RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 42, NUMBER 17 15 DECEMBER 1990-I

# Optical studies of the piezoelectric effect in (111)-oriented CdTe/$Cd_{1-x}Zn_xTe$ strained quantum wells

R. André, C. Deshayes, J. Cibert, Le Si Dang, and S. Tatarenko
*Laboratoire de Spectrométrie Physique, Université J. Fourier, Boîte Postale No. 87,*
*38402 Saint Martin d'Hères, France*

K. Saminadayar
*Département de Recherche Fondamentale, Service de Physique, Physique des Semiconducteurs,*
*Centre d'Etudes Nucléaires, Boîte Postale 85X, 38041 Grenoble CEDEX, France*

(Received 10 September 1990)

We report on the optical properties of (111)-oriented CdTe/$Cd_{1-x}Zn_xTe$ single quantum wells grown by molecular-beam epitaxy on (001) GaAs substrates. Several quantum wells with different widths were coherently grown on a single, thick $Cd_{1-x}Zn_xTe$ buffer layer, which induces the same in-plane strains $\approx 1\%$ in all quantum wells. A strong redshift of the exciton transition is observed. It increases linearly with the well width at a rate of 2.5 meV/Å, so that exciton transitions occur at energies below the gap of bulk CdTe for wider wells. This linear redshift can only be explained by the existence of a dominant piezoelectric field across the strained quantum wells.

Recently it was pointed out that strained heterostructures made from zinc-blende-type semiconductors grown along the [111] axis and the [001] axis should exhibit different behaviors due to the piezoelectric effect.[1] This effect, which vanishes for (001)-strained heterostructures, can generate in II-VI or III-V materials internal electric fields reaching $10^5\ \mathrm{V\,cm^{-1}}$ for strains of about 1%, and thus modifies the electronic structure and optical properties of (111)-strained heterostructures. Moreover large optical nonlinearities are predicted to occur through the modulation of these internal electric fields by photogenerated free carriers, and important shifts of the band edge should be induced by external applied stress or electrical bias, which are of considerable interest for applications.[1] The experimental evidence of piezoelectric fields[2] has been reported for a (111)-oriented $Ga_{1-x}In_xAs$/GaAs strained-layer superlattice (SLS), which exhibited a redshift of the intrinsic transitions when compared to an equivalent (001)-oriented SLS grown simultaneously. Shortly afterwards a direct demonstration of the piezoelectric field was obtained by growing a (111)-oriented $Ga_{1-x}In_xAs$/GaAs quantum well (QW) in the intrinsic region of a pin diode.[3] Then a blueshift was observed for the QW band edge in photoconductivity measurements under appropriate electrical bias. This shows that there exists an electric field across the strained QW without any external bias. Evidence of piezoelectric fields has been reported also for II-VI semiconductors: optical studies of type-II CdS/CdSe SLS's with the Wurtzite structure[4] showed a strong dependence of emission energies and linewidths on the SLS periods, which was satisfactorily interpreted assuming piezoelectric fields as large as $10^6\ \mathrm{V\,cm^{-1}}$.

In this Rapid Communication we report on the optical properties of (111)-oriented CdTe/$Cd_{1-x}Zn_xTe$ strained QW's. The CdTe/ZnTe heterostructure is characterized by a large lattice mismatch $\approx 6\%$ and a small valence-band offset (less than 10% of the gap difference),[5-7] which makes this system particularly sensitive to the piezoelectric effect. To reduce the number of fitting parameters, the same strain state is imposed to the QW's by coherently growing several QW's with different widths on the same $Cd_{1-x}Zn_xTe$ buffer layer. The QW exciton transitions are clearly identified in photoreflectance measurements. They present a strong redshift which increases linearly with the well width at a rate of 2.5 meV/Å: exciton transitions are actually observed below the gap of bulk CdTe for widths larger than about 40 Å. This linear shift can only be explained by the existence of a piezoelectric field across the strained QW's, whose effects dominate over the carrier confinement effects.

Samples were grown by molecular-beam epitaxy on semi-insulating GaAs(001) substrates with a small miscut (usually 4° towards [110]) to avoid the formation of twins in the (111) layers.[8] The (111) growth was initiated by a thin $\approx 1000$ Å layer of CdTe followed by a 2-$\mu$m-thick $Cd_{1-x}Zn_xTe$ buffer layer, with $x \approx 0.16$. Since the buffer thickness greatly exceeds the critical thickness, it is virtually strain free, with only residual strains $\approx 5\times10^{-4}$ induced by the difference in thermal expansion between the substrate and the layer.[9] When a misoriented substrate is used, no oscillations are observed in reflection high-energy electron diffraction as expected if growth proceeds through step propagation. This precludes a direct measurement of the growth rates, and hence of the QW widths, so that one has to rely on calibrations on thick layers. To minimize the problem of estimating the growth rate, several QW's with different widths were grown on the same buffer layer, the successive QW's being separated by 500-Å-thick barriers with the same alloy composition as the buffer: then the relative widths of these QW's are accurately known from the different growth times, with the growth rate being the same for all QW's. Another important advantage of this type of structure is to impose the same strain state in all QW's providing the growth is coherent. Although the critical thickness for

(111) CdTe/$Cd_{1-x}Zn_xTe$ has not been completely determined yet, an estimate can be obtained by a comparative study of the photoluminescence (PL) intensity. Indeed a drop of the PL intensity by 2 orders-of-magnitude was observed for relaxed (001) CdTe/$Cd_{1-x}Zn_xTe$ QW's.[10] The same evolution was observed here for (111) QW's, and the critical thickness estimated to be about 30 monolayers (1 ML $\approx$ 3.74 Å along [111] in unstrained CdTe) for (111) CdTe/$Cd_{0.84}Zn_{0.16}Te$. Therefore as long as the QW width is kept lower than 30 ML, the lattice spacing within the growth plane is constant throughout the structure, and equal to the lattice parameter of the relaxed buffer layer. Thus strains in the QW are determined by the lattice mismatch $\delta a/a \approx 1\%$ between the $Cd_{1-x}Zn_xTe$ buffer layer and the CdTe well. These strains largely exceed thermal strains which will be neglected in the following.

Optical experiments were performed at 1.8 K. Photoluminescence was excited by either an $Ar^+$ laser or a Styryl-8 dye laser focused typically to 1-10 $W/cm^2$. An iodine lamp was used for photoreflectance, in combination with the $Ar^+$ or dye laser.

Figure 1 shows optical spectra for sample No. 3, which contains four single QW's with nominal thicknesses of 4, 8, 12, and 17 ML. The PL spectrum [Fig. 1(a)] presents four lines attributed to the four QW's. Note that PL of 12- and 17-ML QW's occurs at lower energies than the exciton gap of bulk CdTe. For the two narrowest wells (4 and 8 ML), the PL line shape is quite similar to what is observed on equivalent (001)-oriented QW's: an intense free exciton line with a full width at half intensity of about 2 meV and a broader extrinsic line 4 meV lower in energy. The absence of clear exciton lines for broader QW's is consistent with the existence of an internal electric field which tends to separate electrons from holes. Indeed in photoreflectance exciton transitions are only observed for the three narrowest QW's as shown in Fig. 1(b), suggesting again a reduced oscillator strength for excitons in the broadest QW. Finally, the exciton transition detected at $\approx$ 1680 meV is due to the barrier-buffer layer.

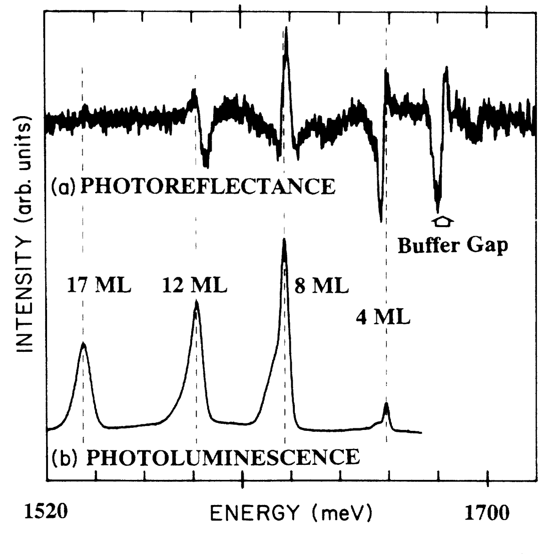

FIG. 1. Optical measurements at $T = 1.8$ K obtained on sample No. 3 which contains four QW's with thicknesses of 4, 8, 12, and 17 monolayers. (a) Photoluminescence excited at 1.746 eV with about 30 $W\,cm^{-2}$; (b) photoreflectance spectrum.

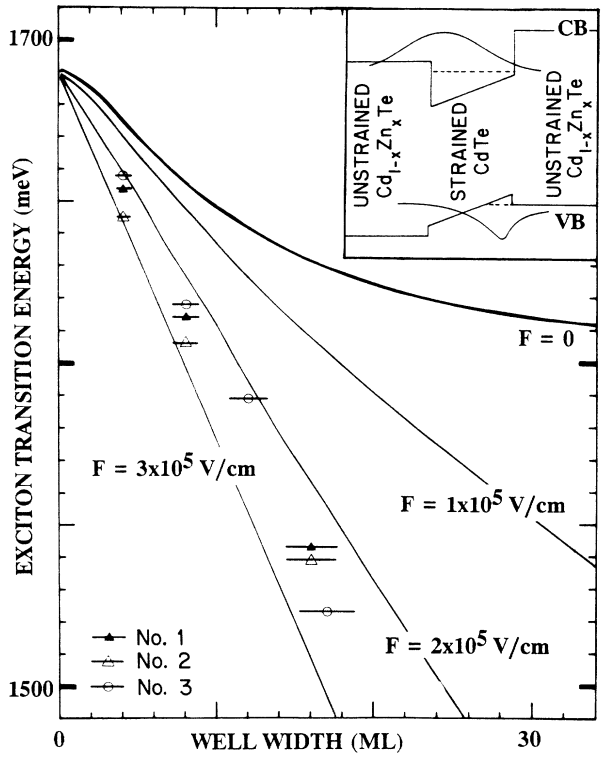

FIG. 2. Dependence of the exciton transition on the QW width (expressed in number of monolayers). Comparison of experiment (open circles and triangles) and calculations with piezoelectric fields $F = 0$, 1, 2, and $3\times10^5$ $V\,cm^{-1}$ (solid lines). Inset shows the model QW used in the calculations.

The dependence of exciton transitions on QW widths is shown in Fig. 2 for three samples with similar $Cd_{1-x}Zn_xTe$ barrier composition ($x \approx 0.16 \pm 0.01$). Horizontal bars represent errors in estimating the well widths. For the broadest QW's ($\approx$ 17 ML), we have plotted positions of extrinsic lines instead of free exciton lines which could not be detected in photoreflectance. The strong redshift with increasing well width is almost linear with a slope of 2.5 meV/Å.

We have used the envelope function approximation[11] to calculate the optical gaps of the QW's. The zero-strain valence-band offset is varied from 0% to 10% of the gap difference, which is the upper limit commonly accepted for CdTe/ZnTe.[5-7] The sign of the zero-strain offset is such that, in the ground state, electrons and holes are in the CdTe and ZnTe layers, respectively. The band structure of CdTe is modified by mismatch strains whose effects can be expressed in terms of the compliance constants $s_{ij}$, and the deformation potentials $a_c$, $a_v$, and $d$. Taking values from Ref. 12, one obtains a well barrier $V_0 = 80 \pm 6$ meV for electrons and $10 \pm 6$ meV for heavy holes (confined in CdTe). Strains also induce an electric field through the piezoelectric effect.[1] This electric field $F$

exists only in the well since the barrier is practically strain free, and the resulting potential is shown in the inset of Fig. 2. To solve the Schrödinger equation, a linear combination of the Airy functions Ai and Bi was used for the wave function inside the well,[13] and decaying exponentials for the wave functions in the barriers. Usual continuity conditions at the two interfaces lead to the following implicit equation for the energy $E$ of bound states:

$$\frac{[(\alpha V_0+x_-)m_2/m_1]^{1/2}\mathrm{Ai}(x_-)-\mathrm{Ai}'(x_-)}{[(\alpha V_0+x_-)m_2/m_1]^{1/2}\mathrm{Bi}(x_-)-\mathrm{Bi}'(x_-)} = \frac{[(\alpha V_0+x_+)m_2/m_1]^{1/2}\mathrm{Ai}(x_+)+\mathrm{Ai}'(x_+)}{[(\alpha V_0+x_+)m_2/m_1]^{1/2}\mathrm{Bi}(x_+)+\mathrm{Bi}'(x_+)}, \tag{1}$$

where $\alpha=(2m_2/\hbar^2q^2F^2)^{1/3}$, $x_\pm=-\alpha(\pm qFL/2+E)$, $m_1$ and $m_2$ are the effective masses in the barrier and in the well, respectively, $V_0$ the well barrier, $L$ the well width, $q$ the electron charge, $F$ the electric field across the well, and Ai′ and Bi′ the Airy derivative functions. We take effective mass values from Neumann, Nöthe, and Lipari.[14] Effective masses in $\mathrm{Cd}_{1-x}\mathrm{Zn}_x\mathrm{Te}$ are linearly scaled from those of CdTe and ZnTe.

Unlike the case of a symmetrical well, bound states may not exist if the piezoelectric field $F$ is too strong. For $F\approx 3\times 10^5$ V cm$^{-1}$ and a valence-band offset equal to zero, there is no bound state for the electron neither for the hole. Decreasing the field to $\approx 2\times 10^5$ V cm$^{-1}$ will introduce a bound state which tends rapidly to that of a triangular well for well widths larger than about 10 ML. The hole bound state (when it exists) is almost in resonance with the barrier band edge so that the hole is mainly localized in the vicinity of the well by the electron Coulomb potential. Since the binding energy of these excitons is not known at present, a value of 10 meV corresponding to bulk CdTe was taken as a first approximation. The solid curves in Fig. 2 represent the calculated exciton transitions for a zero-strain valence band offset equal to zero and for $F=0\text{–}3\times 10^5$ V cm$^{-1}$. Changing the valence-band offset to 10% of the gap difference will only shift the calculated curves by less than 10 meV.

For electric fields larger than about $2\times 10^5$ V cm$^{-1}$, the calculated curves are almost straight lines with slopes equal to the electric fields. This linear dependence of exciton transitions on well widths is the result of a dominant piezoelectric field. This is indeed the case for the data presented in Fig. 2, from which one deduces a piezoelectric field $F=2.5\times 10^5$ V cm$^{-1}$.

For zinc-blende materials grown along the [111] axis, the piezoelectric field is also directed along the [111] axis and given by

$$F=-\frac{2\sqrt{3}e_{14}}{\epsilon_0\epsilon}\frac{\delta a}{a}\frac{s_{44}}{s_{44}+4(s_{11}+2s_{12})}, \tag{2}$$

where $e_{14}$ is the piezoelectric coefficient, $\epsilon$ and $\epsilon_0$ are the low-frequency dielectric constant of CdTe ($\approx 9.8$) and the permittivity of free space, respectively. Taking $e_{14}=0.035$ C/m$^2$,[15,16] $\delta a/a=10^{-2}$, and elastic constant values from Ref. 12, one deduces $F=0.9\times 10^5$ V cm$^{-1}$. The factor of 2.5 between this value and that determined from the fit in Fig. 2 is well beyond our experimental uncertainties. In fact a slightly smaller coefficient was obtained for less strained QW's which were grown on a buffer layer with a smaller Zn content ($x\approx 0.05$). This strongly suggests nonlinear piezoelectric effects and systematic studies of QW's grown on different buffers are in progress to elucidate this point.

One may also question the validity of the flat band configuration we used for the barrier. For narrow wells embedded between thick barriers and highly compensated materials, as is the case here, the potential drop is taken up by charge transfer only over distances long with respect to the well width, and the flat band configuration is a good approximation for the barriers.

In conclusion, we have presented an optical study of (111)-oriented $\mathrm{CdTe/Cd}_{1-x}\mathrm{Zn}_x\mathrm{Te}$ QW's. A strong redshift of the exciton transition is observed, which increases linearly with the well width. This linear dependence is the result of a dominant piezoelectric field $F=2.5\times 10^5$ V cm$^{-1}$ in QW's strained by about $10^{-2}$. Our data also suggest nonlinear piezoelectric effects.

This work has been completed within the CNRS/CEA joint group Microstructures de Semiconducteurs II-VI. We wish to thank Y. Merle d'Aubigné, R. Romestain, and E. Nicholls for fruitful discussions. Laboratoire de Spectrometrie Physique is Laboratoire associé au CNRS (URA 08).

---

[1] D. L. Smith and C. Mailhiot, Rev. Mod. Phys. **62**, 173 (1990).

[2] B. K. Laurich, K. Elcess, C. G. Fonstad, J. G. Beery, C. Mailhiot, and D. L. Smith, Phys. Rev. Lett. **62**, 649 (1989).

[3] E. A. Caridi, T. Y. Chang, K. W. Goossen, and L. F. Eastman, Appl. Phys. Lett. **56**, 659 (1990).

[4] M. P. Halsall, J. E. Nicholls, J. J. Davies, P. J. Wright, and B. Cockayne, Surf. Sci. **228**, 41 (1990).

[5] Y. Merle d'Aubigné, H. Mariette, N. Magnéa, H. Tuffigo, R. T. Cox, G. Lentz, Le Si Dang, J. L. Pautrat, and A. Wasiéla, J. Cryst. Growth **101**, 650 (1990).

[6] H. Mathieu, A. Chatt, J. Allegre, and J. P. Faurie, Phys. Rev. B **41**, 6082 (1990).

[7] T. M. Duc, C. Hsu, and J. P. Faurie, Phys. Rev. Lett. **58**, 1127 (1987).

[8] J. Cibert, Y. Gobil, K. Saminadayar, S. Tatarenko, A. Chami, G. Feuillet, Le Si Dang, and E. Ligeon, Appl. Phys. Lett. **54**, 828 (1989).

[9] Le Si Dang, J. Cibert, Y. Gobil, K. Saminadayar, and S. Tatarenko, Appl. Phys. Lett. **55**, 235 (1989).

[10] J. Cibert, R. André, C. Deshayes, G. Feuillet, P. H. Jouneau, Le Si Dang, R. Mallard, A. Nahmani, K. Saminadayar, and S. Tatarenko, in *Proceedings of the Fifth International Conference on Superlattices and Microstructures, Berlin, 1990* [J. Superlattices Microstruct. (to be published)].

[11] G. Bastard, in *Wavemechannics Applied to Semiconductor Heterostructures* (Les Editions de Physique, Paris, 1988).

[12] J. Allègre, B. Gil, J. Calatayud, and H. Mathieu, J. Cryst. Growth **101**, 603 (1990).

[13] W. W. Lui and M. Fukuma, J. Appl. Phys. **60**, 1555 (1986).

[14] Ch. Neumann, A. Nöthe, and N. O. Lipari, Phys. Rev. B **37**, 922 (1988).

[15] D. Berlincourt, H. Jaffe, and L. R. Shiozawa, Phys. Rev. **129**, 1009 (1963).

[16] P. Maheswaranathan, R. J. Sladek, and U. Debska, Phys. Rev. B **31**, 7910 (1985).