Carrier recombination studies of ZnCdSe/ZnSe single quantum wells grown by molecular beam epitaxy

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Temperature dependent time-resolved photoluminescence has been used to study the excess carrier recombination in $Zn_{0.75}Cd_{0.25}Se/ZnSe$ single quantum well structures grown by molecular beam epitaxy. For temperatures <100 K radiative excitonic recombination appears to dominate, and the photoluminescence (PL) decay time follows the linear dependence on temperature over the range 50–120 K. At higher temperatures the reduction in PL efficiency and decay time indicate that nonradiative processes associated with the ZnCdSe/ZnSe interfaces dominate the recombination. The results are consistent with theoretical predictions. © *1995 American Institute of Physics.*

Recent advances in the growth of II–VI semiconductors such as ZnSe have led to the realization of laser diodes emitting in the blue/blue-green spectral region.[1–4] To reduce the lasing threshold, such devices have used quantum well structures for the active region. One such low dimensional system, based on the ZnCdSe/ZnSe combination has also been used for the fabrication of electroabsorptive modulators[5] and self-electro-optic effect devices (SEEDs).[6] At present, there is still considerable progress to be made in the growth and processing of these materials to obtain the optimum performance from such photonic devices. Since many aspects of device operation are governed by the excess carrier dynamics, a study of these processes in II–VI based quantum well structures is desirable. While some measurements have been made on the narrower gap II–VI materials such as those based on CdTe[7–11] there has been only limited investigation of the wider gap ZnSe based structures.[12,13] In this letter we present a study of the excess carrier dynamics in the ZnCdSe/ZnSe system, using the time-resolved photoluminescence (TRPL) technique, for temperatures in the range 5–300 K.

The measurements were performed on a microscope based instrument (a derivative of an Edinburgh Instruments Lifemap) which has been described in detail elsewhere.[14] Sample excitation is provided at a wavelength of 420 nm by a commercial frequency-doubled picosecond AlGaAs laser diode (pulse duration <20 ps). The actively quenched single photon avalanche diode (SPAD) detector[15] when coupled with the microscope optical system gives a spatial resolution of <5 μm and allows TRPL measurements in the spectral range 420–1100 nm. The instrument uses the time-correlated single photon counting (TCSPC) technique[16] and has an instrumental full width at half-maximum (FWHM) of 50–60 ps. For the measurements presented in this letter, the samples were mounted in a continuous flow helium cryostat (Oxford Instruments model CF1104) which had been modified to allow close optical access to the sample, thus maintaining the high spatial resolution of the microscope system.

The two samples under investigation consisted of a 2 μm thick layer of ZnSe, grown on an n^+ GaAs substrate, and containing a single $Zn_{0.75}Cd_{0.25}Se$ well of (i) 30 Å and (ii) 70 Å thickness, situated approximately 700 Å below the upper ZnSe/air interface. The samples were nominally undoped with an uncompensated donor concentration $N_D - N_A \leq 10^{15}$ cm^{-3}.

TRPL measurements were performed on the two samples in the temperature range 5–300 K, under identical excitation conditions. Figure 1 shows the PL decay corresponding to the quantum well emission for the 30 and 70 Å well structures at a temperature of 130 K over the wavelength ranges 475–485 and 485–495 nm, respectively. The laser excitation was focused to a spot of area ~40 μm^2 on the sample surface and the peak excitation power was ~1.2 mW. Since the excitation wavelength is above the band gap of ZnSe, the high absorption coefficient [typically $\sim 10^5$ cm^{-1} (Ref. 17)] will give a peak photogenerated carrier density of $\leq 10^{16}$ cm^{-3} in the barrier material. The excess carrier density in the well may be significantly higher than this, due to the capture of additional carriers generated in the much thicker barrier material. Spectral discrimination of the PL peak was provided by interchangeable multiple-cavity band pass filters, centered at 10 nm intervals and with a passband of ~10 nm (FWHM). Reabsorption of the PL will be insignificant in these structures, since the emission

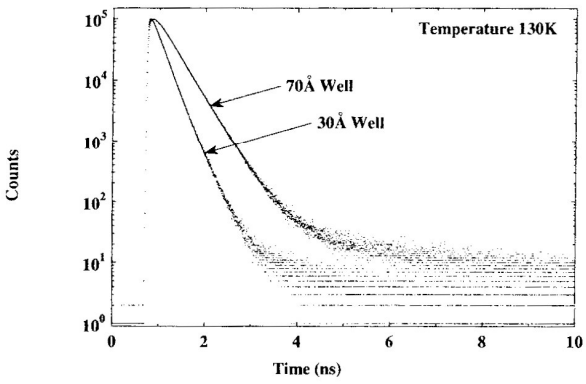

FIG. 1. PL decays from MBE grown $Zn_{0.75}Cd_{0.25}Se/ZnSe$ SQW structures at a temperature of 130 K. Sample excitation was at a wavelength of 420 nm, and the PL detection was over the spectral region 475–485 and 485–495 nm for the structures with 30 and 70 Å wells, respectively. The peak photogenerated carrier density in each case was ~10^{16} cm^{-3}

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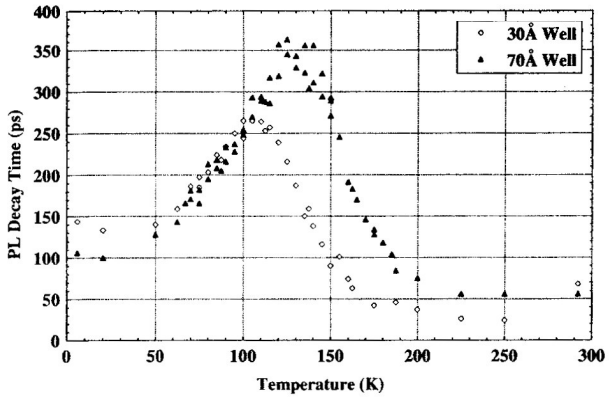

FIG. 2. PL decay time vs temperature for $Zn_{0.75}Cd_{0.25}Se/ZnSe$ SQW structures with 30 and 70 Å wells. The peak photogenerated carrier density in each case was $\sim 10^{16}$ cm^{-3} and the PL was detected over the whole PL band for each well.

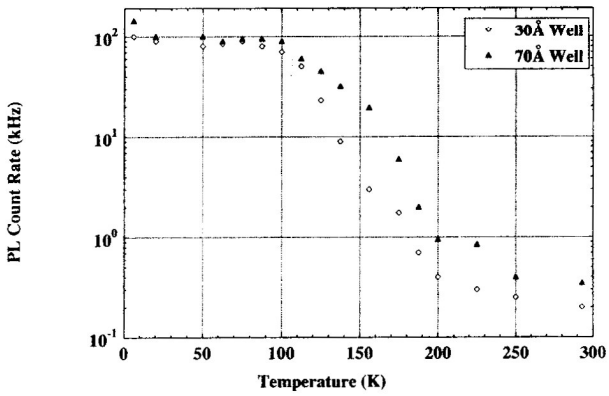

FIG. 3. PL count rate vs temperatures for $Zn_{0.75}Cd_{0.25}Se/ZnSe$ SQW structures with 30 and 70 Å wells. The peak photogenerated carrier density in each case was $\sim 10^{16}$ cm^{-3} and the PL was detected over the whole PL band for each well.

wavelength is greater than that of the absorption edge of the barrier material. The PL decays in Fig. 1 show a single exponential form over more than 3 decades in PL intensity, and have time constants of 185 and 330 ps, respectively, for the 30 and 70 Å wells. Figure 1 also shows the existence of a much weaker emission process which decays on a time scale of tens of ns, and with an intensity ~4 decades lower than the main process. This tail is observed for both samples, over the entire temperature range covered, and is characteristic of deep level reemission processes which have been observed previously in ZnSe based materials.[18] It should be noted, that the observation of such a weak decay requires the use of a technique with a very high sensitivity, such as the TCSPC method used here, which can routinely give a signal dynamic range of $\sim 10^5$.

For temperatures <70 K the PL decay is dominated by an exponential component of ~100 ps with a second much weaker component of ~200 ps, while at higher temperatures the decay is predominantly single exponential. Figure 2 shows the mean PL decay time versus temperature for the two quantum well samples over the temperature range 5–300 K. The general form is the same for both samples and shows that the PL decay time is approximately constant, at ~100 ps, from 5 to 50 K. As the temperature increases further, the PL decay times increase linearly, with gradients of 2.4 ps K^{-1} for the 30 Å structure and 3.1 ps K^{-1} for the 70 Å structure. The decay times for both structures reach a maximum in the temperature range ~100–130 K before decreasing steadily with increasing temperature to values of ~30 and ~60 ps, respectively, for the 30 and 70 Å structures above 200 K. The decay times then remain approximately constant up to room temperature. Figure 3 shows the corresponding temperature dependence of the PL intensity (plotted in terms of the photon count rate). The PL intensity is approximately constant at temperatures <100 K, and decreases steadily as the temperature is increased to room temperature. This indicates that for temperatures <100 K radiative recombination is the dominant carrier decay mechanism and that the variation in the PL decay time is a result of the temperature dependence of the radiative recombination. In this regime the single exponential nature of the decay is consistent with linear excitonic recombination, while the second (slower) component observed at the lowest temperatures is probably due to localized or impurity bound exciton recombination. For temperatures >100 K, the PL intensity decreases with increasing temperature, and thus the corresponding reduction of the PL decay time is consistent with increasing nonradiative recombination. If it is assumed that the quantum efficiency at 5 K is ~100% then Fig. 3 indicates that it has fallen to only ~0.2% at room temperature.

There have been a number of temperature dependent PL decay time studies in both III–V[19–21] and II–VI[10,11] quantum well structures. The theories of Feldmann *et al.*[19] and Andreani *et al.*[22] predict the linear increase in exciton radiative lifetime τ, with temperature T, observed experimentally.[10,11,19,21] Feldmann *et al.* derive their relationship by integrating the zone-center $K=0$ oscillator strength over the homogeneous linewidth $\Delta(T)$, determined by acoustic phonon scattering, and this leads to an expression for free excitons of the form

$$\tau(T) \propto \frac{1}{E_B}\left(\frac{\Delta(T)}{1-e^{\Delta(T)/kT}}\right) \approx \frac{T}{E_B},$$

where E_B is the exciton binding energy. The gradients of the linear regions (50 K<T<100 K) in Fig. 2 thus imply an ~30% increase in the exciton binding energy as the well width is reduced from 70 to 30 Å. For bound or localized excitons, the radiative lifetime is expected to be independent of temperature, consistent with the results for T<50 K.

Room temperature carrier recombination in III–V quantum well structures has in the past been the subject of some debate, but it is now generally regarded that nonradiative centers associated with the well/barrier interface[23] play the major role. We recently reported[24] a room temperature PL decay time on the ns time scale for nominally undoped, bulk ZnSe material grown by molecular beam epitaxy (MBE). The order of magnitude decrease in the PL decay time for quantum well structures would seem to indicate that the well/barrier interface is also determining the PL decay time in these II–VI structures. In addition, the factor of ~2 increase

in PL decay time between the 30 and 70 Å structures, at temperatures >150 K, is consistent with the nonradiative recombination centers being associated with the interfaces and increased interface coupling for narrower wells. Nonradiative recombination from these states is more efficient at higher temperatures due to the higher phonon density.

In conclusion, we have performed TRPL measurements on ZnCdSe/ZnSe single quantum well (SQW) structures, grown by MBE, in the temperature range 5–300 K. Recombination times of ~100 ps were observed below 50 K, rising to ~300 ps at ~120 K and falling back to ~50 ps at room temperature. The results indicate that in the temperature range ~60–120 K the dominant carrier decay mechanism is by radiative excitonic recombination and follows the linear dependence on temperature derived by Feldmann *et al.*[19] At higher temperatures nonradiative recombination, probably associated with the well barrier interface is the dominant carrier decay mechanism.

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