Room-temperature exciton luminescence in II-VI quantum wells

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We observe free excitons in absorption and emission at room temperature in $Cd_{0.25}Zn_{0.75}Te$/ZnTe multiple quantum wells. A large overlap between luminescence and absorption peaks observed at 10 K is maintained up to room temperature showing that the luminescence is predominantly excitonic. From a rate equation analysis we calculate the branching ratio for free carriers relaxing into excitons to free-carrier radiative recombination.

It has been well demonstrated that quantum well structures enhance excitonic effects in semiconductors.[1] In particular there is a remarkable difference in the appearance of bulk GaAs and AlAs/GaAs quantum wells at room temperature, with the quantum wells showing pronounced excitonic resonances in absorption.[1] In contrast, the distinction between excitonic and band-to-band luminescence at room temperature is not so clear. This point has been the subject of some conflicting reports.[2-5] The original reports of room-temperature exciton luminescence[2] in III-V materials have been recently verified.[5] The larger exciton binding energy in II-VI materials should lead to even more pronounced room-temperature exciton effects in II-VI quantum wells. Recent results on a variety of II-VI based quantum wells have shown that the absorption due to excitons at room temperature is indeed larger than in equivalent III-V based structures.[6,7] However the contrast between band-to-band and exciton absorption is not as good as expected from the exciton binding energy.[8] The explanation for this is that at room temperature the exciton transition is broadened by longitudinal-optical (LO) phonon scattering. This effect is enhanced due to the combination of the smaller LO phonon energy (resulting in a larger density of LO phonons) and the stronger exciton LO phonon coupling in II-VI materials.

In this letter we report on room-temperature absorption and luminescence in $Cd_{0.25}Zn_{0.75}Te$/ZnTe multiple quantum wells (MQWs). To our knowledge, this is the first observation of room-temperature exciton luminescence in II-VI quantum wells. We show that there is a large contrast between band-to-band and exciton emission. From our observations the free-carrier recombination and exciton formation rates are estimated.

The MQWs were grown by molecular beam epitaxy on GaAs substrates. Buffer layers of ZnTe, 2 μm thick, were used to reduce strain and dislocations. The well material is $Cd_xZn_{1-x}Te$ with $x = 0.25$, and the barrier material is ZnTe. There is a 1.6% lattice mismatch between well and barrier layers. Samples No. 1 and No. 2 have 50 Å wells, but sample No. 2 was grown with an additional 2 μm buffer layer of $Cd_{0.14}Zn_{0.86}Te$. Assuming psuedomorphic growth, the strain in sample No. 2 should be less than in sample No. 1. The barrier layers were 100 Å thick in both samples. For absorption measurements the substrates were

removed by selective etching. Low-temperature work was carried out at 10 K using a closed-cycle He refrigerator. Spectra were taken with a 0.5 m Spex monochromator. Photoluminescence was excited from the same etched samples with an argon-ion laser.

Figures 1(a) and 2(a) show low-temperature absorption and photoluminescence (PL) spectra for both samples at 10 K. The spectra show well-resolved exciton lines. Light-hole and heavy-hole exciton lines are seen in sample No. 2 in absorption, while only a heavy-hole exciton absorption line is seen in sample No. 1. The wells in these structures are shallow and the valence-band offset is predicted to be small, so that strain rather than quantum confinement is the dominant mechanism for splitting the light-hole and heavy- hole valence bands. Sample No. 2 is grown on a buffer that has an intermediate lattice spacing. Assuming that the quantum well is lattice matched to the $Cd_{0.14}Zn_{0.86}Te$ buffer, the wells in No. 2 should be less strained than in No. 1 leading to a smaller splitting of the light-hole and heavy-hole bands. With larger splitting the light-hole band can become resonant with the unbound heavy-hole states and band mixing may prevent the formation of well-defined light-hole exciton states. Alternatively, reversal of the strain splitting in the barrier regions may lead to a type-II quantum well with light holes confined in the barrier region for electrons. This has been observed in $CdTe/Cd_xZn_{1-x}Te$ MQWs.[9]

At low temperature, 10 K, the peak of the luminescence line is shifted by 2.5 meV from the absorption peak. The shift is low given the large band tailing that is usually seen in bulk mixed crystals. To the low-energy side is a broad defect band which saturates with increasing excitation density. The luminescence lifetime of the defect band is of the order of 10 μs at low excitation intensity (< 10 mW cm^{-2}), suggesting that it is due to donor-acceptor recombination rather than bound excitons.

As the temperature is increased, the exciton lines seen in emission and absorption broaden. Room-temperature absorption and photoluminescence (PL) spectra for samples No. 1 and No. 2 are shown in Figs. 1(b) and 2(b), respectively. The exciton is seen clearly in absorption but is no longer fully resolved from the continuum. The strong exciton line seen in emission at low temperature persist all the way up to room temperature and closely tracks the
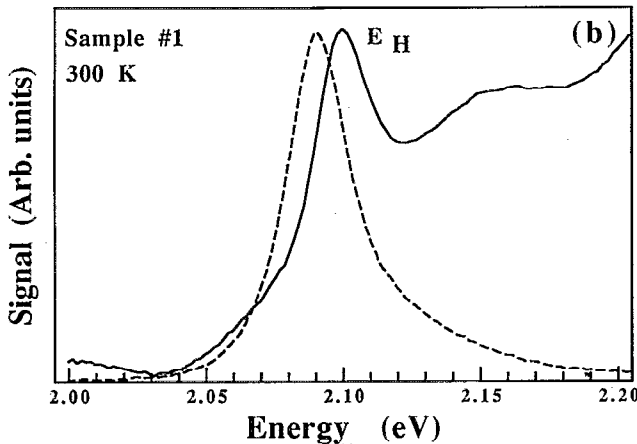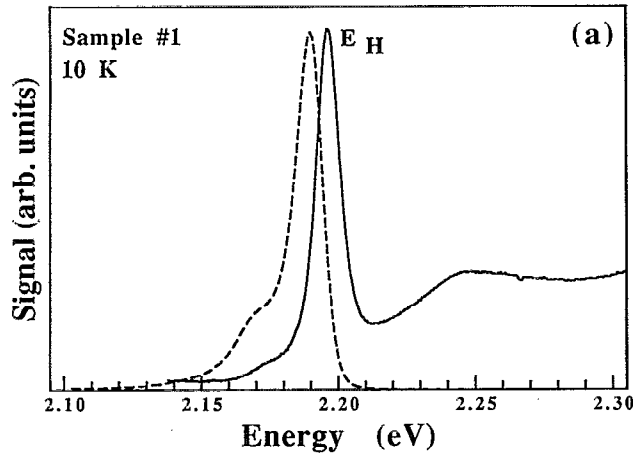
FIG. 1. Absorption (solid line) and photoluminescence (dashed line) from sample No. 1 at (a) 10 K and (b) 300 K, showing the overlap between absorption and emission lines. E_H denotes the $n = 1$ heavy-hole exciton.
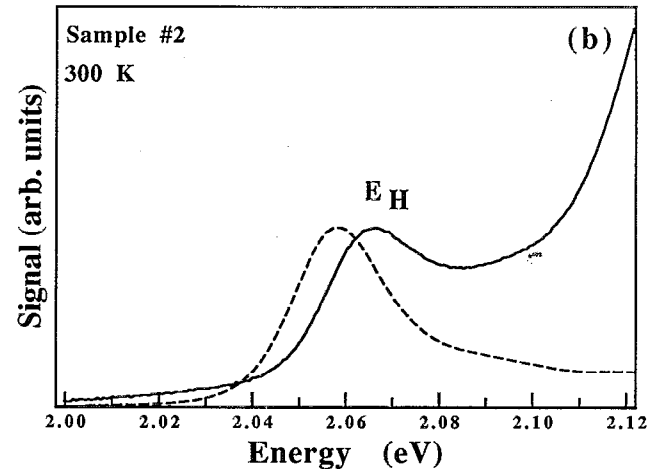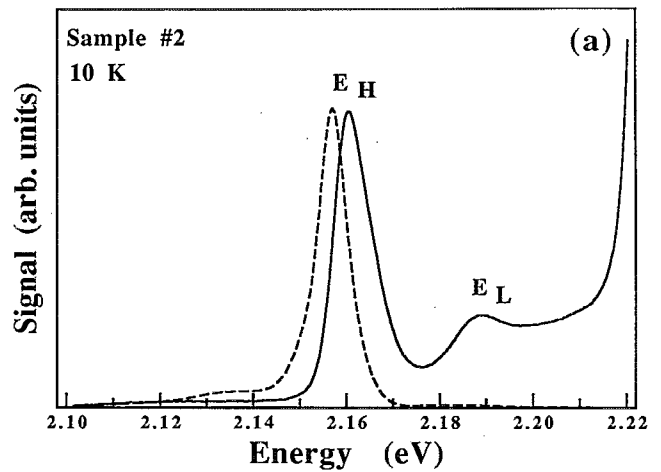
FIG. 2. Absorption (solid line) and photoluminescence (dashed line) from sample No. 2 at (a) 10 K and (b) 300 K, showing the overlap between absorption and emission lines. E_H, E_L denote the lowest energy ($n = 1$) heavy-hole and light-hole excitons, respectively. The large increase in absorption at the high-energy end of the graphs is due to the band edge of the $Cd_{0.14}Zn_{0.86}Te$ buffer layer.

exciton absorption line. The separation between the absorption and emission peaks varies from 2.5 meV at 10 K to 10 meV at room temperature. The emission peak is always to the low-energy side of the absorption peak. Although the absorbing region of these samples is very short (0.225 μm), by taking account of reabsorption the separation between absorption and emission peaks at room temperature becomes negligible. This shows clearly that even at room temperature, the emission line is still predominantly excitonic. There is an asymmetry, however, in the emission line with a tail on the high-energy side. In sample No. 1 this tail can be solely attributed to free-carrier recombination. In sample No. 2 there is an additional contribution to the high- energy tail due to luminescence from the $Cd_{0.14}Zn_{0.86}Te$ buffer layer.

An accepted model for exciton line broadening[10] is that the excitons are scattered from their $k = 0$ states by LO phonons. The halfwidth half maximum (HWHM) linewidth can be expressed as the sum of the low-temperature linewidth (HWHM) plus an interaction factor times the temperature dependent LO phonon occupation number. This interaction factor has been estimated previously in these and similar structures.[8,11,12] The measured inter-

action factors indicate that the exciton lifetime at room temperature is in the range 30–60 fs. Although this lifetime is very short, most of the emission is due to free excitons rather than free carriers.

A simple picture for the dynamics in this system is as follows. For continuous pumping above the band gap, there is an equilibrium number of excitons and free carriers. The free-carrier population is depopulated by radiative recombination, nonradiative recombination at traps, and by the formation of excitons. It is populated by the creation of electron-hole pairs by the pump light and from the ionization of excitons by phonon scattering. Similarly the excitons are depopulated by radiative recombination, nonradiative recombination at traps, and ionization into free carriers and the excitons are pumped just by the relaxation of free carriers.[13] This leads to the rate equations[14] for the number of free-carriers N, and the number of excitons X:

$$\frac{dN}{dT} = P - A_{nr}N - B_r N^2 - C_x N^2 + F_r X, \qquad (1)$$

$$\frac{dX}{dt} = C_x N^2 - D_{nr}X - E_r X - F_i X, \qquad (2)$$

where A_{nr} and D_{nr} are the nonradiative recombination rates for carriers and excitons, respectively; B_r and E_r are their respective radiative recombination rates; P is the rate of creation of free carriers by the pump; C_x is the rate of formation of excitons from electron-hole pairs; and F_i is the rate of exciton ionization. We assume that the numbers of electrons and holes are the same and that higher order processes such as Auger recombination can be neglected. The $C_x N^2$ term for exciton formation is not usually included in the electron rate equations. It arises from the similarity between the requirements for a pair of free carriers to radiate (net momentum ~ 0 and overlapping wave functions) and to form an exciton (net momentum of both carriers close to zero and carriers near enough for capture). This implies that while exciton recombination is a monomolecular process, exciton formation is bimolecular.

Under steady-state conditions, there is no change in either population so $dN/dt = 0$ and $dX/dt = 0$ and Eqs. (1) and (2) can be solved to give the ratio of exciton to free-carrier luminescence:

$$\frac{L_x}{L_{eh}} = \frac{C_x E_r}{(D_{nr} + E_r + F_i)B_r}. \qquad (3)$$

At low temperatures and high radiative efficiency $E_r \gg D_{nr}$, F_i then $L_x:L_{eh}$ becomes C_x/B_r. The strong exciton luminescence seen at low temperatures shows that the free carriers relax into exciton states before they undergo radiative (or nonradiative) recombination. At high temperatures (300 K) the exciton ionization rate dominates over the radiative and nonradiative rates ($F_i \gg D_{nr}$, E_r). The ratio of exciton to free-carrier luminescence then becomes $C_x E_r/F_i B_r$. Time-resolved PL measurements at 10 K yield an exciton lifetime of ~ 100 ps.[15] If this changes little with temperature, then E_r is $\sim 1/100$ ps^{-1}. The homogeneous broadening of the exciton line implies that $F_i = 1/50$ fs^{-1}. From the room-temperature PL spectrum, Fig. 1(b), the ratio $L_x:L_{eh}$ can be calculated by assuming that the asymmetry on the high-energy side of the luminescence line is due to free-carrier recombination.[16] This probably overestimates the contribution from free carriers so we say that the ratio $L_x:L_{eh}$ is greater than 10. With these values the ratio C_x/B_r at room temperature is over 2×10^4. In other words, the probability that an electron-hole pair will form an exciton is over 2×10^4 times greater than the probability of radiative recombination. This figure agrees qualitatively with what is observed at low temperature, i.e., virtually no free-carrier luminescence.

By considering the case of thermodynamic equilibrium, the relation between the exciton creation rate $C_x N^2$ and the exciton ionization rate $F_i X$ can be calculated using Eq. (2):

$$\frac{C_x}{F_i} = \frac{\exp(E_x/kT)}{N_x}, \qquad (4)$$

where E_x is the exciton binding energy and N_x is the temperature-dependent joint effective density of states (N_x

$= \sqrt{N_e N_h}$, where N_e and N_h are the effective density of states for electrons and holes, respectively). Setting E_x to 15 meV and using F_i as before, then the exciton formation coefficient C_x is 2.7×10^{-5} cm^3 s^{-1}. Combining this figure with the ratio C_x/B_r found above gives a value for the free-carrier recombination coefficient B_r of 1.4×10^{-9} cm^3 s^{-1}. This is somewhat larger than the value of 1.7×10^{-10} cm^3 s^{-1} found in GaAs quantum wells[17] as expected from the stronger Coulomb interaction in II-VI semiconductors.

These figures give a reference from which other II-VI materials and structures can be compared. They also show that in emission the effect of the increased exciton binding energy dominates over exciton line broadening from LO phonon scattering when it comes to separating band-to-band and excitonic contributions. This distinction is clearer than in equivalent III-V structures.

To conclude, in Cd$_{0.25}$Zn$_{0.75}$Te/ZnTe MQWs we can observe free excitons in absorption and emission at room temperature. The strong overlap between the photoluminescence and the absorption peaks shows that the luminescence at room temperature is predominantly excitonic. Using a simple model we can calculate the branching ratio for free-carriers relaxing into excitons to free-carrier radiative recombination.

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