High-pressure study of the deformation potentials of $Cd_{1-x}Zn_xTe/ZnTe$ quantum wells via photoluminescence

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Low-temperature photoluminescence spectra from $Cd_{0.395}Zn_{0.605}Te/ZnTe$ multiple quantum-well heterostructures were measured in vacuum and under high hydrostatic pressures. Theoretical calculations were performed using model-solid theory and results were compared to experiment. High-pressure measurements yielded excellent agreement with relative deformation potentials calculated by Christensen and Christensen [Phys. Rev. B **33**, 4739 (1986)] using self-consistent relativistic linear-muffin-tin-orbital theory and the valence-band offsets calculated by Van de Walle [Phys. Rev. B **39**, 1871 (1989)].

I. INTRODUCTION

Recently, new semiconductor heterostructures have attracted considerable interest. Multiple quantum-well structures and superlattices of II-VI compounds are the subject of intensive study because of their interesting optical properties. With these structures, energy gaps ranging from the UV to IR are accessible.[1,2] They also offer an exceptional degree of freedom in tailoring device characteristics to specific requirements through the fact that these semiconductor heterostructures are usually lattice mismatched. The lattice mismatch results in accommodated elastic strain in individual layers, which modifies the band alignments, and hence modifies the device's optical properties.[3–5]

It is clear that the knowledge of band alignments (i.e., discontinuity of valence and conduction bands at interfaces) is essential in designing heterostructures with desired optical features. Theoretical calculations based upon local-density-functional theory and *ab initio* pseudopotentials have become possible only recently. Such calculations have been performed by different groups for both lattice matched[6,7] and strained-layer interfaces.[7–9]

The high computational complexity of these calculations, however, makes them impractical in everyday applications. As an example, strained-layer interfaces offer an infinite number of strain configurations; carrying out first-principle self-consistent calculations for every configuration is an unfeasible task. For practical purposes a simpler but reliable model is needed.

One possible answer is the so-called model-solid theory, described in detail by Van de Walle.[3] The theory supplies two kinds of parameters of interest. First, band-edge energies are calculated for different semiconductors with respect to a fixed reference point. Second, the strain dependence of these energies is determined. These calculations are still based on first principles and are rather complex, but once armed with unstrained band-edge values and their strain dependence it is straightforward to predict band alignments in semiconductor heterostructures of any kind.

We used parameters published by Van de Walle,[3] Van de Walle and Martin,[8] Mathieu *et al.*,[5] and Christensen and Christensen[9] to perform these straightforward calculations for specific heterostructures ($Cd_{1-x}Zn_xTe/ZnTe$ multiple quantum wells) and compared our results to photoluminescence (PL) measurements. Experiments were also performed as a function of high pressure, which enabled us to directly (and independently) evaluate the relative strain dependence of energy-band positions.

II. EXPERIMENTS

Our sample was grown by molecular-beam epitaxy on a semi-insulating (001) GaAs substrate. The structure consists of a 3-μm-thick ZnTe buffer layer, five thin $Cd_{1-x}Zn_xTe$ quantum wells ($x=0.605$) separated by 300-Å-thick ZnTe barrier layers and finally a 300-Å-thick ZnTe cap layer. The nominal thicknesses of the quantum layers are 50, 40, 30, 20, and 10 Å, the 50-Å quantum well being closest to the buffer layer.

The thicknesses of individual layers were selected such that the buffer and barrier ZnTe layers are much thicker, whereas the $Cd_{1-x}Zn_xTe$ layers are thinner, than the critical thickness.[10] We were concerned that some of the thickest quantum wells might have relaxed, but photoluminescence experiments indicated that relaxation had not occurred (as discussed below).

Samples were investigated by the standard photoluminescence technique. The sample was illuminated by intense monochromatic light from an argon ion laser (different wavelengths are used, mostly 4765 and 4579 Å; incident intensities varied from 1 to 100 mW).

Emitted light was focused into a double monochromator and photons were detected by a photomultiplier-photon counting electronics system.

In zero-pressure measurements, the sample was directly mounted on the cold finger of a closed-cycle helium cryostat. PL experiments were conducted at 15–20 K,

measured by a thermocouple attached to the cold finger.

In high-pressure experiments near-hydrostatic conditions were created up to ≈4 GPa (1 GPa = 9869 atmospheres of pressure) using a miniature Merrill-Bassett diamond anvil cell.[11,12] The samples (about $100\times100\times30$ μm^3) were contained in a 200–300-μm hole drilled onto a hardened steel gasket and the pressure-transmitting medium was argon. For pressure calibration within the cell, the positions of the R_1 and R_2 photoluminescence peaks from small pieces of ruby crystal placed next to the sample was measured.[13] The ruby spectrum was also used for determining the temperature inside the cell by measuring the ratio of the intensities of the R_1 and R_2 peaks.[14] The temperature was between 20 and 25 K for all high-pressure experiments.

III. EXPERIMENTAL RESULTS

Figure 1 shows a typical PL spectra of our sample at 1.93 GPa. Individual peaks are identified on the figure and the experimental uncertainty in the peak position is estimated to be ±10 meV. At the low-energy part of the spectrum, the wide feature is composed of five peaks. Decomposition was made by a numerical fitting program. The five peaks are shown (when compared to theoretical calculations) to belong to heavy-hole–electron annihilations from the five different quantum wells.

On the high-energy part of the spectrum are the light-hole–electron recombination peaks. The peak from the 40-Å quantum well is very weak. It can only be identified visually with a large uncertainty in position (≥ 30 meV). The light-hole peak from the 50-Å quantum well should be even weaker and it is predicted to be at approximately the same position as the heavy-hole peak from the 10-Å well; it is, therefore, not visible. Because of these difficulties, no analysis is reported for the light hole in the 40- and 50-Å quantum wells.

Figure 2 shows the energy of identified PL peaks measured as a function of pressure. Experimental results are well represented by straight lines. The slopes of best fits to these results are given on the figure in meV/GPa and in Table III.

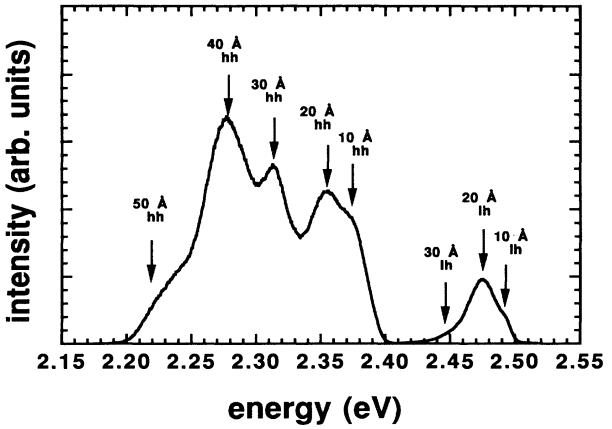

FIG. 1. Typical photoluminescence spectrum at 1.93 GPa and 20 K.

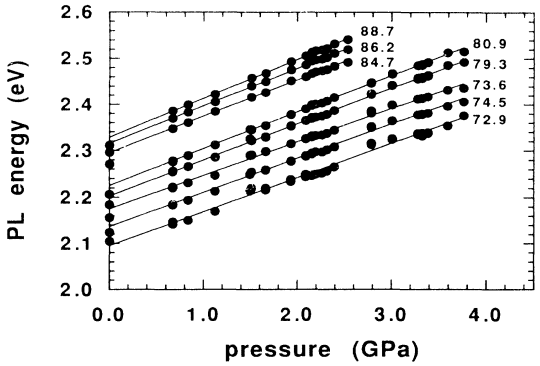

FIG. 2. Pressure dependence of the measured photoluminescence peaks. The slopes of best fits are given on the figure in meV/GPa. The uncertainty in the PL energies is estimated to be ±10 meV (the size of the symbols).

IV. ANALYSIS

The effect of strain on the energy levels inside the quantum wells is calculated in the manner of Van de Walle.[3] Since the well material is a ternary alloy ($Cd_{1-x}Zn_xTe$), the band gap E_{gap} and average valence energy $E_{v,av}$ are determined from Cardona and Christensen[15] and Nimtz.[16] This analysis shows that heavy- and light-hole band alignments are both type I in our sample (Table I, Fig. 3). Since the barriers of our samples are much thicker than the wells, we assume that all of the strain is accommodated in the wells.

When calculating PL energies we had to take into account that the energies of the electrons and holes are modified by their confinement. Calculations of ground-state confinement energies are performed numerically. The effective-mass jump at the barriers has been taken into account by using the envelope-function method of

TABLE I. Deformation potentials, energy-band shifts, and energy-band positions in the studied multiple quantum-well structure (in eV's). Parameters used are from Van de Walle (Ref. 3) and Duc, Hsu, and Faurie (Ref. 27). $x=0.605$.

	ZnTe	CdTe	$Cd_{1-x}Zn_xTe$
E_{gap}	2.394	1.606	2.0206
$E_{v,av}$	0.03	0.21	0.1114
Δ	0.91	0.93	0.9179
a_v	0.79	0.55	0.6952
a_c	−5.83	−3.96	−5.0914
b_u	−1.26	−1.10	−1.1968
δE_u			−0.0636
E_c	2.7273		2.5314
E_{hh}	0.3333		0.4682
E_{lh}	0.3333		0.3504
E_c offs.			0.1959
E_{hh} offs.			0.1349
E_{lh} offs.			0.0170

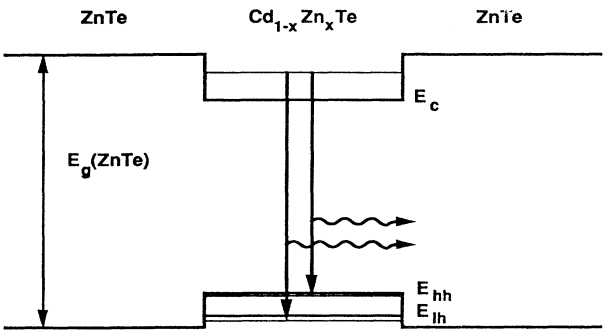

FIG. 3. Band alignment in $Cd_{1-x}Zn_xTe$/ZnTe quantum-well structures with the assumption that all of the strain is accommodated in the thin $Cd_{1-x}Zn_xTe$ layers.

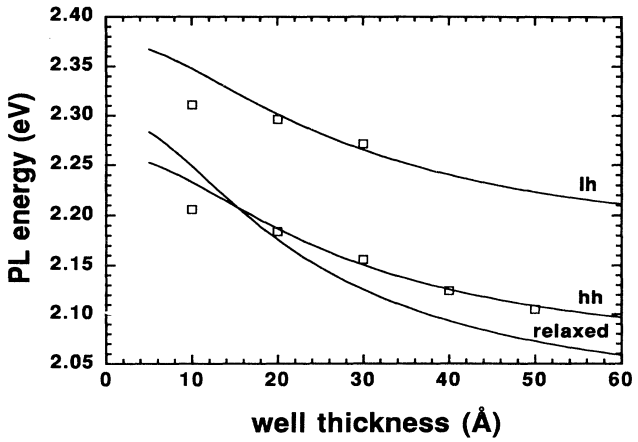

FIG. 4. Photoluminescence energy vs well thickness. Solid lines are calculations for heavy-hole and light-hole recombination in strained or relaxed layers. Open squares are experimental results.

Bastard.[17] The confinement energy of holes are neglected, because heavy and light holes are much more massive than electrons, and the valence-band wells are relatively shallow compared to the conduction-band well.

As for the exciton binding energy, it is 12 and 13 meV in bulk CdTe and ZnTe, respectively.[18] For confined excitonic systems, however, this value can be considerably higher. In case of ideal two-dimensional confinement, the ground-state binding energy is four times the three-dimensional (bulk) value. In real heterostructures the confinement is not perfect, but binding energies as much as three times the bulk value have been observed.[4,20]

Much work has been done on confined excitonic systems,[19–23] but because of both theoretical and experimental difficulties the exact dependence of exciton binding energy on quantum-well parameters is not known. Experimental results suggest that the exciton binding energy peaks at a well width of about 10–20 Å.[20,24,25] For narrower quantum wells, penetration into the barrier becomes important and the three-dimensional binding energy is recovered, as predicted by theory and verified by experiments.[18,20]

We used a standard value of 12 meV for exciton binding energy in our calculations, keeping in mind that for narrow quantum wells this value can be as high as 40 meV.

Different deformation potentials and band parameters have been tested from different authors.[3–5] Parameters from Table II were used in the calculations for which results are shown on Fig. 4. The predicted PL energy is plotted as a function of well width (solid lines), along with experimental data (open squares). In order to show that our quantum layers are not relaxed, the PL energy expected from a relaxed well is also plotted.

TABLE II. Deformation potentials of ZnTe, CdTe, and of the ternary alloy in our sample ($x=0.605$). A combination of parameters calculated by Van de Walle (Ref. 3), Christensen and Christensen (Ref. 9), and Duc, Hsu, and Faurie (Ref. 27) are presented here.

	ZnTe	CdTe	$Cd_{1-x}Zn_xTe$
$E_{v,av}$	0.03	0.21	0.111
Δ	0.91	0.93	0.918
a_v	0.79	0.55	0.695
a_c	−3.56	−2.1	−3.003
a_v-a_c	4.35	2.70	3.698

As shown in Fig. 4, the agreement between theory and experiment for no applied pressure seems to be remarkable. It must be noted, however, that very different parameters published by different authors worked equally well. This is mainly due to the fact that in our sample the electrons are strongly confined into the narrow quantum wells, therefore, the PL energy is not very sensitive to the exact conduction-band position inside the quantum well. The worst agreement between experiment and theory is observed for the 10-Å well. As noted earlier, such narrow wells have been observed to have very large exciton binding energies.

A numerical calculation was performed to determine PL energies as a function of applied hydrostatic pressure, which causes a change in the relative volume as given by the bulk modulus. The exact change in the volume of the sample will depend on whether the elastic properties of the entire quantum-well structure are dominated by the thick ZnTe buffer layer or by the GaAs substrate, which composes ~90% of the sample. Our calculations have been performed for both cases, as reported in Table III. The applied hydrostatic pressure will also change the relative lattice mismatch between the wells and the barriers since the two materials have different elastic moduli. The calculation took into account (1) the shift of energy levels due to uniform volume compression; (2) the change in strain conditions inside the quantum wells due to the fact that the bulk moduli of CdTe and ZnTe are different; (3) the change in confinement energy as the quantum-well width decreases; and (4) the change in the mass of the charge carriers as derived by Lefebvre, Gil, and Mathieu[26] from Kane's $\mathbf{k}\cdot\mathbf{p}$ theory. Effects 1 and 2 were calculated in the manner described by Van de Walle.[3] It was found that the pressure dependence of PL energies is

TABLE III. Calculated and experimental $\partial E_{PL}/\partial P$ slopes in meV/GPa. Parameters are taken from the indicated sources. Values listed first are for dominating ZnTe buffer layer. Results with dominating GaAs substrate are listed second.

Thickness	Van de Walle[a]	Mathieu *et al.*[b]	Christensen and Christensen[c]	Experimental
10-Å hh	126.7/120.7	98.7/95.3	82.6/81.0	80.9
20-Å hh	123.2/118.2	95.9/93.2	79.8/78.9	79.3
30-Å hh	121.2/116.7	94.5/92.1	78.2/77.7	73.6
40-Å hh	120.2/115.9	93.8/91.5	77.4/76.9	74.5
50-Å hh	119.6/115.4	93.4/91.2	76.9/76.6	72.9
10-Å lh	125.3/108.0	97.3/83.4	81.2/68.3	88.7
20-Å lh	121.8/105.5	94.5/81.3	78.3/66.2	86.2
30-Å lh	119.8/104.0	93.1/80.2	76.7/65.0	84.7
40-Å lh	118.8/103.2	92.4/79.6	75.9/64.3	
50-Å lh	118.2/102.7	92.1/79.3	75.5/63.9	

[a]See Ref. 3.
[b]See Ref. 5.
[c]See Ref. 9.

essentially linear, therefore, we calculated the slopes of the best-fit straight lines to our theoretical predictions.

Different deformation potentials and band parameters published by different authors were tested. Some of the results (slopes of best fits) are listed in Table III. Two different values are listed for all references, the first was obtained by assuming that the overall elastic properties of the system are determined by the ZnTe buffer layer, the second is based on the assumption that the GaAs substrate dominates the system's elastic behavior.

V. DISCUSSIONS

Previous studies of II-VI semiconductor multiple quantum well and superlattice heterostructures have dealt with type-I heavy-hole and type-II light-hole band alignments.[1,4,5] Therefore, direct observation of the E_{hh}-E_{lh} splitting was not possible. In our samples heavy and light holes are both type I, which enables us to observe heavy- and light-hole decays simultaneously; the separation between heavy- and light-hole peaks can be used to determine the value of the uniaxial deformation potential b_u directly. In fact, if we neglect the coupling of the spin-orbit splitting and the uniaxial strain splitting (the error introduced by this approximation is less than 3 meV), the expression for heavy- and light-hole energies reduces to

$$E_{hh}=E_{v,av}+\tfrac{1}{3}\Delta+a_v\mathrm{Tr}(\hat{\varepsilon})-\delta E_u \ ,$$

$$E_{lh}=E_{v,av}+\tfrac{1}{3}\Delta+a_v\mathrm{Tr}(\hat{\varepsilon})+\delta E_u \ ,$$

where $E_{v,av}$ is the average zero-strain valence-band energy, Δ is the energy of the spin-orbit splitting, a_v is the absolute deformation potential of the valence band, and δE_u is the splitting between the heavy- and light-hole bands due to uniaxial strain. In this approximation, the separation between peak pairs is uniquely determined by the strain splitting:

$$\Delta E=2\delta E_u=2b_u(x)(\varepsilon_\perp-\varepsilon_\parallel) \ .$$

For our sample, the average separation is $\Delta E=114\pm6$ meV in vacuum, the uniaxial component of the strain is $\varepsilon_\perp-\varepsilon_\parallel=0.0531$, which yields a uniaxial deformation potential of $b_u(x)=-1.07\pm0.06$ eV (following the general sign convention). This is close to the value of -1.11 eV that can be calculated from the uniaxial deformation potentials used by Mathieu *et al.*,[5] but smaller than -1.197 eV, predicted by Van de Walle.[3]

As far as calculations of the energy-band alignments are concerned for the samples in vacuum, the agreement between theory and experiment seems remarkable. It is worth noting, however, that significantly different hydrostatic deformation potentials yield almost equally consistent results. In fact, Van de Walle estimates the inaccuracy of his deformation potentials to be on the order of ±1 eV, which is quite large compared to his deformation potential values themselves, which are on the order of a few eV's (0.055–5.83 eV).

The real probes of the hydrostatic deformation potentials are the high-pressure experiments. A significant difference was found between our experimental values and these ones calculated by using Van de Walle's theoretical or Mathieu's semiempirical parameters (Table III). However, our result seems to be in remarkable agreement with calculations performed using Christensen and Christensen's[9] relative deformation potentials (assuming dominant ZnTe buffer layer).

Therefore, we suggest the deformation potentials listed in Table II. We have kept the absolute deformation potentials for valence bands by Van de Walle, since his valence-band-edge calculations are believed to be reliable and agree well with experiments.[3,4] We added, however, Christensen and Christensen's[9] relative deformation potential to these values in order to obtain absolute deformation potentials for conduction bands.

VI. SUMMARY

Low-temperature PL was measured from $Cd_{0.395}Zn_{0.605}Te/ZnTe$ multiple quantum-well hetero-

structures as a function of pressure. The energy of the observed PL peaks were found to be in excellent agreement with the valence-band offsets calculated by Van de Walle[3] and relative deformation potentials calculated by Christensen and Christensen.[9]

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