Carrier-density dependence of the photoluminescence lifetimes in ZnCdSe/ZnSSe quantum wells at room temperature

C. Jordan, J. F. Donegan,[a] J. Hegarty, and B. J. Roycroft
Physics Department, Trinity College, Dublin 2, Ireland

S. Taniguchi, T. Hino, E. Kato, N. Noguchi, and A. Ishibashi
Research Centre, Sony Corporation, 174-Fujitsuka-cho, Hodogaya-ku, Yokohama 240, Japan

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Photoluminescence lifetimes have been measured at room temperature as a function of carrier density in ZnCdSe/ZnSSe quantum wells. We show that, at low carrier density (5×10^9–$5\times10^{10}\,\mathrm{cm}^{-2}$), nonradiative recombination dominates, while radiative recombination becomes more dominant as the carrier density is increased from 5×10^{10} to $5\times10^{11}\,\mathrm{cm}^{-2}$. Above $\sim5\times10^{11}\,\mathrm{cm}^{-2}$, band filling effects are shown to produce a saturation of the lifetimes. A simple rate equation model approach can be used to describe the carrier density dependence of the photoluminescence decay data obtained on a wide range of samples. A representative band-to-band recombination coefficient of $8\times10^{-4}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ and a Shockley–Read–Hall rate of $7.3\times10^7\,\mathrm{s}^{-1}$ were determined for one of the better samples studied. We believe that the excellent quality of our samples has allowed for the radiative recombination coefficient to be characterized accurately at room temperature. © *1999 American Institute of Physics.* [S0003-6951(99)03622-0]

The operating lifetime of ZnSe-based laser diodes has shown a consistent improvement over time[1,2] with devices operating for over 400 h now achieved. In relatively long-lived devices, nonradiative recombination at point defects is believed to enhance significantly the defect mobility, resulting in the formation and growth of defect complexes.[1–3] Since nonradiative recombination is central to the defect dynamics in II–VI lasers, the characterization of the carrier recombination in the state-of-the-art material is of prime importance.

In this letter we present a study of the carrier recombination dynamics through time-resolved photoluminescence (TRPL) measurements performed at room temperature and as a function of carrier density in $Zn_{1-x}Cd_xSe$/ZnSSe/ZnMgSSe separate confinement heterostructures. For the purpose of our study we chose to characterize samples with similar parameters but grown at different times. We see a gradual reduction in the nonradiative recombination rate from older to newer samples.

The samples, grown by molecular beam epitaxy, were nominally undoped and consisted of a single $Zn_{1-x}Cd_xSe$ quantum well (QW) whose parameters are listed in Table I. Our measurements were made using a time-correlated single-photon counting system providing a time resolution of $\sim$100 ps. The excitation was provided by a synchronously pumped mode-locked dye laser producing 5 ps pulses at 76 MHz. The dye laser wavelength was tuned to 464 nm, below the gap of the ZnSSe barriers (460 nm) in order to generate carriers in the quantum well only.

As recombination takes place on a much longer time scale than the laser pulse duration, the initial sheet carrier density n_0 is proportional to the average laser power P and is given by $n_0=0.68A(1-R)P/(\hbar\omega S\gamma)$, where $\hbar\omega$ is the photon energy, S is the excited area, and γ is the laser repetition rate. The prefactor arises because the carrier distribution is nearly Gaussian, as measured by imaging the PL profile. The laser intensity was varied between 5 and $5\times10^3\,\mathrm{W/cm}^2$. Taking the reflection coefficients $R=23\%$ and the absorbance as $A=(3.2\pm0.7)\%$,[4] the initial carrier density in the QW was thus varied between 5×10^9 and $5\times10^{12}\,\mathrm{cm}^{-2}$.

The PL lifetime was obtained by fitting the initial part of the PL decay with a single exponential (this is reasonable since the decays show an initial exponential component over at least 1 order of magnitude). The variation of the PL lifetime with carrier density is plotted in Fig. 1 for three different QW samples. The newest sample (QW1) exhibits the longest luminescence lifetimes, reaching 6.5 ns at low carrier density. In contrast, the lifetimes are shorter and show very little dependence on carrier density in sample QW5, grown before QW4 and QW1. We see that the samples show more pronounced differences in PL decay time at low carrier densities (5×10^9–$5\times10^{10}\,\mathrm{cm}^{-2}$), i.e., where nonradiative recombination is expected to dominate.

Radiative recombination in QW structures is complex and involves different excitation states such as free carriers, heavy and light free excitons, and bound excitons, whose

TABLE I. Sample characteristics and parameters for the band to band (B) and nonradiative (A) coefficients obtained from fits to the data in Fig. 1. The error in the B parameter arises from the uncertainty associated with the determination of the initial carrier density.

Sample	Well width (nm)	Cd content	$B(10^{-4}\,\mathrm{cm}^2/\mathrm{s})$	$A(10^8/\mathrm{s})$
QW1	3.5	0.34	8±2	0.73
QW2	6	0.23	2.2±0.7	0.75
QW3	6	0.25	6.5±1.5	1.45
QW4	6	0.25	2±0.6	1.7
QW5	6	0.25	2±0.6	2.8

[a]Electronic mail: jdonegan@tcd.ie

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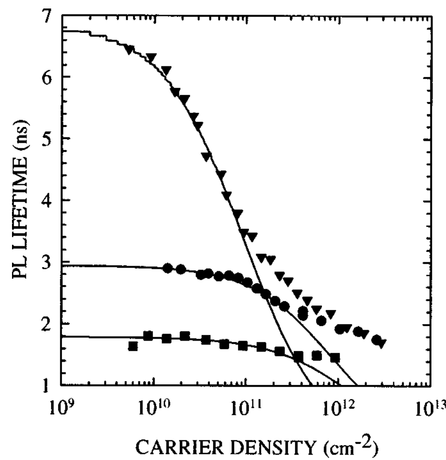

FIG. 1. Photoluminescence lifetime vs carrier density for samples QW1 (triangles), QW4 (circles), and QW5 (squares). The fit to Eq. (2) is shown as the full line.

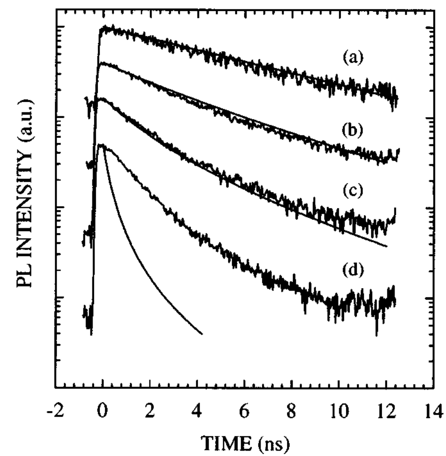

FIG. 2. Photoluminescence decays for samples QW1 for different carrier densities. The fit to the solution of Eq. (1) is shown as the full line: (a) 4×10^9 cm^{-2}, (b) 5×10^{10} cm^{-2}, (c) 4×10^{11} cm^{-2}, and (d) 2.5×10^{12} cm^{-2}.

relative contribution depends on temperature. In II–VI QW materials excitons play an enhanced role in the optical properties compared with similar narrow-gap III–V structures due to an increased Coulomb interaction between electrons and holes.[5] Neglecting nonradiative recombination and considering the ideal case of no correlation between excitons, exciton-dominated recombination is a monomolecular process which gives rise to single exponential PL decays, independent of the density. In contrast, band-to-band recombination is bimolecular and leads to nonexponential decays where the PL decay time depends on the carrier density.[6,7] The decrease in PL lifetime with increasing excitation for samples QW1 and QW4 (Fig. 1) suggests that in our samples the dominant radiative recombination mechanism at room temperature involves free carriers instead of excitons. This, however, does not mean that Coulomb effects are absent. Coulomb effects will only be completely screened above the Mott density.

To account for the variation of the PL decay time with carrier density, we thus used a rate equation model where the decay of excess carrier density n is expressed as the sum of a bimolecular-type radiative term and a nonradiative term

$$\frac{dn}{dt}=-Bn^2-An, \tag{1}$$

where B is the band-to-band radiative recombination rate coefficient and A is the capture rate coefficient associated with nonradiative centers of recombination. Using Eq. (1) implies that the nonradiative centers are saturated at our regime of excitation (the effect of background doping, with a density of 10^9 cm^{-2} in a 6 nm well, can also be neglected, i.e., the electron and hole densities in our materials are comparable). We also note that the effect of Coulomb enhancement can readily be included in the radiative recombination term B of Eq. (1).[6–8] From Eq. (1), the instantaneous PL lifetime τ_{PL} as a function of n_0 is given by

$$\frac{1}{\tau_{\mathrm{PL}}}=\left|\frac{d\log(I_{\mathrm{PL}})}{dt}\right|_{t=0}=2(Bn_0+A), \tag{2}$$

where $I_{\mathrm{PL}}=Bn^2$ is the PL intensity.

Results of the fits to Eq. (2) for the PL lifetimes are shown in Fig. 1 as a solid line and fitting parameters are given in Table I. Using the values of A and B deduced from the fits we show in Fig. 2 experimental PL decays for sample QW1 at different excitation intensities together with the PL decays obtained by solving Eq. (1). We see that our simple model can account very well for the variation of the PL lifetime between 5×10^9 and 5×10^{11} cm^{-2}. The observed and predicted decays are exponential at low density but develop into a nonexponential form at higher densities. Above $\sim5\times10^{11}$ cm^{-2} the measured lifetimes are longer than the predicted ones and tend to saturate at values of about 1.7 ns for samples QW1, QW3–4, and of about 2.2 ns for sample QW2.

Assuming that our samples contain the same type of defect, we see from Table I that the gradual reduction in the value of the nonradiative coefficient A over time directly reflects the improvement in growth quality. Despite the fact that the PL lifetimes are the longest reported to date for a ZnCdSe QW, they are still significantly shorter than in good quality III–V QWs. Room temperature lifetimes in excess of tens of ns have been measured in these materials,[9,10] corresponding to an A coefficient more than one order of magnitude smaller than the values given in Table I. This shows that the defect density is still relatively high in ZnCdSe QW structures compared with GaAs-based III–Vs.

The exponential decays observed at low carrier densities (Fig. 2) are a direct consequence of the domination of nonradiative recombination for this regime of excitation. As the carrier density is increased from 5×10^9 to 5×10^{10} cm^{-2} the variation in PL decay time allows the band-to-band coefficient B to be determined. Unlike sample QW5, where the nonradiative lifetime dominates the whole excitation range, B is well determined for the other samples. Note that the relatively large error on B arises from the uncertainty in the estimation of the carrier density through the absorbance A. Although slightly higher, we found that our values for B compare well with values of $1.1-1.9\times10^{-4}$ cm^2/s obtained at room temperature in a 7 nm AlGaAs quantum well.[10] In contrast, previous estimates of B in bulk ZnSe[11–13] and in n-type ZnCdSe/ZnSe QWs[14] are about one order of magnitude higher than these values. It was concluded[11,14] that Cou-

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lomb enhancement was responsible for the higher recombination rate in II–VI's. However these measurements were performed in samples with subnanosecond recombination times at room temperature. Nonradiative recombination would likely dominate in these samples, making any study of the radiative processes difficult. We believe that the growth quality achieved in our samples enabled us to determine B with much better accuracy. The larger value for B for the higher Cd content sample (QW1) is unexpected. At present, we do not have the range of well width and Cd content samples necessary to quantify this interesting effect.

The fact that our value for B is of the same order as the values obtained in III–V QW materials does not imply that Coulomb effects are absent from our samples. An elaborate model which includes Coulomb enhancement has been used to predict gain in these same materials.[15] This model predicts B values of 9.8×10^{-4} and 1.7×10^{-4} cm^2/s with and without Coulomb enhancement, respectively (the calculations were carried out at a carrier density of $6\times10^{11}\,cm^{-2}$ for a 6 nm $Zn_{0.8}Cd_{0.2}Se/ZnSe$ QW). We see that these values lie within the experimental uncertainty of B and so do not allow for Coulomb enhancement to be correctly characterized by our measurements.

From Figs. 1 and 2 one can see that above $\sim5\times10^{11}\,cm^{-2}$ the measured lifetimes are longer than the predicted ones. It is clear that nonradiative Auger recombination is not involved as it would produce a rapid reduction in the measured PL lifetime at high carrier density.[16] We also believe that photon-recycling effects will be negligible for our single QW samples. It was suggested[13] that at very high carrier density the formation of an electron–hole plasma can induce a rapid expansion of the carriers outside the excited spot and thereby increase the recombination time. Measurements of the PL spot profile did not show any evidence for such an effect in our samples.

The carrier density profile in our excitation spot is Gaussian. At high carrier density, we would expect that the recombination at the center of the spot would be faster than at the edges where the carrier density is much lower. Efforts to quantify this effect by measuring the PL through a small pinhole were not successful due to low light levels.

We believe that the saturation effect results principally from band filling effects. If we consider the system to be a purely two-dimensional (2D) semiconductor, the carrier density required to reach degeneracy is given by the 2D effective density of states N_{2D}.[17] Due to their smaller effective mass the electron population will become saturated at a carrier density of $1.8\times10^{12}\,cm^{-2}$. The bimolecular term in Eq. (1) has therefore to be replaced by $BN_{2D}n_0$ and the PL lifetime in Eq. (2) then becomes $1/(BN_{2D}+A)$. The range of B values given in Table I gives a range of 0.6–2 ns for the saturated lifetime in reasonable agreement with the data in Fig. 1.

In summary, we have made a detailed study of the recombination dynamics in ZnCdSe QWs at room temperature. We find that the amount of nonradiative recombination is smaller in newer samples, reflecting the improvement in the growth of these materials. From the simple rate equation model, we have been able to determine the radiative and the nonradiative recombination coefficients to be 8×10^{-4} cm^2/s and $7.3\times10^7/s$ in the best material. A saturation of the PL lifetimes at densities above $\sim5\times10^{11}\,cm^{-2}$ was also measured, reflecting the onset of degeneracy. Our analysis suggests that a bimolecular recombination model is appropriate to describe the radiative recombination at room temperature in II–VI QWs, although Coulomb enhancement effects are likely to be present.

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