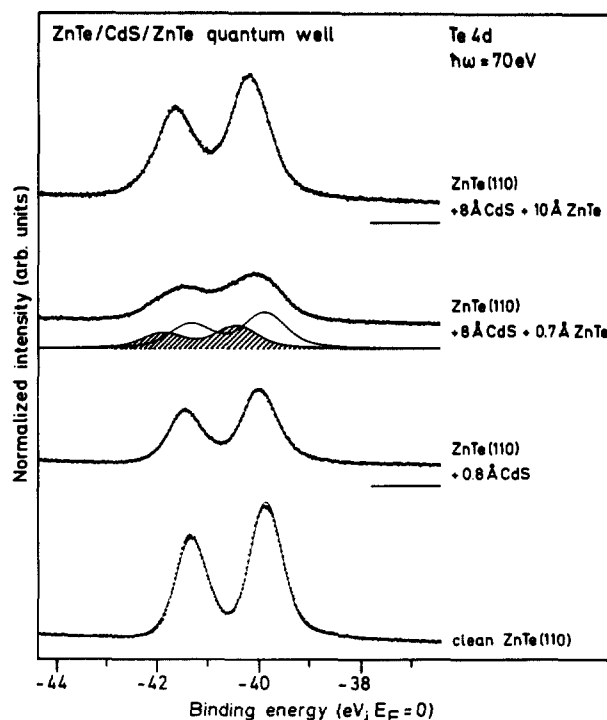


FIG. 2. Closeup spectra of the Te 4d peak, recorded for different coverages of CdS and ZnTe. The line indicates the fit curve as described in the text. The hatched doublet in the third curve indicates emission from a new chemical species (see the text). Photon energy, 70 eV.

and electron analyzer resolution as well as other effects (phonon broadening, inhomogeneous pinning, etc.). The fit parameters were subjected to a least-squares optimization routine based on the Marquardt algorithm.¹³ In all but the first spectrum, the fit curve is almost indistinguishable from the data points, indicating the good quality of the fit.

Based on results from other (110) surfaces of the III-V compound semiconductor surfaces,^{14,15} we would have expected to find clear evidence for surface atom emission to be shifted with respect to the bulk emission [toward lower binding energies in this case of the anion (Te 4*d*) level], to be visible in the raw data, let alone in the line shape analysis. Despite several attempts involving different ZnTe crystals, using different photon energies and electron collection angles, however, no clear surface core level shift (SCLS) could be identified. Although it is difficult to give a lower limit for the magnitude of SCLS, they would certainly have to be < 100 meV to escape detection in our data analysis. This result is most surprising in view of the widely accepted model which identifies surface Madelung energy as the main contributor to the SCLS,^{15,16} since ZnTe, being a II-VI compound, should have a higher ionicity and therefore, a higher surface Madelung contribution and SCLS. This result certainly warrants further study. We note that agreement between the fit curve and the data is not perfect in the clean surface spectrum, particularly with respect to the shape of the 4*d*_{5/2} peak. This may be related to a different intrinsic width of the *d*_{3/2} and *d*_{5/2} level, which were constrained to the same value in the fitting procedure; the fit did not improve when a second Lorentzian doublet was included.

Deposition of 0.8 Å CdS gives rise to a small shift in peak energy and a decrease of intensity. In some cases, deposition of overlayers has been used to identify the SCLS by their intensity decrease.^{15,17} The failure to observe clear changes in the Te 4*d* line shape supports our above claim that the SCLS have to be small. This discussion of SCLS is not peripheral to the central topic of our investigation, i.e., the study of valence band offsets, since the input parameters for the core level analysis are important for a subsequent determination of coverage-dependent band bending, which directly enters into the value for ΔE_v . While little change in line shape occurs on the Te 4*d* level up to the highest coverages, the situation changes when ZnTe is deposited onto the CdS "quantum well" overlayer. This is shown in the third spectrum of Fig. 2. The rather broad peak shape can be well-reproduced by two doublets, one of which (shown hatched) is shifted by 0.6 eV with respect to the bulk Te emission. The second component obviously stems from a reacted interface component, because the final spectrum shows a well-resolved doublet which is very similar to the one from the substrate surface; the reacted component is therefore confined to the interface region. From the binding energy of the new Te 4*d* component, 39.23 eV, we conclude that CdTe is formed, since the binding energy value reported for the Te 4*d* level in CdTe(100) is 39.34 eV¹⁸ [both referenced to the valence band maximum (VBM)]. The enthalpy of formation for CdTe is only 60% of that for CdS (−161.9 kJ mol^{−1}), but these bulk thermodynamic values may not be applicable to the present interface situation. Since we

were limited to photon energies below ~120 eV, it was not possible to determine whether an accompanying zinc-sulfur reaction took place because of the binding energy of the sulfur 2*p* level ($E_b = 163$ eV). In view of the fact that equal arrival rates occur in the case of congruent evaporation used here, such reaction appears likely; however, the Zn 3*d* peak cannot be used for chemical analysis because of the band character of this level (see above). From the intensity of the new line, we estimate that the corresponding amount may be approximately one to two monolayers equivalent. The reacted component is buried at the interface as indicated by the top spectrum in Fig. 2; this shows the Te 4*d* peaks recorded from a 10 Å thick overlayer of ZnTe on the CdS well layer, which can again be described by only one Lorentzian.

The valence band maximum emission such as shown in Fig. 3, used in combination with band bending shifts deduced from the Te 4*d* core level, provides a basis for the determination of the valence band offset ΔE_v . On the left-hand side, the major features of the valence band are seen, and it is obvious that considerable changes occur as the CdS layer is formed. The bottom spectrum exhibits the features of clean ZnTe(110); with increasing deposition, the peak shapes change, and in the 8 Å CdS spectrum, an entirely different shape is observed. As the subsequent ZnTe overlayer builds up, the spectrum reverts to the initial shape, although with less well-defined shape on each of the peaks. This is more likely due to a high degree of disorder in the overlayer. Considering a lattice mismatch of 4.5% between ZnTe and CdS, the critical thickness beyond which the strain in the overlayer is released by dislocations, is fairly small, probably ~20 Å.¹⁹ Thus it is reasonable to assume that the spectrum, which is characterized by direct transitions, will have a higher proportion of contributions from other crystal orientations, and/or a higher amount of scattering of the photoelectron due to these lattice imperfections. The main ingredients of the ZnTe valence level spectrum may still be distinguished in the topmost spectrum, however.

From the valence band maximum region shown on the right-hand side, an energy difference of ~1 eV between the VBM of ZnTe and CdS is derived. The VBMs, evaluated by linear extrapolation, are combined with the band bending changes upon layer deposition to give the valence band offset in Fig. 4. Different symbols refer to each of the five quantum wells; in one of the experiments, a thin ZnTe buffer layer was grown on the cleaved ZnTe crystal in order to ascertain that growth conditions resulted in the production of well-defined ZnTe layers. Results from this buffer layer were found to be indistinguishable as compared with fresh cleaved crystals. Figure 4 shows the emergence of the new valence band maximum as a function of overlayer thickness; this quantity was derived, for CdS layers, from the decrease of Te 4*d* intensity as a function of deposition time, and calibrated into thicknesses using a semilogarithmic plot and tabulated photoelectron mean free path lengths. For the subsequent ZnTe growth, we relied on deposition rates evaluated from a previous ZnTe MBE growth experiment,¹⁰ because core level attenuation based on the Cd 4*d* level was deemed not accurate enough because of its overlap with the Zn 3*d* peak. Because of the direction of ΔE_v for CdS/ZnTe, emission from

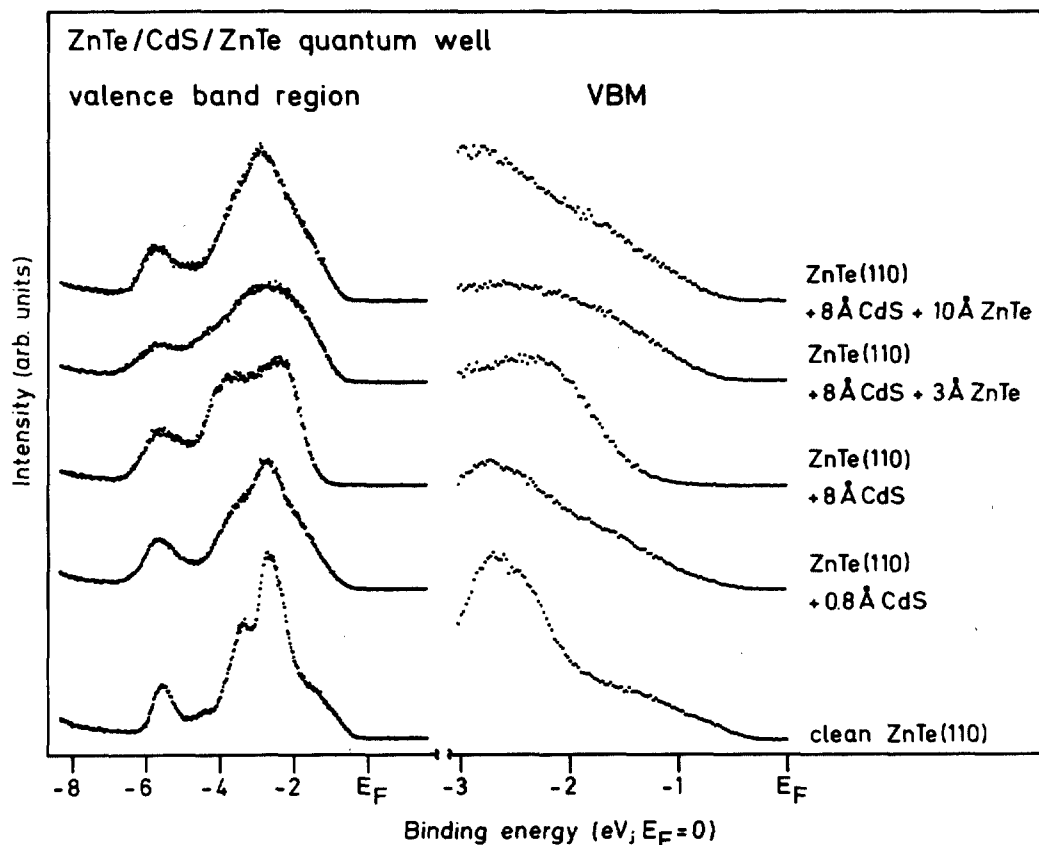


FIG. 3. Valence band spectra for ZnTe(110) and CdS as well as ZnTe overlayers, showing the changeover from the characteristic feature of ZnTe, to those of CdS. The final layer of ZnTe exhibits similar but broadened features compared with those of the substrate. Photon energy 70 eV, normal electron emission.

the ZnTe VBM (at lower binding energies than from the CdS VBM) will be detected up to fairly high layer thicknesses. The gradual emergence of ΔE_v as presented in Fig. 4 should not be mistaken as indicating the real establishing of ΔE_v ; rather, Fig. 4 represents the evolution of the *experimental* parameters by which it is determined. There is one feature of the ΔE_v versus coverage curve which merits attention; this is the initial increase of the valence band maximum value measured at the very lowest CdS deposition. While the effect is small ($\sim +0.1$ eV), it is clearly distinguishable and present in all experiments. Further, we have found a similar "overshoot" of the VBM at low depositions also in our previous investigation of ZnTe/GaSb(110) (Ref. 10) and

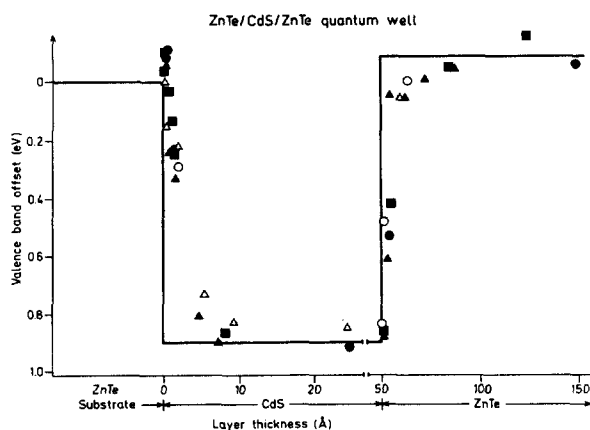


FIG. 4. Evolution of the valence band offset in ZnTe/CdS/ZnTe as a function of overlayer thickness.

CdS/InP(110).¹¹ This phenomenon can be explained by an upward bending of the substrate bands due to CdS deposition, which is detected by the shift in the core level peak; the VBM emission being already shifted by the added emission from the CdS overlayer, such that the band bending effect (which should also be observed here) is obscured by the deposition. Support for this explanation comes from the absence of this overshoot in the second junction (see Fig. 4). Here, the CdS overlayer is too thin for band bending to occur, such that no shift can take place.

The final value of the valence band offset is found to be established after the deposition of ~ 10 to 15 Å of material. This is not meant to indicate that the formation of the heterojunction actually needs layers of such a comparatively large thickness. Rather, it represents our experimental limitation in determining such offsets. One can infer from the course of the VBM in Fig. 4 that any band offset determination by photoelectron spectroscopy will have to consider this problem connected with overlap of valence band emission from both substrate and overlayer (except in those cases where the offset is positive, i.e., emission from the overlayer occurs at lower binding energies than that of the substrate, such as in the case of Ge on ZnSe²⁰). Determinations of ΔE_v based on overlayer thicknesses as low as 8 Å (Ref. 8) may therefore be subject to a small error. The size of the deviation from the true offset will depend on the photon energy used, due to the characteristic escape depth of the photoelectrons for a given $\hbar\omega$. The offset at the CdS/ZnTe interface is similarly affected by the overlap of the valence band maxima. From the plot in Fig. 4, the magnitude of ΔE_v can be derived. For the first ZnTe/CdS interface, a value of $\Delta E_v = 0.90$ eV

is obtained. The second interface has a valence band offset of very similar magnitude, $\Delta E_v = 0.99$ eV. While there is some scatter in the magnitude of ΔE_v for the second interface for high values of ZnTe layer thickness, it is certainly higher than the value for the first junction as evident from the data points in Fig. 4.

The error in the determination of ΔE_v needs some consideration at this point. The valence band offset is derived from the shift in energy of the substrate bulk Te 4d core level, which is derived through the fitting routine with an absolute precision (fit routine confidence interval for 1σ deviation) of ± 0.01 eV; the precision for the shifts due to band bending is even better. Probably, the largest error is introduced through the determination of the valence band maximum, for which we use the linear extrapolation of the spectral region near the VBM. This involves a sizable absolute error; its magnitude, as determined from different extreme possibilities for linear extrapolation, is estimated to be 30 to 50 meV. Again, the relative error is smaller, but combined with the error for the core level line we arrive at an overall precision of approximately ± 50 meV. Taking this uncertainty into account, the difference between the values for ΔE_v (0.09 eV) is seen to lie just within the error margins for the determination of the two band offsets.

Apart from the measurement of the valence band offset, the photoemission technique also gives access to other important characteristics of the heterojunction. This is displayed in Fig. 5, where the valence band discontinuity of Fig. 4 is shown together with the conduction band offset as derived from the magnitude of the fundamental gap E_g for the two semiconductors; for CdS, we have used E_g for the wurtzite structure, although we infer from our LEED photographs that CdS grows pseudomorphically in the zincblende structure on ZnTe(110), similar to what is observed on InP(110). The course of the valence and conduction bands across the quantum well shows that the ZnTe/CdS heterojunction is of the staggered type (also called type II).

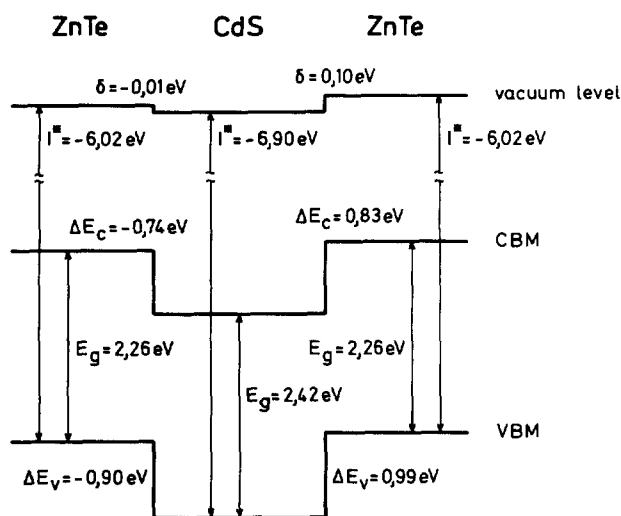


Fig. 5. Alignment of valence and conduction bands in the ZnTe/CdS/ZnTe quantum well with a well thickness of 50 Å. Also shown is the change in the vacuum level (work function change) at the two interfaces (see the text).

This rare way of valence and conduction band alignment has so far been observed only once experimentally, in the case of ZnSe/MnSe/ZnSe reported by Asonen *et al.*⁸ While in the present case, the discontinuity is distributed rather evenly in both valence and conduction bands, Asonen *et al.* found a very small valence band offset and a larger conduction band offset. From the total width of the photoelectron spectra and by precisely measuring the photon energy, we can derive the ionization energy I^* for the surface under study. For clean ZnTe(110), this is shown in Fig. 5; I^* is 6.02 eV, somewhat larger than the value found on ZnTe layers (5.56 eV) in a previous band offset study.¹⁰ For the CdS overlayer, $I^* = 6.90$ eV, very close to the value for CdS overlayers on InP(110) [7.00 eV (Ref. 11)]. At the ZnTe/CdS interface, this gives a very small change in the dipole part of the vacuum level (change in work function) of 0.01 eV; this value has increased to 0.1 eV at the CdS/ZnTe interface.

Having established the valence band offset, we compare its magnitude with different schemes for predicting ΔE_v . The semiempirical scheme of Katnani and Margaritondo⁵ has been widely used for such predictions; it is based on the concept of transitivity (another feature common to all linear theories), and involves the deposition of Si and Ge overlayers on a wide variety of semiconductor surfaces. Their semiempirical table, which was improved by taking into account more recent experimental values,³ yields $\Delta E_v = -0.74$ eV for ZnTe/CdS, certainly within the limits of the overall accuracy of approximately 0.15 eV which the authors quote. Another way of estimating band offsets is based on the analogy between Schottky barrier formation and heterojunctions drawn by Tersoff²¹ who, starting from earlier work by Heine,²² postulated the existence of a charge neutrality level (CNL) that serves to adjust the valence levels on either side of the heterojunction. Because of tunneling of states from one side of the junction to the other, a charge transfer dipole will occur. Using the values for the Schottky barrier height of gold for *p*-type material as a measure for the CNL,²³ a value of $\Delta E_v = 0.98$ eV is found, i.e., very close to our experimental result. In Harrison's tight-binding theory,²⁴ the valence band maxima result from a superposition of the *p* levels of the free cation and anion, combined with a universal interatomic coupling term which only contains the bond length. Assuming the interface dipoles are negligible, the so-called "natural lineup" is obtained; its magnitude is -1.62 eV. Current thinking stresses the importance of the interface dipoles, however; in a later paper, Harrison and Tersoff²⁵ include this dipole, and find a valence band offset of -0.74 eV. This shows that for the present system in particular a large difference occurs when dipoles are included. Finally, among these theories based on bulk semiconductor properties, the Frenley-Kroemer pseudopotential model²⁶ gives $\Delta E_v = -0.68$ eV for ZnTe/CdS, but without including interface dipoles. It is difficult to estimate the confidence margin for these predictions. Due to the fact that the junction is not well lattice matched, supercell calculations (such as performed by Christensen for a number of junctions³) are not available, and neither are values derived from the dielectric midgap energy model of Cardona and Christensen.² We are therefore left with the above comparisons, which give

good agreement, in contrast to what is sometimes found for other systems. Part of the good agreement may be due to the fact that only a small dipole layer exists at the ZnTe/CdS interface.

Tests of valence band offset commutativity are of central importance for an assessment of the validity of the basic linearity assumption, which is common to all present theories for the prediction of the band lineup. Having established the band offset on both sides of the ZnTe/CdS/ZnTe quantum well, we will now discuss these results in the light of current theoretical concepts of band discontinuities. Results for Schottky barrier heights as well as heterojunctions have shown that the concept of a specific charge neutrality level (CNL), which acts as a reference level for the alignment of the band structures of the two semiconductors upon contact, can explain much of the experimental data for these systems, sometimes with surprising accuracy. The influence of this level may be compared with that of the Fermi level in metal-to-metal junction. In such a contact, charge will flow, resulting in a dipole that cancels the difference in work function of the two metals, such that the interface will be in equilibrium. The situation in a contact between two insulators will be different; here, no charge flow occurs, such that the discontinuity will occur between the two CNLs, and the vacuum levels will be aligned; there is no dipole. The situation in a semiconductor will be somewhere in between these two limiting cases. While some charge flow will occur, causing a dipole to be formed that will compensate the difference in the vacuum levels, it is also reasonable to assume that the CNLs will not be perfectly adjusted. Since we refer the valence band maxima to the CNL, this has a direct influence on the ΔE_v . Restated in a simple way, the factors affecting the valence band offset divide up into a dipole term between the vacuum levels and an energy difference between the neutrality levels. This situation is visualized in Fig. 6. The question is then how close the case of two semiconductors is to either limiting cases. For III-V semiconductors, Tejedor and Flores have estimated that the situation is closer to the case of two metals, with energy differences between the two CNLs of up to ~ 0.2 eV.²⁴

So far, there is no difference between the ΔE_v 's at the two sides of a quantum well. Consider, however, the case of an additional sheet of dipoles introduced at the interface, either through an interface reaction occurring at only one of the two sides, or through intentional deposition of some material at the interface.²⁵ Tersoff has considered this case in a thought experiment. He argues that embedding a sheet of dipoles δ_x in a semiconductor leads to a net screened dipole $\delta = \delta_x/\epsilon$, where ϵ is the static long-wavelength dielectric constant. Since the screening charge in a semiconductor is confined to a region of a few angstroms around the charge being screened, the extra observable valence band discontinuity by the sheet of dipoles corresponds to the net screened dipole. This extra dipole will thus change the balance between CNL energy difference and vacuum level "offset" mentioned above. We contend that this behavior is precisely what we observe in the case of the ZnTe/CdS/ZnTe quantum well. The second valence band offset is larger than the first by ~ 0.1 eV, and this increase is reflected in the change

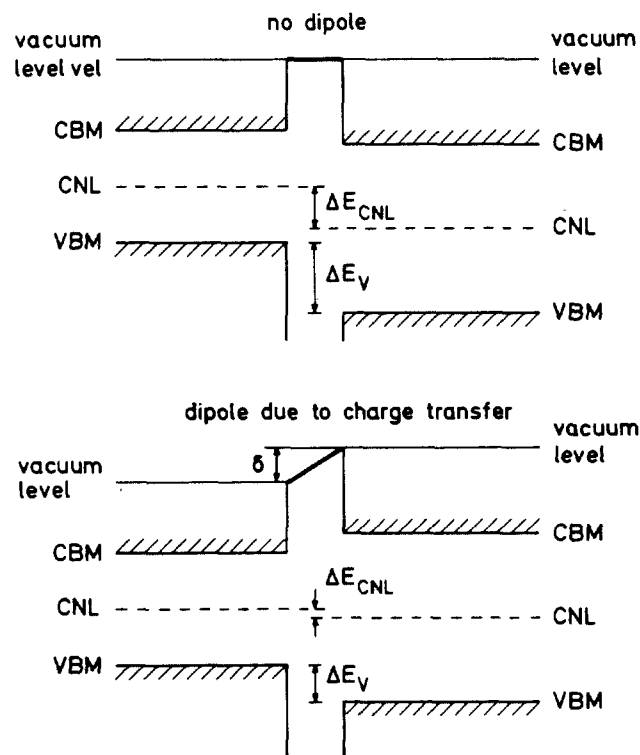


FIG. 6. Schematic diagram of energy levels at a heterojunction. (a) No charge transfer between the constituents, and thus, no dipole. (b) Realistic case with charge transfer. The energy differences are seen to divide up into a dipole part which shifts the vacuum level, and an energy difference between the charge neutrality levels (CNL). After Tersoff, Ref. 21.

of the vacuum levels (work function) at the second interface, which is also larger by 0.1 eV, as it should be from the reasoning outlined above. Since the reacted Te 4d photoemission line only occurs at the second interface, we argue that the reaction products introduce a sheet of dipoles that affect the band offsets in the way described above; such an influence of interlayers in heterojunctions has previously been reported by Perfetti *et al.*²⁸ It is worth noting that, in this present system, the differences between the band offsets on both sides of the quantum well are small, close to the combined experimental accuracy; however, the systematic occurrence of differences in ΔE_v and the vacuum level is strong evidence in favor of an explanation of the observed differences in terms of the influence of dipole layers caused by interface reactions.

If the band offset is influenced by the presence of dipole layers due to interface reaction products and/or foreign species, as suggested from our data and the above discussion, deviations from commutativity would find a natural explanation. Unfortunately, there are only a few studies of this aspect of band alignment in the literature. We will first discuss the only other *in situ* study of commutativity by Asonen *et al.*⁸ using ZnSe/MnSe/ZnSe quantum wells grown on a GaAs substrate, and then consider several examples for III-V semiconductors. A comparison of our data with those by Asonen *et al.* is particularly interesting since their system also involved II-VI semiconductors with large band gaps, and the lattice mismatch is also very similar (4.7%). They find no deviation from commutativity within their error lim-

it, and no change in band bending upon interface formation. Being restricted to laboratory photon sources (He I), they base the band bending evaluation on the Zn 3d level, which at least for ZnTe has still valence band character.¹² One might argue that the center of gravity of the peak will not change during interface formation, since the bulk band states will not be strongly affected. However, it would be difficult to extract from this peak the kind of chemical information that we have seen to be related to interface reactions in several systems^{10,11} including the present one, and a separation into band bending and chemically induced is obviously particularly difficult in a peak where a clear spin-orbit splitting cannot be identified. Asonen *et al.* have used very thin (6 Å) quantum wells, and the final ZnSe overlayer was of similar thickness. From the evolution of the experimental value for the band offset, such as shown in Fig. 4 (as well as similar data for other junctions^{10,11}), we can infer that the major part of the band offset is accessible even at these low thicknesses, although at such low photon energies the sensitivity for the underlying bulk emission is greater. In view of the small valence band offset (0.16 eV) the error introduced by the use of very thin quantum wells is probably less important. It must also be noted that in such a system with a common anion, chemical reactions are probably less important than in our present case.

Other tests of commutativity have been performed using the concept of transitivity in junctions involving a group of three semiconductors A, B, and C, i.e.,

$$\Delta E_v^{(A-B)} = \Delta E_v^{(B-C)} + \Delta E_v^{(C-A)}. \quad (2)$$

Obviously, transitivity is a concept intrinsic to all linear theories and is interrelated with commutativity. Tran Minh Duc *et al.*²⁹ have studied these relations in the three semiconductors CdTe, HgTe, and ZnTe. In establishing ΔE_v for all three interfaces between these compounds, they found that Eq. (2) was fulfilled, despite the strain introduced in these lattice mismatched junctions. In the light of our present results, it is interesting to note that Tran Minh Duc *et al.* found a small deviation from commutativity for ZnTe–CdTe(111), i.e., a surface orientation on which, because of its polar nature, reaction-dependent changes in the dipole layer are more likely than on the nonpolar (110) surface. This small deviation (50 meV) is at the limit of the experimental uncertainties. Again, the system studied by these workers is of the common anion type.

Other tests of linearity have involved interfaces between Si and Ge and a large group of III–V and II–VI semiconductors.⁵ For these room-temperature grown junctions, Katnani and Margaritondo found an *average* deviation of 0.09 eV per system. Tests of linearity were carried for a few specific systems, among them for the technologically important AlAs–GaAs(110). Kowalczyk *et al.*⁶ found a difference of 0.23 eV in ΔE_v when the growth sequence of this junction was reversed. The magnitude of this effect, which is far above the uncertainty of the experiment, suggests a massive difference in interface structure for the two junctions. Note that Niles *et al.*,³⁰ by introducing ultrathin (2 Å) Al layers into a ZnSe–Ge heterojunction, were able to change ΔE_v by 0.2 to 0.3 eV. For AlAs–GaAs(100), Katnani and Bauer

later performed another commutativity test of these junctions, but using the (100) surface;⁷ they found a negligible difference in the band offsets. Taken at face value, these data suggest that there are large influences of surface orientation and/or orientation-induced or growth condition-related chemical changes that cause the observed differences. Experiments for other systems also point to large deviations from linearity. Waldrop *et al.*,³¹ studying pairs of interfaces containing GaAs, ZnSe, and CuBr, found deviations from transitivity of 0.70 eV, i.e., an average deviation of 0.23 eV, certainly beyond any experimental uncertainty. Thus, while the deviation from linearity has been established for a few systems, not enough data are available for an assessment of the causes in a particular system; this is clearly desirable, in particular for such important junctions as GaAs–AlAs. The influence of ultrathin interlayers such as reported by Perfetti *et al.*²⁸ and Niles *et al.*³⁰ assert that dipole effects caused by such preparations can in fact cause fairly large changes in ΔE_v .

In summary, we have characterized the ZnTe–CdS heterojunction by valence and core level photoemission, using an *in situ* grown quantum well. The valence band offset is of type II (staggered) rarely encountered in experimental studies. We find differences in the chemical reactions at the interface. The band offset at both sides of the CdS quantum well exhibit small differences, which are also reflected in the dipole contribution at the interfaces. These results, while reporting only small deviations from commutativity, suggest that the dipole contribution of varying magnitude caused by such reactions influence the magnitude of the band offset in semiconductor heterojunctions.

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