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Luminescence from quantized exciton-polariton states in $Cd_{1-x}Zn_xTe/CdTe/Cd_{1-x}Zn_xTe$ thin-layer heterostructures

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Photoluminescence spectra, very different from those given by bulk CdTe, are obtained at 1.8 K, for two $Cd_{0.92}Zn_{0.08}Te/CdTe/Cd_{0.92}Zn_{0.08}Te$ quantum-well heterostructures. The thicknesses of the CdTe layers are 500 and 1000 Å, respectively, intermediate between a quasi-two-dimensional quantum well and the bulk. Zero-phonon free-exciton luminescence predominates over bound-exciton recombination; phonon replicas of the free-exciton luminescence are not visible. Satellite peaks are observed over a 10-meV range on the high-energy side of the free-exciton peak. These are attributed to quantized states of the exciton-polariton confined inside the CdTe layer. A simple theory is given for the relative emission probabilities associated with the quantized states; their energy positions are fitted with a series of indexed, discrete points on a polariton dispersion curve.

We report here a study of the exciton-related photoluminescence of $Cd_{1-x}Zn_xTe/CdTe/Cd_{1-x}Zn_xTe$ quantum-well heterostructures. This study has a twofold interest. First, very little spectroscopy has been done on quantum wells fabricated with II-VI compounds. Second, our CdTe confined layers are of "intermediate" thickness, being located between the quasi-two-dimensional quantum well, in which quantized energy levels are well separated, and the bulk. This region of thickness has not received much attention even for the much studied III-V compounds. Our results allow a precise analysis of the early effects of the confinement-induced quantization as the sample thickness is reduced.

Our samples consist of one CdTe layer confined between two 800-Å-thick $Cd_{0.92}Zn_{0.08}Te$ layers. They were grown at the Laboratoire d'Infrarouge by molecular-beam epitaxy on {100}-oriented $Cd_{0.96}Zn_{0.04}Te$ substrates. Nominal thicknesses of the CdTe layers are 500 and 1000 Å; the thickness is known to an accuracy of ± 15%. The CdTe layer is uniformly strained because of the 0.23% lattice parameter mismatch with the $Cd_{0.96}Zn_{0.04}Te$ substrate (the structure's thickness is less than the critical thickness at which the strain relaxes).[1,2] The optical gap of the CdTe layer (1.61 eV) is approximately 45 meV smaller than that of the $Cd_{1-x}Zn_xTe$ barriers.

Luminescence was excited above the CdTe layer's optical gap with a krypton laser and observed perpendicular to the layers making up the well. The samples were immersed in pumped helium at 1.8 K. Intense luminescence in the excitonic spectral region is obtained for the confined layers. We discuss three important differences with respect to the luminescence of bulk[3] or thick-layer[4] samples of CdTe.

First, as already noted by Magnea *et al.*,[5] who studied the same samples, *intrinsic* luminescence is dominant for the confined layers. Figure 1 illustrates this point: The luminescence of the $Cd_{1-x}Zn_xTe$ substrate (i.e., a bulk sample) is dominated by the D^0X and A^0X emissions (excitons bound to donors and acceptors, respectively) whereas the CdTe layer's luminescence is dominated by

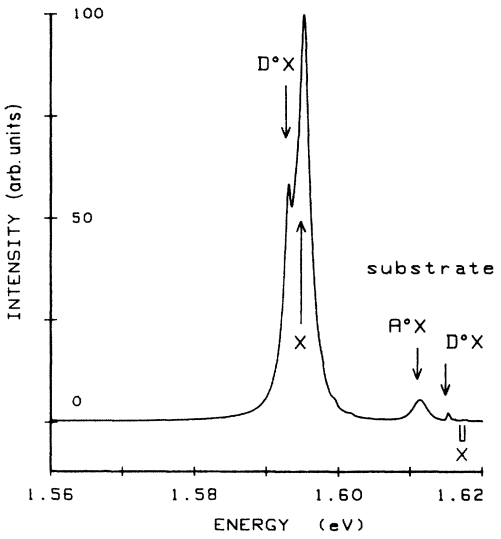

FIG. 1. Luminescence spectrum of the 1000-Å-thick well showing emissions D^0X and X from the CdTe confined layer and A^0X, D^0X, and X from the $Cd_{1-x}Zn_xTe$ substrate simultaneously.

the line labeled X associated with free exciton recombination.

Second, although the free exciton line X is very intense for the confined layer, phonon replicas of this line are not observed; see Fig. 1 where the first LO phonon replica should lie at $1595-21=1574$ meV. This contrasts with bulk CdTe, where the LO-phonon replicas are moderately intense and stronger than the very weak zero-phonon free exciton luminescence.[3]

The third point that we discuss is the most interesting one: for both the 1000-Å confined layer (see Fig. 2) and the 500-Å layer, the high-energy side of the excitonic line of the luminescence spectra shows a series of satellite peaks. Related oscillations have been observed in transmission, excitation, and reflectivity spectra of these samples.[6]

For the 1000-Å-thick confined layer, peak X lies at 1594.8 meV and we detect eight satellite lines at 1596.0, 1596.6, 1597.3, 1598.2, 1599.1, 1600.2, 1601.4, and 1604.2 meV (the first derivative of the luminescence spectra proved useful for determining the precise energy positions, see Fig. 2). A very interesting feature here is that the line intensities are alternatively weak and strong (see Fig. 2).

For the 500-Å-thick confined layer, the peak X lies at 1595.2 meV and we detect four satellite lines at 1597.1, 1598.6, 1600.6, and 1602.6 meV. The resolution is not as good as in the previous case. We do not observe any noteworthy alternation in the line intensities for this thickness.

The satellite peaks are observable over a surprisingly large range of ≈ 10 meV (i.e., $k_B \times 120$ K) above the peak X, even though the sample is held at helium temperature. This shows that the thermalization of the excitonic satellite states is not very efficient.

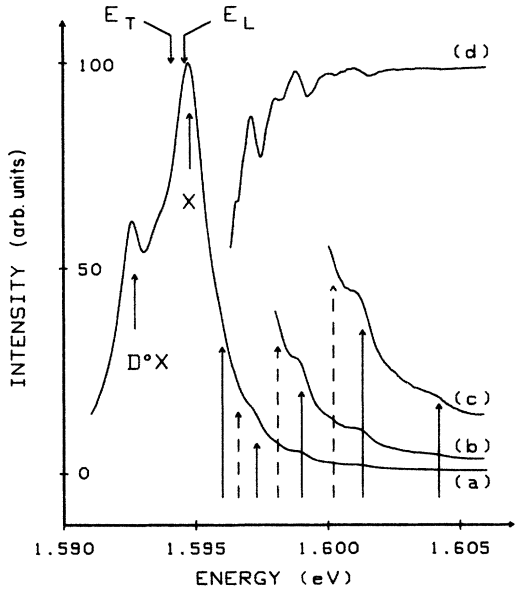

FIG. 2. Luminescence spectrum of the 1000-Å-thick well showing lines corresponding to recombination of free excitons (X) and of excitons bound to donors (D^0X). The high-energy side of line X shows a series of satellite peaks with alternating intensities (solid arrows mark stronger peaks, dotted arrows mark weaker peaks). In (a), (b), and (c) the gain is 1, 5, and 20, respectively. Curve (d) is the first derivative of the spectrum.

We attribute the presence of satellite peaks on the high-energy side of the free exciton line, with spacing and relative intensities that depend on the thickness of the CdTe layer, to the quantification of the exciton. That is, despite their relatively large thickness, one can consider these samples to be quantum wells. The situation studied here, however, is rather different from the extensively studied case of much thinner GaAs wells, where exciton states E_iH_j are formed by binding an electron from an electron subband E_i and a hole from a hole subband H_j.[7]

In our case (thicker layers, larger electron mass), the confinement energies for an electron and a hole (approximately 1.3 and 0.2 meV, respectively, for the 500-Å layer), are small in relation to the exciton binding energy of about 10 meV. The electron-hole Coulomb interaction then completely mixes the subbands and we have to directly consider the quantification of the exciton itself. More strictly, at least for energies near E_L, E_T (the energies of longitudinal and transverse excitons with $k=0$), we must consider the quantification of the excitonic polariton.

Polariton quantification was first observed in extensive reflectivity studies of thin platelet crystals of CdS and CdSe.[8] More recently, Schultheis and Ploog observed the effects of polariton quantification in reflectivity and excitation spectra of confined GaAs layers.[9] However, quantification effects were not evident in their emission spectra: A series of polariton emission peaks as reported here was not resolved.

Figure 3 shows the anticrossing between the parabolic dispersion curve for the heavy-hole exciton and the straight-line $E(k)$ relation for a photon in the CdTe layer. We need not consider the light-hole exciton, raised 12.3 meV above the heavy-hole exciton by the mismatch-induced strain.[2] We take E_{LT}, the longitudinal-transverse splitting, to be the bulk-crystal value 0.65 meV (Ref. 10) reduced by a factor $\frac{3}{4}$ (representing the heavy exciton's share of the oscillator strength of the $M=\pm 1$ states of the cubic exciton).

Around the anticrossing region for both branches and above it for the lower branch, a polariton wave created in the well is strongly reflected at the well-barrier interfaces. Standing wave states then exist for $N\lambda/2=L$, where N is a nonzero integer, λ is the polariton wavelength, and L is the well thickness. Consequently, the continuous polariton curve $E(k_z)$ becomes a series of discrete points at $k_z=N\pi/L$, resolvable when their spacings exceed the damping-related broadening.

Prediction of the relative intensity associated with each quantized mode is a complex problem, even independent of the question of their occupancy. The simple theory we give here, first used by Merle d'Aubigné *et al.*[6] to describe the absorption of light by the same samples, is appropriate to the region well above E_L, where the lower branch polariton is essentially an exciton and the upper branch polariton is essentially a photon. Transitions occur between the two branches with a probability given by perturbation

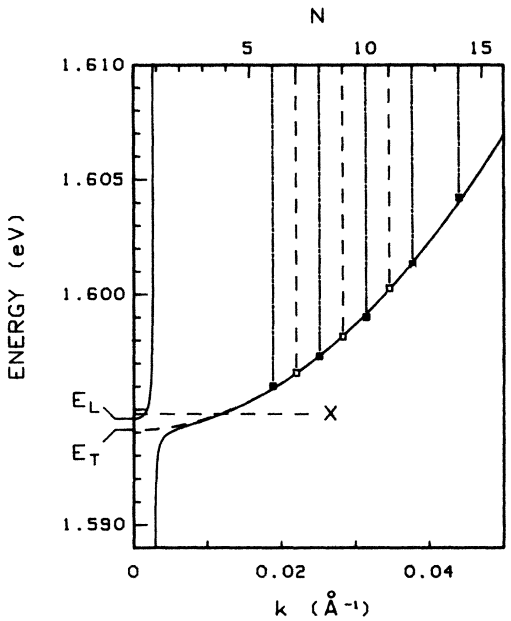

FIG. 3. Drawn on a polariton dispersion curve $E(k_z)$, the squares represent the positions of the satellite lines for the well of 1000-Å nominal thickness (filled squares: more intense peaks; open squares: less intense peaks). N is the number of half wavelengths of the polariton in the confined layer. The horizontal line at $E=1594.8$ meV indicates the position of peak X (the luminescence intensity maximum). The dispersion curve is calculated with $E_T=1.5941$ eV; the fit corresponds to $L=1040$ Å.

theory.

The wave function $T_N(z)$ for the center-of-mass motion of the exciton is taken to be zero for $|z|>L/2$. Within the well, it has the even symmetry form $\cos(N\pi z/L)$ for odd N and the odd symmetry form $\sin(N\pi z/L)$ for even N. The transition probability per unit time is $W_t=|C|^2|F_N(k_{ph})|^2$, where $F_N(k_{ph})$ is the Fourier component of $T_N(z)$ at the wave vector $k_{ph}=2\pi/\lambda_{ph}$ of the photon in CdTe ($\lambda_{ph}\approx 2500$ Å). (We neglect here the effect of the reflection of the emitted photon at the barrier-vacuum interface.) The valence-band to conduction-band electric dipole-matrix element is included in C as well as the factor relating the oscillator strength of the free exciton to the envelope function describing the relative motion of the electron and hole.[11] The Fourier components are

$$F_N^2(k_{ph})=\begin{cases}A_N^2\cos^2(k_{ph}L/2) & \text{for odd } N\ ,\\ A_N^2\sin^2(k_{ph}L/2) & \text{for even } N\ ,\end{cases} \tag{1}$$

where

$$A_N^2=\{(N\pi/L)/[(N\pi/L)^2-k_{ph}^2]\}^2(2/L)\ .$$

Expressions (1) lead to the following selection rules. For $k_{ph}L=2\pi,4\pi,\ldots$ there is no emission for even N, whereas for $k_{ph}L=\pi,3\pi,\ldots$ there is no emission for odd N. For $k_{ph}L=\pi/2,3\pi/2,\ldots$ the modes corresponding to even N and odd N have the same recombination probability. In our case, $k_{ph}L=\pi/2$ is equivalent to $L=620$ Å, close to 500 Å. This explains why we do not observe any marked alternation in the line intensities of the 500-Å-thick sample's spectrum. On the other hand, $k_{ph}L=\pi$ is equivalent to $L=1240$ Å, close to 1000 Å. This shows that the more intense lines of the 1000-Å-thick sample's spectrum should correspond to even N modes.

Our problem was to fit the resolved satellite peaks to such standing wave modes or, in other words, to index the satellites with the correct corresponding values of N. The fit was done as follows: We assigned trial sets of indices N to the peaks and tried to draw a polariton dispersion curve through all the points by varying E_T and the thickness L, with E_{LT} and the exciton's mass $M^*=m_e^*+m_h^*=(0.088+0.6)m_0$ (Ref. 12) kept fixed.

For the 500-Å-thick sample, the only reasonable fit gave the following results: $E_T=1595.0$ meV and $L=500$ Å.

For the 1000 Å thick sample, two fits corresponding to two different indexations of the satellite lines appeared possible (using two different values of the thickness L within its uncertainty range). But taking into account the selection rules discussed above, we could eliminate one solution and obtained $E_T=1594.1$ meV and $L=1040$ Å (see Fig. 3).

Around the main peak X, the quantized states can no longer be resolved; also the upper polariton branch might be involved for this energy region. Therefore, it does not appear useful to try to assign a value of N to peak X for either sample.

According to our results, there is a difference of 1.1 ± 0.3 meV between the values of $E_T+\hbar^2\pi^2/2L^2M^*$ (the energy of the uncoupled transverse exciton) for the two wells. This is close to the calculated difference between their optical gaps (1.06 meV) which indicates that there is very little change in exciton binding energy when L decreases from 1000 to 500 Å.

We will now argue that the thickness dependence of the optical selection rules is very important for explaining the other features distinguishing the luminescence of our confined layers from that of bulk samples, i.e., predominance of free exciton luminescence and absence of phonon replicas of this luminescence.

We begin, however, by recalling an explanation often given for similar effects in III-V compounds.[13] For a bulk sample, only those polaritons that reach the surface and have $k\approx k_{ph}$ can give rise to external photons. Because the polariton mean free path is very short near $k=k_{ph}$, the zero-phonon polariton luminescence is very weak compared with the intensity of the LO phonon, D^0X and A^0X processes, which generate photons in the bulk. When the sample's thickness becomes smaller than the polariton mean free path, this obstacle no longer exists and the free polariton emission can be very intense at the expense of the trapped exciton lines and the LO-phonon replicas.

While this kind of explanation seems applicable for the energy region around the anticrossing in the polariton dispersion diagram, we believe it does not completely describe our case. We measure substantial intensity (the satellite peaks) well up into the energy region where the polariton is essentially an exciton; indeed, for the 1000-Å thick layer, even the main peak X lies above E_L (Figs. 2

and 3). Above E_L, excitons and photons become weakly coupled, a description in terms of polaritons is less useful and Eqs. (1) are applicable. For a bulk sample, optical transitions are forbidden in this energy region; indeed, the factor A_N [Eqs. (1)] tends towards zero when L becomes infinite, which amounts to saying that optical transitions must satisfy the k-vector conservation law. On the other hand, in the case of a confined layer, Eqs. (1) show that optical transitions become allowed for discrete values of k_z different from k_{ph}; this very strongly reinforces the luminescence intensity in this region, again at the expense of nonradiative processes, trapping on impurities, LO-phonon-assisted processes, etc.

In summary, these samples have shown very clearly the early effects of quantification on exciton states as one sample dimension is reduced. Thus, they give interesting information about the transition between the three-dimensional semiconductor and a very thin layer where the exciton would become perfectly two dimensional.

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[1]C. Fontaine, J. P. Gailliard, S. Magli, A. Million, and J. Piaguet, Appl. Phys. Lett. **50**, 903 (1987).

[2]N. Magnea, F. Dal'Bo, C. Fontaine, A. Million, J. P. Gailliard, Le Si Dang, Y. Merle d'Aubigné, and S. Tatarenko, J. Cryst. Growth **81**, 501 (1987).

[3]For example, P. Hiesinger, S. Suga, F. Willmann, and W. Dreybrodt, Phys. Status Solidi B **67**, 641 (1975); J. M. Francou, Ph.D. thesis, University of Grenoble, 1985 (unpublished).

[4]Z. C. Feng, A . Mascarenhas, and W. J. Choyke, J. Lumin. **35**, 329 (1986).

[5]N. Magnea, F. Dal'Bo, J. L. Pautrat, A. Million, L. Di Cioccio, and G. Feuillet, in *Materials for Infrared Detectors and Sources, 1986,* edited by R. F. C. Farrow, J. F. Schetzina, and J. T. Cheung, Materials Research Symposia Proceedings, Vol. 90 (MRS, Pittsburgh, 1987), p. 455.

[6]Y. Merle d'Aubigné, Le Si Dang, A. Wasiela, N. Magnea, F. Dal'Bo, and A. Million, in *Proceedings of the Third Conference on Modulated Semiconductor Structures, Montpellier, 1987* (Les Editions de Physique, Paris, in press).

[7]R. Dingle, W. Wiegmann, and C. H. Henry, Phys. Rev. Lett. **33**, 827 (1974).

[8]See, for example, V. A. Kiselev, B. S. Razsbirin, and I. N. Ultrasev, Pis'ma Zh. Eksp. Teor. Fiz. **18**, 504 (1973) [JETP Lett. **18**, 296 (1973)]; Phys. Status Solidi B **72**, 161 (1975).

[9]L. Schultheis and K. Ploog, Phys. Rev. B **29**, 7058 (1984).

[10]J. C. Merle, R. Sooryakuma, and M. Cardona, Phys. Rev. B **30**, 3261 (1984).

[11]R. J. Elliot, in *Polarons and Excitons,* edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, Edinburgh, 1961), p. 269.

[12]Le Si Dang, G. Neu, and R. Romestain, Solid State Commun. **44**, 1187 (1982).

[13]See, for example, W. L. Bloss, E. S. Koteles, E. M. Brody, B. J. Sowell, J. P. Salerno, and J. V. Gormley, Solid State Commun. **54**, 103 (1985); C. Weisbuch, R. C. Miller, R. Dingle, A. C. Gossard, and W. Wiegmann, *ibid.* **37**, 219 (1981).