Measurement of the CdSe/ZnTe valence band offset by x-ray photoelectron spectroscopy

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We have used x-ray photoelectron spectroscopy (XPS) to measure the valence band offset *in situ* for CdSe/ZnTe (100) heterojunctions grown by molecular-beam epitaxy. XPS measurements were performed for films of CdSe (100) and ZnTe (100), and for heterojunctions consisting of either ~25 Å of CdSe grown on ZnTe or ~25 Å of ZnTe grown on CdSe. Observations of reflection high energy electron diffraction patterns indicated that CdSe films deposited on ZnTe were grown in cubic zinc blende form, rather than the natural wurtzite structure of CdSe. Our measurements yielded a CdSe/ZnTe valence band offset $\Delta E_v = 0.64 \pm 0.07$ eV. The corresponding conduction band offset for CdSe/ZnTe is $\Delta E_c = 1.22 \pm 0.07$ eV for room temperature band gaps for ZnTe and for cubic CdSe of 2.25 and 1.67 eV, respectively.

I. INTRODUCTION

The inability to dope ZnTe *n* type has frustrated attempts to fabricate ZnTe-based green light emitters using simple ZnTe *p–n* homojunctions. Heterojunction structures have been proposed as a particularly promising alternative for injecting electrons into *p*-type ZnTe and achieving visible electroluminescence;[1-3] the CdSe/ZnTe material system has been considered as a possible candidate for the fabrication of green light emitters based on heterojunction injection of electrons into *p*-type ZnTe. CdSe is an attractive candidate for this application because it can be doped *n* type and, although its equilibrium crystal structure is wurtzite, it can be grown in the cubic zinc blende structure on ZnTe with a lattice mismatch of only ~0.44%. However, the feasibility of this approach depends critically on the conduction band offset in the CdSe/ZnTe heterojunction system.

In addition, the band offset in the CdSe/ZnTe heterojunction is of interest for the information its value might provide about band offsets for other heterojunction systems involving Se and Te compounds, such as ZnSe/ZnTe. The "common anion rule" of McCaldin, McGill, and Mead[4] states that, for a wide range of semiconductor compounds (materials containing Al being the most notable exception), the valence band offset between two materials will depend only on the anion contained in each compound. The physical motivation for this rule arises from well-established theoretical evidence that, in compound semiconductors, the valence band states are derived primarily from *p*-like atomic orbitals of the anion. One might therefore expect that the position of the semiconductor valence band edge on an absolute energy scale, and consequently the band offset value between two semiconductors, would be determined primarily by the energies of the outermost (valence) electrons of the anion. The value of the CdSe/ZnTe valence band offset might provide insight into the general validity of the common anion rule, and possibly a basis for determining band offset values in other heterojunction systems containing Se and Te.

II. SAMPLE GROWTH

The samples prepared for this study were grown by molecular-beam epitaxy (MBE) in two Perkin–Elmer 430P MBE systems. An MBE chamber dedicated to the growth of III–V semiconductors was used to grow GaSb buffer layers on GaSb (100) substrates, providing a smooth starting surface for growth of the ZnTe and CdSe layers. All samples were grown on *p*-type GaSb (100) substrates, with $p \approx 1 \times 10^{17}$ cm^{-3}. Following oxide desorption at 530 °C, a GaSb buffer layer was grown at 100 Å/min with the substrate at 475 °C. Once the GaSb buffer layers were grown, the samples were transferred under ultrahigh vacuum (UHV) conditions to an MBE chamber devoted to the growth of II–VI materials. ZnTe layers were grown at rates of 50–75 Å/min, and with the substrate at 270 °C; a growth rate of ~60 Å/min and a substrate temperature of 270 °C were used for growth of the CdSe layers.

The Te $4d_{5/2}$ core level to valence band edge binding energy was measured in two 275 Å films of ZnTe; details of these measurements have been reported elsewhere.[5] To measure the Se $3d_{5/2}$ core level to valence band edge binding energy in CdSe, two samples were grown, each consisting of ~400 Å of CdSe grown on ZnTe. Reflection high-energy electron diffraction patterns monitored during growth of the CdSe layers showed very little deviation from the initial (2×1) ZnTe surface pattern, indicating that the CdSe film was growing in cubic zincblende form rather than its natural wurtzite structure. X-ray diffraction measurements reported for cubic zinc blende CdSe epilayers grown on GaAs (100) substrates have yielded[6] a cubic lattice constant $a_{CdSe} = 6.077$ Å; the lattice mismatch between cubic CdSe and ZnTe ($a_{ZnTe} = 6.104$ Å) should therefore be only ~0.44%.

The Se $3d_{5/2}$ to Te $4d_{5/2}$ core level energy separation was measured in two heterojunctions consisting of ~25 Å of CdSe grown on ZnTe, and in two heterojunctions consisting of ~25 Å of ZnTe grown on CdSe. Immediately following

all growths, the samples were transported under UHV conditions to the x-ray photoelectron spectroscopy (XPS) chamber for analysis. The ability to perform both sample growth and XPS characterization without exposing samples to atmosphere allowed us to eliminate experimental uncertainties associated with surface passivation and subsequent evaporation of protective capping layers. This aspect of the experiment was of considerable importance, in light of evidence that interdiffusion of atoms and the resulting formation of intermediate compounds or a solid solution can occur at the CdSe/ZnTe interface.[7-11]

III. XPS MEASUREMENTS AND DATA ANALYSIS

Figure 1 shows a schematic energy band diagram for the CdSe/ZnTe heterojunction. Strain-induced effects on the electronic band structure of the two materials have been neglected, due to the small lattice mismatch (0.44%) between cubic CdSe and ZnTe. As shown in the figure, the valence band offset is given by

$$\Delta E_v = (E^{\rm ZnTe}_{{\rm Te}4d_{5/2}} - E^{\rm ZnTe}_v) + (E^{\rm CdSe}_{{\rm Se}3d_{5/2}} - E^{\rm ZnTe}_{{\rm Te}4d_{5/2}}) - (E^{\rm CdSe}_{{\rm Se}3d_{5/2}} - E^{\rm CdSe}_v). \quad (1)$$

XPS measurements were obtained using a Perkin–Elmer Model 5100 analysis system with a monochromatic Al $K\alpha$ x-ray source ($h\nu = 1486.6$ eV). The measured linewidth for Au $4f$ core level peaks was ~ 0.75 eV, and the pressure in the analysis chamber was typically $\sim 5\times10^{-10}$ Torr. The analysis chamber is connected to the MBE growth chambers via UHV transfer tubes, allowing samples to be grown and characterized without being exposed to atmosphere.

Representative XPS spectra for bulk CdSe, bulk ZnTe, and a CdSe/ZnTe heterojunction are shown in Figs. 2(a), 2(b), and 2(c), respectively. The valence band spectrum for the bulk ZnTe sample is also shown on an enlarged intensity scale, as indicated in the figure. As seen in Fig. 2, the Cd $4d$ and Zn $3d$ atomic core levels overlap in energy, making the determination of the Cd $4d$ to Zn $3d$ core level energy separation in the CdSe/ZnTe heterojunction relatively difficult. We have therefore chosen, as indicated by Eq. (1), to use the Se $3d_{5/2}$ and Te $4d_{5/2}$ atomic core levels as reference energy levels in CdSe and ZnTe, respectively.

Core level peak positions were obtained by subtracting from each core level peak a background function proportional to the integrated photoelectron intensity, and fitting the resulting core level spectra to characteristic peak shape functions consisting of two identically shaped Voigt functions separated by a fixed spin-orbit splitting, whose relative heights scaled as $(2J+1)$. For the Cd $4d$ and Zn $3d$ core levels, the peak position was taken to be the average of the positions of the spin-orbit-split components, weighted by the degeneracy $(2J+1)$. The relatively large spin-orbit splittings of the Se $3d$ and Te $4d$ atomic core levels ($\Delta_0^{\rm Se3d} = 0.86$ eV and $\Delta_0^{\rm Te4d} = 1.46$ eV) allowed us to resolve clearly the spin-orbit-split components of each core level peak; the Se $3d_{5/2}$ and Te $4d_{5/2}$ core level peak components were therefore used as reference levels for the band offset measurement. The uncertainty in measured core level energy separations was estimated to be ± 0.02 eV, and measurements of core level energy separations were typically reproducible to approximately ± 0.01 eV.

The position of the valence band edge in each bulk XPS

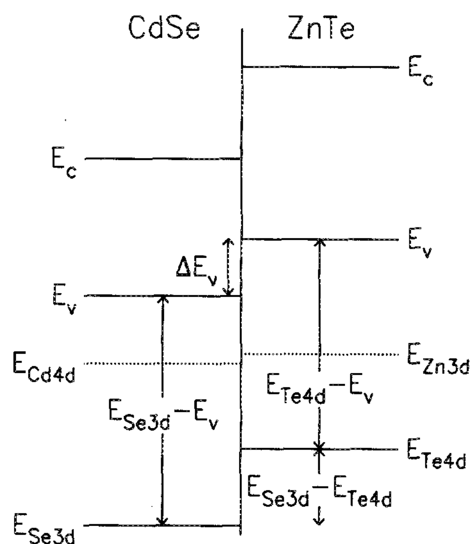

FIG. 1. Schematic energy band diagram for the CdSe/ZnTe heterojunction. Because the Cd $4d$ and Zn $3d$ core level peaks overlap in energy, the Se $3d$ and Te $4d$ core levels in CdSe and ZnTe, respectively, have been used to measure the valence band offset.

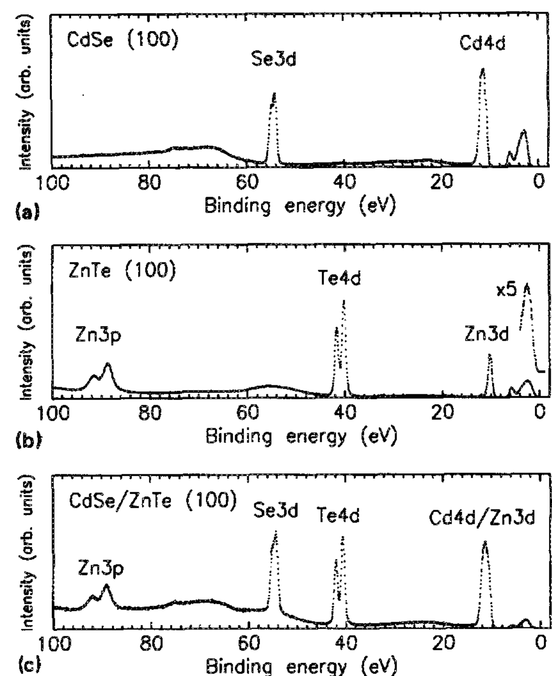

FIG. 2. Representative binding energy XPS spectra for (a) bulk cubic CdSe (100), (b) bulk ZnTe (100), and (c) a CdSe/ZnTe (100) heterojunction. The Se $3d_{5/2}$ core level to valence band edge binding energy is measured in the bulk cubic CdSe samples, the Te $4d_{5/2}$ core level to valence band edge binding energy in the bulk ZnTe samples, and the Se $3d_{5/2}$ to Te $4d_{5/2}$ core level energy separation in the CdSe/ZnTe heterojunctions. Longer sampling times have been used in the vicinity of the valence band edge for the spectra in (a) and (b). The valence band spectrum for the bulk ZnTe sample is also shown on an enlarged intensity scale, as indicated in the figure.

spectrum was determined using the precision analysis technique of Kraut *et al.*[12] In this approach, the XPS spectrum near the valence band edge is modeled as a convolution of a theoretical valence band density of states with an experimentally determined XPS instrumental resolution function. This model function is then fitted to the experimental data to give the position of the valence band edge. The XPS instrumental resolution function was determined from measured XPS spectra for Au 4*f* core level peaks, for which the inherent linewidth due to lifetime broadening is known.[13] The theoretical valence band density of states was calculated using the empirical pseudopotential method;[14] spin-orbit interactions[15] and a nonlocal effective mass parameter[16] were included in these calculations. The empirical pseudopotential parameters were obtained by optimizing the calculated band structure to give the best agreement at the Γ, *X*, and *L* points in the Brillouin zone with previously calculated band structures and measured critical point energies for CdSe (Ref. 17) and ZnTe.[14,18-20] Figures 3(a) and 3(b) show the valence band spectra, model functions fitted to the XPS data, and calculated valence band densities of states for cubic CdSe (100) and ZnTe (100), respectively. The valence band edge in these figures, as determined by the fitting procedure described above, is taken to be at 0 eV.

IV. RESULTS AND DISCUSSION

Measurements obtained from the two bulk cubic CdSe samples yielded a Se $3d_{5/2}$ core level to valence band edge binding energy of 52.51 ± 0.05 eV. The separation between the Se $3d_{5/2}$ and Cd 4*d* was determined to be 42.78 ± 0.03 eV, yielding a Cd 4*d* to core level to valence band edge binding energy of 9.73 ± 0.05 eV. To our knowledge, these are the first measurements of atomic core level binding energies in cubic CdSe.

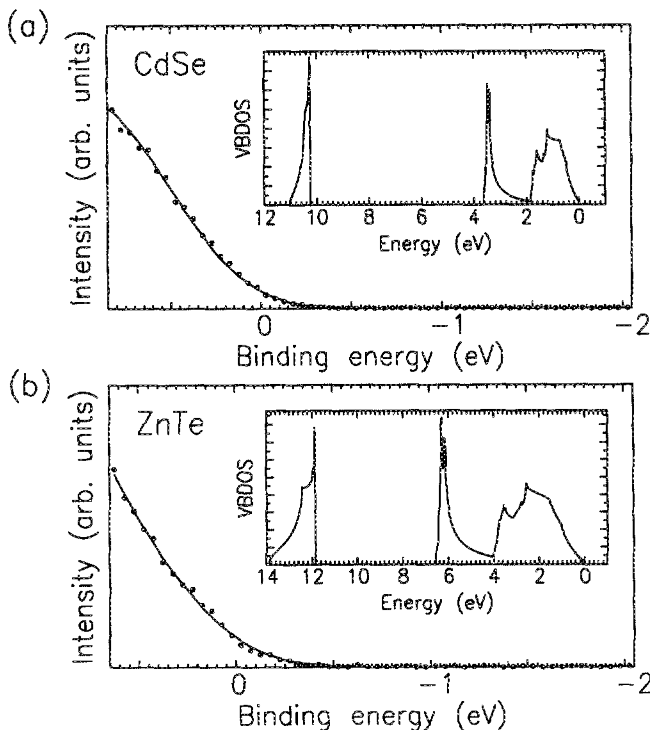

FIG. 3. Typical XPS valence band spectra and model functions fitted to the experimental data for (a) cubic CdSe (100) and (b) ZnTe (100). The theoretical valence band densities of states used to construct the model functions are shown in the insets to each figure. These model functions are used to determine the position of the valence band edge in each spectrum.

Measurements on bulk ZnTe samples yielded values of 9.42 ± 0.04 eV and 30.02 ± 0.02 eV for the Zn 3*d* core level to valence band edge binding energy and the Te $4d_{5/2}$ to Zn 3*d* core level energy separation, respectively. These values correspond to a Te $4d_{5/2}$ core level to valence band edge binding energy in ZnTe of 39.44 ± 0.04 eV. Comparison of these results with previous measurements is difficult; reported values[21-23] for the Zn 3*d* core level to valence band edge binding energy range from 9.1 to 9.84 eV.

The Se $3d_{5/2}$ to Te $4d_{5/2}$ core level energy separation was measured in two heterojunctions consisting of ~25 Å of CdSe grown on ZnTe, and in one heterojunction consisting of ~25 Å of ZnTe grown on CdSe. For these three heterojunctions, the core level energy separation was measured to be $(E^{\rm CdSe}_{{\rm Se}3d_{5/2}} - E^{\rm ZnTe}_{{\rm Te}4d_{5/2}}) = 13.71 \pm 0.02$ eV, yielding a valence band offset $\Delta E_v = 0.64 \pm 0.07$ eV. A measurement of the Se $3d_{5/2}$ to Te $4d_{5/2}$ core level energy separation was also made in one additional heterojunction consisting of ~25 Å of ZnTe grown on ~120 Å of CdSe that was deposited on a thicker CdSe film that had been used for bulk CdSe XPS measurements. This heterojunction yielded a core level energy separation $(E^{\rm CdSe}_{{\rm Se}3d_{5/2}} - E^{\rm ZnTe}_{{\rm Te}4d_{5/2}}) = 13.85 \pm 0.02$ eV, suggesting that adverse growth conditions might influence band offset values in the CdSe/ZnTe material system. Earlier observations of interdiffusion and the formation of solid solutions at the CdSe/ZnTe interface[7-11] lend support to the possibility that specific growth conditions might influence the detailed structure of the interface, and thereby induce shifts in band offset values.

A wide range of theoretical predictions have been reported for the CdSe/ZnTe valence band offset,[4,24-32] from the value of Harrison and Tersoff,[30] $\Delta E_v = 0.31$ eV, to Kraut's calculation,[27] using Harrison's theory[26] with Hartree–Fock rather than Herman–Skillman atomic term values, of 1.11 eV for the CdSe/ZnTe valence band offset. In the latter case, Kraut's observation that poorer agreement with experiment is obtained by using Hartree–Fock rather than Herman–Skillman values is supported by our measurement. Figure 4 shows the range of values proposed for the CdSe/ZnTe valence band offset, and also includes the valence band offset value we obtained from our measurements. The large discrepancies among the theoretical values in Fig. 4 make apparent the need for reliable experimental measurements of band offsets for CdSe/ZnTe and other novel heterojunction systems.

Using room-temperature band gaps for ZnTe and for cubic CdSe[6] of 2.25 and 1.67 eV, respectively, we obtain a conduction band offset ΔE_c(CdSe/ZnTe) = 1.22 ± 0.07 eV, corresponding to a type II, staggered band alignment. The size of the conduction band offset indicates that injection of electrons directly from *n*-CdSe into *p*-ZnTe is probably not practical. However, electron injection from, for example, *n*-$(\rm CdSe)_{1-x}(\rm ZnTe)_x$ into *p*-ZnTe remains a possibility, depending on the dopability of *n*-$(\rm CdSe)_{1-x}(\rm ZnTe)_x$ alloys. Figure 5 shows the valence and

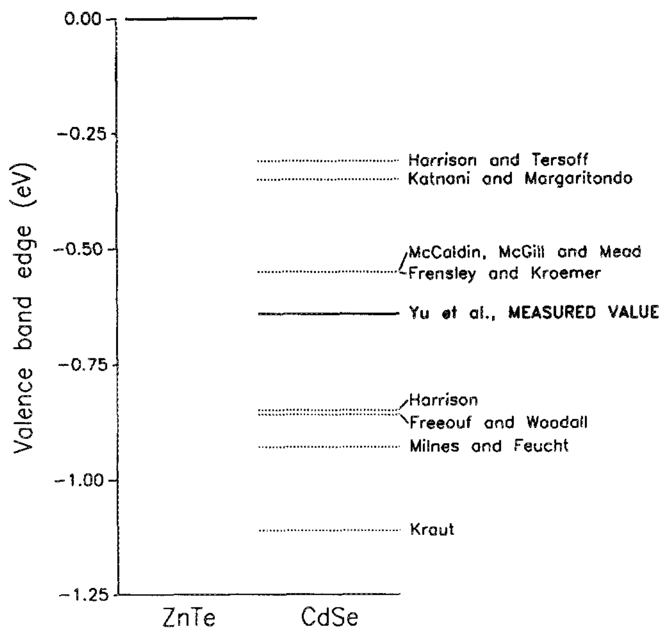

FIG. 4. Valence band offset values for the CdSe/ZnTe heterojunction predicted by several theories,[4,24-32] and the valence band offset value obtained from our measurements, $\Delta E_v = 0.64 \pm 0.07$ eV.

conduction band alignments for the CdSe/ZnTe heterojunction obtained from our measurements.

Our measurement of the CdSe/ZnTe valence band offset also allows us to examine the validity of the common anion rule for heterojunctions containing Se and Te compounds. The value we have measured for the CdSe/ZnTe valence band offset differs significantly from the valence band offset value obtained for the ZnSe/ZnTe heterojunction by Rajakarunanayake *et al.*[33] by analyzing the optical experiments of Kobayashi *et al.*[34] and interpreting their data using theoretical calculations of superlattice band structure. The analysis of Rajakarunanayake *et al.* yields a ZnSe/ZnTe valence band offset of 0.98 ± 0.10 eV, compared to our value of 0.64 ± 0.07 eV for the CdSe/ZnTe valence band offset. Based on the common anion rule,[4] one would expect the valence band offsets for the ZnSe/ZnTe and the CdSe/ZnTe heterojunctions to be quite close. Our results and those of Rajakarunanayake *et al.* therefore appear to demonstrate a substantial deviation from the common anion rule. A potential source of complications, however, is the presence of strain in the ZnSe/ZnTe heterojunction, which is lattice mismatched by over 7%. The band offset value obtained by Rajakarunanayake *et al.* is the discontinuity in the average position of the light-hole, heavy-hole, and split-off valence bands in each material, a quantity that is expected to depend only weakly on strain.[35,36] Nevertheless, it is possible that a dependence of the average valence band offset on strain might significantly augment an actual deviation from the common anion rule to produce the discrepancy we have observed between the CdSe/ZnTe and ZnSe/ZnTe valence band offsets.

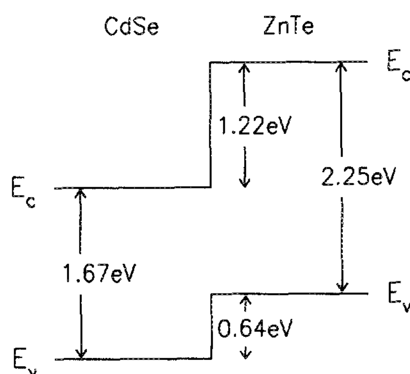

FIG. 5. Conduction and valence band alignments determined by our measurements for the CdSe/ZnTe heterojunction. We obtained $\Delta E_v = 0.64 \pm 0.07$ eV, corresponding to $\Delta E_c = 1.22 \pm 0.07$ eV, yielding a type II, staggered band alignment. As seen in the figure, the conduction band offset is too high to allow efficient injection of electrons directly from *n*-CdSe into *p*-ZnTe.

V. CONCLUSIONS

We have presented a measurement of the CdSe/ZnTe (100) heterojunction valence band offset by x-ray photoelectron spectroscopy. The CdSe/ZnTe material system is of potential interest for heterojunction injection of electrons into *p*-ZnTe to achieve visible electroluminescence in ZnTe. In addition, the CdSe/ZnTe valence band offset could provide insight into the validity of the common anion rule for valence band offsets, and possibly information about band offsets in other material systems containing Se and Te, such as ZnSe/ZnTe.

We have been able to grow cubic zinc blende CdSe on ZnTe with a lattice mismatch of only ~0.44%, and have performed the first measurements, to the best of our knowledge, of atomic core level binding energies in cubic CdSe. Our measurements of the Se $3d_{5/2}$ and Te $4d_{5/2}$ core level to valence band edge binding energies in CdSe and ZnTe, respectively, and of the Se $3d_{5/2}$ to Te $4d_{5/2}$ core level energy separation in CdSe/ZnTe heterojunctions, have yielded a valence band offset $\Delta E_v(\text{CdSe/ZnTe}) = 0.64 \pm 0.07$ eV, corresponding to a conduction band offset $\Delta E_c(\text{CdSe/ZnTe}) = 1.22 \pm 0.07$ eV. The size of the CdSe/ZnTe conduction band offset obviates the possibility of achieving practical electron injection directly from *n*-CdSe into *p*-ZnTe; other schemes, however, such as electron injection from *n*-$(\text{CdSe})_{1-x}(\text{ZnTe})_x$ into *p*-ZnTe remain possible, depending on the dopability of *n*-$(\text{CdSe})_{1-x}(\text{ZnTe})_x$ alloys. We have also observed evidence that details of growth conditions might affect band offset values for the CdSe/ZnTe interface; this possibility is supported by earlier observations of atomic interdiffusion and the formation of solid solutions and intermediate compounds in CdSe/ZnTe heterojunctions. Finally, a comparison of our result for the CdSe/ZnTe valence band offset with a determination of the ZnSe/ZnTe average valence band offset appears to yield a substantial deviation from the common anion rule. However, complications due to strain in the ZnSe/ZnTe heterojunction system may be partially responsible for this discrepancy.

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