PHYSICAL REVIEW B VOLUME 45, NUMBER 11 15 MARCH 1992-I

Excitonic effects in separate-confinement quantum-well heterostructures CdTe/(Cd,Zn)Te

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(Received 19 November 1991)

Optical experiments, performed at 1.7 K, on three CdTe/(Cd,Zn)Te quantum-well separate-confinement heterostructures, reveal a type-I behavior of the 1*s* light-hole excitonic recombination line, although the band-to-band potential could be type II due to the strains. This behavior is explained in terms of the Coulombic interaction between the localized electrons and the light holes. Comparison between experimental and theoretical results provides a value for the strain-free relative valence-band offset: $q_v^0 \approx 20\%$.

Among various II-VI systems, the growth by molecular-beam epitaxy of CdTe/(Cd,Zn)Te samples is now well controlled. Optical studies have been performed in high-quality quantum-well or superlattice structures.[1,2] The results are consistent with a low valence-band offset discontinuity ΔE_v: it is found that the relative valence-band offset $q_v = \Delta E_v / \Delta E_g$ (ΔE_g is the band-gap discontinuity) lies between -10% and 10%.[2] In order to determine more precisely this ratio, we have performed optical experiments in so-called quantum-well separate-confinement heterostructures (QWSCH), which have already been used to determine accurately the band alignment in GaAs/(Ga,Al)As systems.[3] To interpret the experimental data, we will use a calculation of the exciton binding energy, adapted to this structure, whose valence-band offset is small and possibly negative. This calculation will allow us to show that the Coulomb interaction between an electron confined in the CdTe well and a light hole can provide a type-I behavior, although the strain-induced band alignment could be type II for free light holes, due to the strain effects. This property will allow us to determine the value of the strain-free relative valence-band offset q_v^0.

Our three QWSCH structures consist of a CdTe quantum well (thickness d_w) embedded in $Cd_{1-y}Zn_yTe$ layers (thicknesses d_{int1} and d_{int2}, called intermediate barriers), the latter being clad between $Cd_{1-x}Zn_xTe$ layers (called barriers), a buffer whose thickness is 2 μm and a cap layer whose thickness is typically 800 Å. The nominal values of the Zn concentration (x_{nom} and $y_{nom} = x_{nom}/2$) of the alloys, obtained from x-ray data, and layer thicknesses, which are controlled *in situ* during the growth by reflection high-energy electron diffraction (RHEED), are reported in Table I. Note that two of them (SCH2 and SCH3) have small intermediate barriers whereas SCH1 has thick intermediate barriers. These structures are grown by molecular-beam epitaxy on a (001)-oriented $Cd_{0.96}Zn_{0.04}Te$ substrate.[4]

Photoluminescence and excitation spectroscopy at low temperature (1.7 K) have been performed for each sample and Fig. 1 shows the obtained spectra for SCH1. The (X) line, present in the three photoluminescence (PL) spectra, is clearly identified by excitation spectroscopy as the 1*s* heavy-hole recombination. The excitation spectra exhibit several excitonic transitions, whose light- or heavy-hole nature is determined by a spin-orientation experiment,[5] which is reported for SCH1 on Fig. 1 (dashed-dotted line). The positive (negative) polarization peaks are the signature of the heavy- (light-) hole nature of the transition. The first light-hole peak in the excitation spectra of the three samples is identified without ambiguity as the 1*s* light-hole recombination E_1L_1. We assign the EL and EH intense peaks to the light- and heavy-hole excitonic recombinations in the $Cd_{1-x}Zn_xTe$ barrier layer. The nature of these two transitions has been confirmed by piezomodulated reflectivity experiments.[6] The assignment of the other peaks is consistent with the calculation of the excitonic transition energies, as explained at the end of this paper.

The energy of the heavy-hole excitonic EH transition,

TABLE I. Characteristics of the three samples, as explained in the text.

Sample	SCH1	SCH2	SCH3
d_{int1} (Å)	195	36	36
d_w (Å)	36	36	36
d_{int2} (Å)	195	52	36
x_{nom} (%)	16	16	12
x_{opt} (%)	13.77	16.19	11.37
ε_{bar}	1.16×10^{-3}	1.04×10^{-3}	5.18×10^{-4}
a (Å)	6.4365	6.4266	6.4414

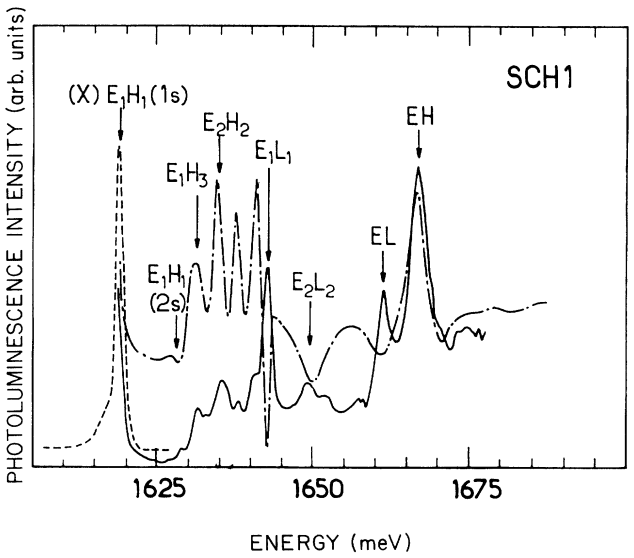

FIG. 1. Photoluminescence spectra (dashed line), photoluminescence excitation spectra (solid line) of the (*X*) line, and optical pumping spectra (dashed-dotted line) of the sample SCH1. The arrows indicate the experimental positions of the different optical transitions, the peaks are labeled following the calculation of the excitonic transitions, as explained in the text.

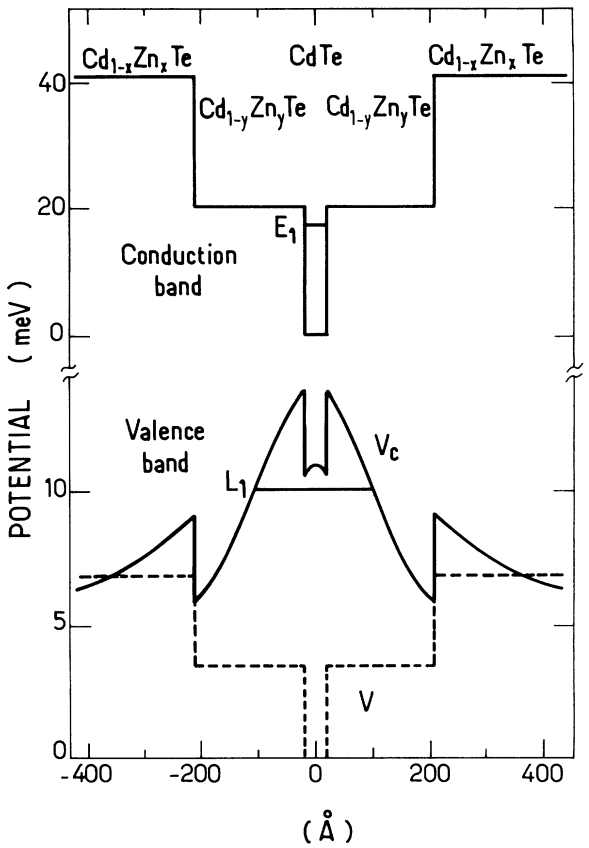

FIG. 2. Potential profile along the growth axis seen by the electrons and by the light holes (for SCH1) in the case of an assumed relative valence-band offset $q_v^0=25\%$, with strains but without Coulombic interaction, $V(z)$ (dashed line); with strains and Coulombic interaction, $V_c(z)$ (solid line).

which is known not to be very sensitive to the strain in this system,[1] allows the precise determination of the Zn concentration in the barrier layer: x_{opt} (Table I, and $y_{opt}=x_{opt}/2$), knowing the band-gap energy, $E_g=1606+525x$ meV, and the exciton binding energy in the bulk material, $E_x^{bulk}=11$ meV.[7] The EH-EL splitting is due to the residual tension of the $Cd_{1-x}Zn_xTe$ layer on the $Cd_{0.96}Zn_{0.04}Te$ substrate: EH-EL $=4.8226\varepsilon_{bar}$ meV where ε_{bar} is the residual strain in the barrier, $\varepsilon_{bar}=[a-a^0(x)]/a$, a is the mean parameter in the strained $Cd_{1-x}Zn_xTe$ layer and $a^0(x)$ is the strain-free parameter of $Cd_{1-x}Zn_xTe$: $a^0(x)=6.481-0.3773x$ Å.[7] The expression of EH-EL has been obtained from calculation of the influence of the strains on the band structure, detailed in Ref. 1, using the elastic constants $S_{11}=3.581$ MPa^{-1}, $S_{12}=-1.394$ MPa^{-1}, the deformation potentials $a_\varepsilon=a_c-a_v=-3.27$ eV and $b_v=1.06$ eV, and the distribution of the deformation potential a_ε between the valence and conduction bands: $a_v/a_c=-0.38$.[8] The experimental value of EH-EL allows the determination of ε_{bar} and of the mean lattice parameter in the $Cd_{1-x}Zn_xTe$ layers: a, whose values are reported in Table I for each sample. Assuming an elastic accommodation of the $Cd_{1-y}Zn_yTe$ and CdTe lattice parameters with the barrier one, the effect of the strains on the band structure of the materials can be deduced.[1,2] We find that the structure exhibits a type-I band alignment for the heavy holes for $q_v^0>-20\%$, whereas for the light holes, the band alignment is type II for $q_v^0<34\%$ and type I for $q_v^0>34\%$ (the calculated value of q_v^0 for which the type-I band alignment becomes type II is almost the same for the three samples).

To interpret the experimental data, the knowledge of the Coulombic interaction (i.e., the excitonic effect) is necessary because of the small and possibly negative valence-band offset. We have calculated it in terms of a variational method[9] where the hole wave function $\chi_H(z)$ is numerically calculated in a potential profile $V_c(z)$. The latter is the sum of the QWSCH band-edge profile $V(z)$, including the strain effect and of the Coulomb interaction averaged over the electron probability density $\chi_E^2(z)$ along the growth axis and over the $1s$ wave function. The reduced exciton motion in the layer plane is taken as $(2/\pi a_B^2)^{1/2}\exp(-\rho/a_B)$, where ρ is the in-plane electron-hole distance and a_B is the variational parameter. The potential profile $V_c(z)$ for the light holes is reported in Fig. 2 for $q_v^0=25\%$ as well as $V(z)$ without Coulomb interaction (but with strain effect) for SCH1. The effect of the Coulomb interaction here is to transform the nature of a type-II band alignment (due to the strain), for which the light-hole wave function is localized in the $Cd_{1-x}Zn_xTe$ layers, to a type-I one, for which the light-hole wave function is localized in the separate confinement quantum well.

We have calculated the variation of the quantity $f=|\langle\chi_E(z)|\chi_H(z)\rangle|^2/(a_B^2/\lambda^2)$, where $\lambda=\kappa a_0/m_c$ (a_0 is the hydrogenic Bohr radius) vs q_v^0. The quantity f_{lh} gives a relative estimate of the oscillator strengths of the E_1L_1

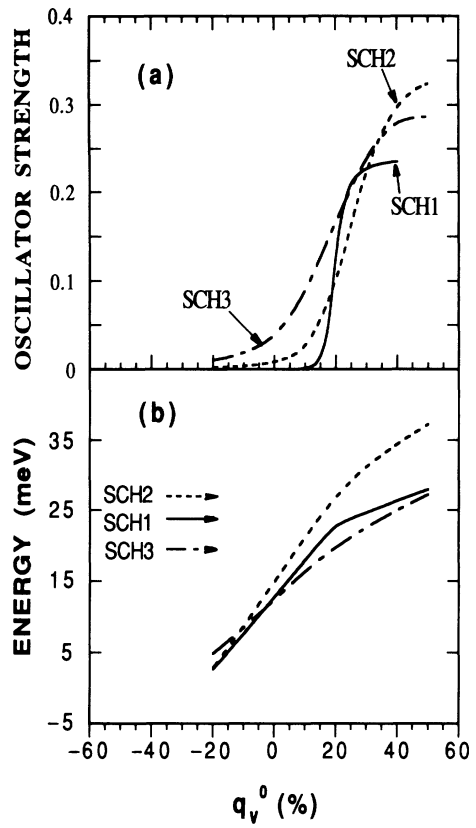

FIG. 3. (a) Oscillator strengths f_{lh} of the E_1L_1 excitonic recombinations vs q_v^0, for the three samples. (b) Calculated energy difference E_1L_1-E_1H_1 vs q_v^0 for the three samples. The arrows indicate the experimental values of E_1L_1-E_1H_1.

excitonic transitions, reported for the three samples in Fig. 3(a). The exciton binding energies of the E_1L_1 transitions: $E_x(E_1L_1)$, which present a behavior versus q_v^0 which is similar to the behavior of f_{lh} versus q_v^0 and the variation of f_{hh} and $E_x(E_1H_1)$, which are not particular, are not reported here. The parameters used in this calculation are $m_e=0.096m_0$, $m_{hh}=0.6m_0$, $m_{lh}=0.11m_0$ (m_0 is the mass of the free electron) for the electron, and heavy- and light-hole masses along the growth axis, respectively, $\gamma_1=5.38$ and $\gamma_2=1.86$ for the Luttinger parameters of the valence band, and $\kappa=10.6$ for the relative dielectric constant.[7] The oscillator strength f_{lh} and the binding energy of the light-hole exciton $E_x(E_1L_1)$ exhibit a strong decrease when q_v^0 decreases, corresponding to the fact that the barrier of the light-hole type-II band alignment increases. For SCH1, the type-II band alignment induced by the strains gives an oscillator strength, whose value is inferior to 10% of the maximum value f_{lh}^{max}, for $q_v^0<18.5\%$. Note that the decrease of f_{lh} is drastic around this value of q_v^0. For $q_v^0<18.5\%$, the thick intermediate barriers maintain the hole wave function localized in the $Cd_{1-x}Zn_xTe$ layers, far away from the electronic wave function, localized for a great part in the CdTe layer; thus, the overlap between these two wave functions is small. Due to the small intermediate barriers in SCH2 and SCH3, allowing a stronger overlap of the hole and electronic wave functions for a smaller q_v^0, we find that f_{lh} is smaller than $f_{lh}^{max}/10$ when $q_v^0<-4\%$ for SCH3 and when $q_v^0<12\%$ for SCH2. It has to be pointed out that these numerical results depend on the strain parameters used in the calculation. The deformation potential has been precisely measured,[8,10] but the distribution of the hydrostatic component between the conduction and valence bands is not well known,[8,11] for example, for SCH1, by changing a_v/a_c ($a_v/a_c=-0.5$, we find that $f_{lh}<f_{lh}^{max}/10$ when $q_v^0<21.5\%$. Moreover, by using the following parameters, $S_{11}=4.144\times10^5$ MPa^{-1}, $S_{12}=-1.703\times10^5$ MPa^{-1},[12] $a_v-a_c=3.85$ eV, $b_v=1.2$ eV,[10] and $a_v/a_c=-0.38$,[8] we find that $f_{lh}<f_{lh}^{max}$ when $q_v^0<24\%$.

Experimentally, the excitation spectrum of the sample SCH1, which has thick intermediate barriers, exhibits a light-hole peak E_1L_1, which intensity is large and comparable to that of E_1H_1. The experimental type-I behavior of the E_1L_1 excitonic recombination line, compared to the theoretical behavior of the oscillator strength with q_v^0 (drastic decrease around $q_v^0=18.5\%$), allows us to assert that $q_v^0>18.5\%$. To deduce a more precise value of q_v^0, the calculation of the transition energies is necessary. Figure 3(b) exhibits the variation of the calculated energy difference between the two excitonic transitions E_1L_1 and E_1H_1:E_1L_1-E_1H_1, vs q_v^0. A comparison between the experimental and theoretical values for the three samples leads to $q_v^0=20\pm3\%$. The comparison is performed on the relative quantity E_1L_1-E_1H_1 and not on the absolute values of E_1L_1 and E_1H_1 in order to weaken the importance of the uncertainties on the layer thicknesses (one or two monolayers).

The energy positions of the other experimental peaks in the excitation spectrum of SCH1 are consistent with our exciton binding energy calculation, exactly for the E_1H_1-$2s$ and E_1H_3 peaks, within an uncertainty of a few meV for the E_2H_2 and E_2L_2 peaks. This uncertainty is due to the fact that our theoretical model is not good for the calculation of the E_2H_2 and E_2L_2 exciton binding energies, because it is not possible to assume that the electronic wave function is unaffected by the Coulomb interaction. The description of these transitions could be performed in the frame of the quantification of the center of mass.[13] We are currently developing a theoretical model in order to calculate these exciton binding energies and thus to improve our determination of q_v^0 (E_2L_2 in SCH1 is sensitive to q_v^0).

In conclusion, we have observed the type-I behavior of the $1s$ E_1L_1 excitonic line in CdTe/(Cd,Zn)Te separate confinement quantum wells with large and small thickness of the intermediate barriers. We have shown that this type-I behavior could be due to the Coulombic interaction between the light holes and the localized electrons and that it can be present even if the band-to-band potential profile induced by the strain is type-II-like. The experimental results obtained on three samples by optical investigations have allowed the determination of q_v^0, $q_v^0=20\%$ with an uncertainty of $\pm3\%$, with the parameters mentioned in the text. A more sophisticated exciton calculation will allow the explanation of all the peaks observed in the excitation spectra and will ascertain our q_v^0 value.

We would like to thank G. Bastard for discussions on the theoretical aspects of this work and M. Voos for his constant interest in this work. The Laboratoire de Physique de la Matière Condensée de l'Ecole Normale Supérieure is Laboratoire associé au Centre National de la Recherche Scientifique et à l'Université Paris VI.

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