Band offset determination of $Zn_{0.53}Cd_{0.47}Se/Zn_{0.29}Cd_{0.24}Mg_{0.47}Se$

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The interband transitions of a single quantum well structure of $Zn_{0.53}Cd_{0.47}Se/Zn_{0.27}Cd_{0.23}Mg_{0.50}Se$ (lattice matched to InP) were evaluated using contactless electroreflectance at room temperature. From a comparison of the measured optical transitions with those calculated using the envelope function approximation we determined that the conduction band offset for this system is given by the parameter $Q_c = \Delta E_c / \Delta E_0 = 0.82 \pm 0.02$, which yields ΔE_c of 590 meV. Such a large conduction band offset may be useful for the design of quantum cascade lasers and other devices based on intersubband transitions. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1606875]

The growing interest in quantum cascade lasers[1] (QCLs) and other intersubband (IS) devices emphasizes the need to research relevant fundamental parameters of heterostructures such as band offsets (BOs). Considerable advances have been achieved in the development of the QCLs, however, there are still many limitations of these lasers. A critical one is the unavailability of QCLs operating in continuous wave (cw) mode at room temperature (RT). Another is the absence of QCLs operating at short wavelengths, such as 1.55 μm, needed to develop ultrafast optical communications. Both limitations are related to the relative small conduction band offset (CBO) present in the most frequently used systems based on GaAs and InP, which imposes the shortest wavelength limits of 8 (Ref. 2) and 3 μm,[3] respectively, for QCLs made from these materials. In order to overcome these limitations studies of IS transitions have been recently extended to other systems based on GaN,[4,5] GaSb,[6,7] Si,[8] and II–VI compounds.[9–12] Among the most relevant parameters for the IS devices are the BOs. A material that has been recently investigated for the growth of visible light emitters is the ZnCdMgSe alloy grown on InP substrates.[13] The subset of compositions of this alloy system that are lattice matched to InP possess a range of band gaps between 2.1 and 3.3 eV, thus a large CBO is expected. In this work, we determined the CBO for a $Zn_{0.53}Cd_{0.47}Se/Zn_{0.27}Cd_{0.23}Mg_{0.50}Se$ single quantum well (QW) structure at RT using contactless electroreflectance (CER). Our results suggest that this system is of potential interest for QCLs and other IS devices.

The details of the molecular beam epitaxy (MBE) system used and the growth of these materials are described in Ref. 14. The specific structure used in this work was grown on a semi-insulating InP(100) substrate and consisted of a lattice matched InGaAs buffer layer ($\sim 0.1 \mu$m), a ZnCdSe interfacial layer ($\sim$70Å) and the II-VI QW structure. This structure consisted of ZnCdMgSe ($E_0 = 2.8$eV at RT) barriers and a QW of $Zn_{0.53}Cd_{0.47}Se$. The nominal thickness of the QW, bottom and top barriers are 50Å, 0.5 and 0.1μm, respectively. Finally, the structure was capped by a 70-Å-thick pseudomorphic ZnCdSe cap layer to protect ZnCdMgSe from oxidation by atmospheric oxygen. The growth rates of the quaternary and ternary layers was 0.9 and 0.4 μm per hour, respectively. The beam equivalent pressure ratio VI/II was about 3. These steps have been previously used to achieve a low defect density and high crystalline quality in these materials.[14] These nominal thicknesses were calculated using thick-calibration samples grown during the same run.

The ZnCdMgSe barrier and the QW layers were nearly lattice matched to InP, with $\Delta a/a = 0.05\%$, and $\Delta a/a = 0.1\%$, respectively. The QW layer mismatch was determined on a thick ZnCdSe sample grown during the same run. The QW structure was characterized by photoluminescence (PL) measurements using the 325 nm line of a HeCd laser for excitation. The QW PL peaks were observed at 2.242 and 2.162 eV at 77 and 300 K, respectively, while the PL peak for the barrier was at 2.880 eV at 77 K. At RT the barrier signal was quenched and we were not able to observe its PL signal.

The interband transitions in this structure were determined using CER, which is a modulated technique[15,16] that measures the changes in the optical reflectance of the material with respect to a modulating electric field. The experimental details and principles of CER are described in Ref. 17.

The solid line in Fig. 1 is the measured RT CER spectrum. The energies corresponding to the transitions observed were obtained using a fit, shown by the dashed line, based on the first derivative of a Gaussian line shape.[15,18] The values obtained from this fit are indicated by arrows in Fig. 1 and presented in Table I. The notation $EnH(L)m$ in Fig. 1 indicates that the transitions are from the nth conduction subband to the mth valence subband of heavy (H) or light (L) hole character, respectively.

Assignment of the transitions was done according to the following considerations. The identification of the signal from the barrier at 2.8 eV was straightforward when we considered the 77 K PL signal at 2.88 eV and its thermal energy shift. The intensities of the transitions at 2.159 and 2.192 eV

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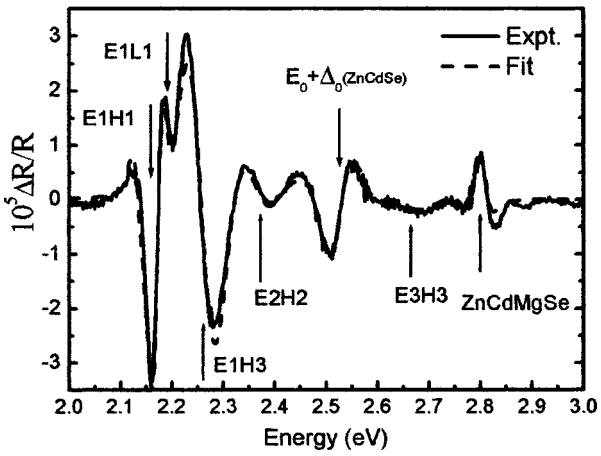

FIG. 1. Solid line represents the experimental $\Delta R/R$ spectra. Dashed line is a fit yielding the energies indicated by the arrows.

exhibit a ratio close to 3, suggesting that they are associated with the heavy and light hole transitions, respectively.[15,18] The band gap of the $Zn_{0.53}Cd_{0.47}Se$ was determined by CER measurements on a thick sample grown during the same run. The value that we found was $E_0=2.080\pm0.005$ eV, in good agreement with Ref. 19, which reported $E_0=2.078\pm0.002$ and spin-orbit splitting $\Delta_0=0.442\pm0.02$ eV. Using our value for the band gap and this value for Δ_0 we obtain $E_0+\Delta_0=2.522$ eV, which agrees well with the experimental value of Table I.

In order to calculate the energies corresponding to the observed transitions we have performed a calculation based on the envelope approximation.[20,21] In these calculations it is necessary to know the values of the effective masses as well as Δ_0. However, there are no reports for the effective masses of these compounds. In order to approximate the required masses we followed two steps: first, for ZnSe, we took the average value between the maximum and minimum reported values, shown in parentheses in Table II, while for MgSe and CdSe the data were taken from Refs. 22 and 23, respectively. We did not find any report for the value of the effective mass of the light hole of CdSe, so observing that the electron and heavy hole masses for CdSe are approximately two thirds of those corresponding to ZnSe we assumed that this proportion is valid for the light hole masses, too. Second, using these values for the binaries and a weighted composition average, we obtained the corresponding values for our compounds, also shown in Table II.

TABLE I. Experimental and calculated interband energies.

Transition	Experiment (eV)	Theory (eV)
E1H1	2.159 ± 0.005	2.158
E1L1	2.192 ± 0.005	2.180[a]
		2.185[b]
E1H3	2.259 ± 0.005	2.261
E2H2	2.369 ± 0.005	2.371
E3H3	2.660 ± 0.005	2.664
$E_0+\Delta_0$	2.525 ± 0.005	2.522[c]
E_0 (barrier)	2.800 ± 0.005	

[a]Calculation without considering the compressive strain.
[b]Calculation considering the compressive strain.
[c]Calculated using Δ_0 of Ref. 19 and our value for E_0.

Using the data listed in Table II, we calculated the energies of the different transitions as a function of the parameter $Q_c=\Delta E_c/\Delta E_0$. Figure 2 shows the results of this strain-free calculation in solid lines for the transitions that fit better the experimental values of the transitions, represented by the horizontal dashed lines. These transitions correspond to the symmetry allowed ($n=m$) and symmetry forbidden but parity allowed ($n=m\pm2,4,...$) ones. As indicated in Fig. 2 by the dotted vertical line, the best agreement between the calculated and the experimental values for all the transitions was found for $Q_c=0.82\pm0.02$ ($\Delta E_c=590$ meV). As shown from Figs. 1 and 2, and Table I, there is very good overall agreement. There is only a small discrepancy in the E1L1 transition, which we attribute to the facts that the light hole mass of the CdSe approximation may not be very accurate and that the small strain present in this structure shifts the calculated E1L1 transition. In order to estimate the band-gap changes in ZnCdSe due to the strain present in this structure we followed Ref. 24, which provides the expressions that describe the band-gap changes as a function of the elastic

TABLE II. Values of the parameters used in the calculation.

Parameter	ZnSe	CdSe	MgSe	$Zn_{0.27}Cd_{0.23}Mg_{0.50}Se$	$Zn_{0.53}Cd_{0.47}Se$
E_0 (eV)				2.800[a]	2.080[a]
m_e	0.15[b] (0.13–0.17)	0.11[c]	0.23[d]	0.18	0.13
m_{hh}	0.66[b] (0.57–0.75)	0.44[c]	0.78[d]	0.67	0.56
m_{lh}	0.145	0.09	0.33[d]	0.22	0.11
Δ_0 (eV)	0.43[e]	0.42[e]	0.40[d]	0.414[f]	0.442[a]
QW thickness (Å)			50 (expt.)	51.9 (calculated)	
$Q_c=\Delta E_c/\Delta E_0$			0.82 ± 0.002		

[a]Experimental value.
[b]Average of the values shown in parentheses, these values were obtained from Ref. 23.
[c]Reference 23.
[d]Reference 22.
[e]Reference 30.
[f]Interpolated value using the binary values.

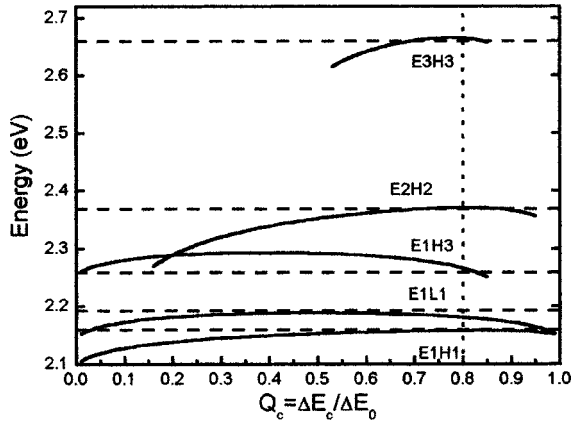

FIG. 2. Energies of the transitions determined by the envelope function approximation vs Q_c $(=\Delta E_c/\Delta E_0)$.

constants C_{11}, C_{12} and deformation potentials a and b. The required constants for this calculation were obtained from Refs. 24–26. These calculations show that the heavy and light hole band gaps are changed by 2 and 5 meV. The change for the heavy hole band gap is smaller than the experimental error and, therefore, can be disregarded. However, the change for the light hole gap is equal to the experimental error and must be added (since the QW is under compressive strain) to the energy of the transition E1L1 previously calculated, obtaining a better agreement with the experimental results.

Our result is in agreement with the common anion rule,[21,27] which states that two semiconductors with a common anion and lattice matched should have most of the band discontinuity in the conduction band.

As stated previously, the unavailability of QCLs operating in cw mode at RT is due to difficulties to minimize the threshold current, which depends inversely on the electron confinement (related to CBO). In addition, the shortest wavelength that a QCL can emit for a given material system is also inversely proportional to the CBO. An important advantage of the QCLs is their intrinsic high speed.[28,29] Thus, a possible application of the ultrafast intersubband devices will be in optical communications at 1.55 μm. This kind of application requires semiconductor systems with a large conduction band discontinuity. One system, currently investigated for this purpose is GaN/GaAlN, where IS optical absorption at 1.35, 1.41, and 1.52 μm has been reported[4,5] in ultrathin (10–15 Å) multiple quantum wells. However, the growth of III-nitride multiplayer structures is especially challenging due to the lack of a lattice-matched substrate, which produces serious concerns about their crystalline quality. Other systems that have shown potential applications for QCLs at 1.55 μm are the wide-band-gap II–VI compounds, such as (CdS/ZnSe)/BeTe and ZnSe/BeTe in which intersubband transitions as short as 1.6 μm have been reported.[9,10] The identification of other near-lattice-matched systems with large conduction band offsets, such as the one presented here, may yield practical alternatives for the design of these complex device structures.

Using CER and the envelope function approximation we have determined that the conduction band offset of $Zn_{0.53}Cd_{0.47}Se/Zn_{0.27}Cd_{0.23}Mg_{0.50}Se$ lattice matched to InP is given by $Q_c=0.82\pm0.02$, yielding a value of ΔE_c of 590 meV. This large band offset suggests that this system may be a good candidate for IS devices.

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