ELSEVIER

Journal of Crystal Growth 159 (1996) 402–405

JOURNAL OF CRYSTAL GROWTH

A study of the excess carrier dynamics in ZnSe based structures grown by molecular beam epitaxy

J.S. Massa *, G.S. Buller, A.C. Walker, J. Simpson [1], G. Horsburgh, J.T. Mullins [2], K.A. Prior, B.C. Cavenett

Department of Physics, Heriot-Watt University, Riccarton, Edinburgh, EH14 4AS, UK

Abstract

In this paper we present photoluminescence decay measurements from n-type, iodine-doped, ZnSe and nominally undoped $Zn_{0.25}Cd_{0.75}Se/ZnSe$ single quantum well structures grown by molecular beam epitaxy. In the temperature range 70–500 K, the iodine-doped material shows evidence of the trapping and re-emission of carriers from three deep acceptor levels at 80, 120, and 350 meV above the valence band. Recombination in the quantum well material is dominated by radiative processes for temperatures < 100 K, whilst at room temperature measurements indicate that the non-radiative processes are considerably worse than in bulk material.

A knowledge of the excess carrier dynamics in semiconductor structures is of considerable importance for the design and fabrication of photonic devices such as light emitting and laser diodes, modulators and self-electro-optic-effect devices (SEEDs). In the low injection level regime ($< 10^{16}$ cm^{-3}) the carrier dynamics are influenced considerably by the material quality, since the presence of impurities and lattice defects in the material can act as traps or centres for nonradiative recombination. In this paper we report time-resolved photoluminescence (TRPL) studies of device quality, n-type (iodine-doped) ZnSe, and nominally undoped ZnCdSe/ZnSe single quantum well (SQW) structures grown by molecular beam epitaxy (MBE).

The instrument used to perform the measurements in this study is microscope-based (a derivative of an Edinburgh Instruments Life-Map) and has been described in detail elsewhere [1]. Sample excitation is at a wavelength of 420 nm, by a commercial frequency-doubled picosecond AlGaAs laser diode (pulse duration < 20 ps). The detector is an actively quenched silicon single-photon avalanche diode (SPAD) [2] with an active area ~ 7 μm diameter. Using appropriate imaging and polarisation optics, TRPL measurements can be performed with a spatial resolution of < 5 μm [3] and over a spectral range 430–1100 nm. The instrument uses the time-correlated single photon counting technique [4] and has an instrumental full width at half maximum (FWHM) of ~ 50 ps. For these experiments the laser excitation was focused to a spot of area ~ 40 μm^2 giving an estimated peak photogenerated carrier density of $\sim 10^{16}$ cm^{-3}.

* Corresponding author. Fax: +44 131 451 3136; E-mail: phyjsm@bonaly.hw.ac.uk.

[1] Present address: Defence Research Agency, Malvern, Worcestershire, WR14 3PS, UK.

[2] Present address: Department of Physics (SECS), University of Durham, Durham, DH1 3LE, UK.

SSDI 0022-0248(95)00690-7

In this investigation the doped samples consisted of MBE-grown layers of ZnSe of ~2 μm thickness, grown on a semi-insulating GaAs substrate, and with uncompensated donor concentrations ($N_D - N_A$) in the range 1×10^{15}–2×10^{19} cm^{-3}. The quantum well material 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 either 30 or 70 Å thickness, approximately 700 Å below the upper ZnSe/air interface. The quantum well samples were nominally undoped with an uncompensated donor concentration $N_D - N_A \leq 10^{15}$ cm^{-3}.

Fig. 1 shows the PL decay spectrally integrated over the range 445–460 nm, from a nominally undoped ZnSe layer at temperatures of 70, 190 and 293 K. The room temperature decay (293 K) is nonexponential and has a form which is characteristic of bimolecular emission by a diffusing carrier distribution. As the temperature is reduced to ~70 K, the decay gradually becomes a single exponential as would be expected for a process involving emission by free or bound excitons. The inset in Fig. 1 indicates that the mean PL decay time steadily increases with temperature, from ~200 ps at 70 K to ~800 ps at 293 K.

For the n-type doped material at room temperature, the band-edge photoluminescence (PL) decay shows an increase in decay rate as the sample doping density increases. The PL decays have an approximately exponential form, indicating a linear recombination process, as would be expected for recombination in the minority carrier regime. The exponential time constants for the decays from the 1.3×10^{17} and 1.5×10^{18} cm^{-3} doped samples are ~335 and ~240 ps respectively. For the heavily doped samples, additional broadband emission is observed over the spectral region 500–700 nm. This emission decays on a microsecond timescale and is non-exponential, corresponding to a nonlinear recombination process. It was concluded in previous work [5] that carrier recombination at room temperature was dominated by minority carrier trapping by deep acceptors and that this mid-gap emission was due to the recombination of the trapped carriers with electrons on distant donors.

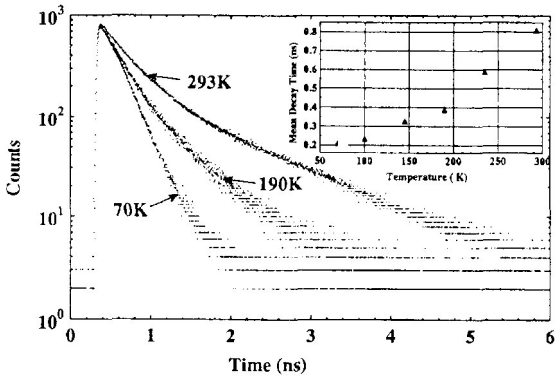

Fig. 1. PL decays, spectrally integrated over the range 445–460 nm, from nominally undoped MBE-grown ZnSe at various temperatures. The inset indicates the mean PL decay time.

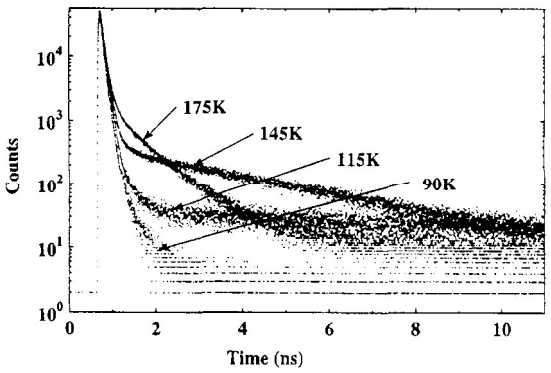

Fig. 2. PL decays from iodine doped ZnSe with $N_D - N_A \approx 1.5 \times 10^{18}$ cm^{-3} for temperatures in the range 100–190 K. The PL was collected over the spectral range 445–455 nm.

The bandedge PL decay for the iodine-doped material changes significantly with temperature as is shown by Fig. 2 for the 1.5×10^{18} cm^{-3} doped sample. Below 100 K the form of the decay is invariant with temperature and follows a single exponential over more than three decades in PL intensity. The exponential time constant for this decay is ~20–30 ps. At ~100 K, a much longer, single exponential component appears with a decay time > 50 ns. This second component increases in amplitude as the temperature is increased, and becomes progressively more rapid before merging into the main PL decay at a temperature of ~190 K. This cycle is repeated a second time in the temperature range ~160–250 K, and a third time in the range 360–500 K. Similar temperature dependent behaviour was observed with the 1.3×10^{17} cm^{-3} doped material but the initial decay time was ~60 ps, and the amplitude of the longer lifetime compo-

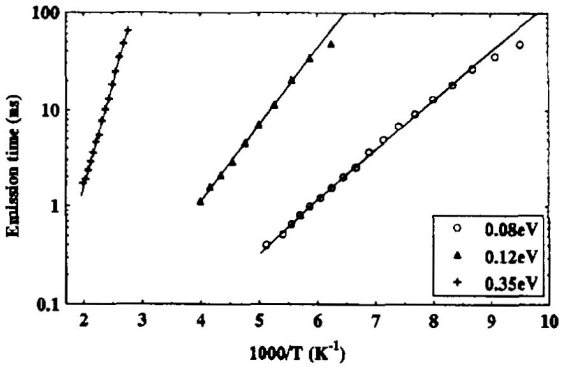

Fig. 3. Arrhenius plots for the three acceptor levels observed in iodine doped ZnSe. The data shown was obtained from the temperature dependence of the re-emission in the sample with $N_D - N_A \approx 1.5 \times 10^{18}$ cm^{-3}.

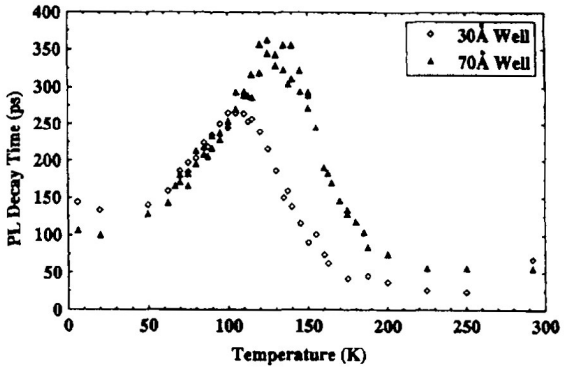

Fig. 4. PL decay time versus temperature for $Zn_{0.75}Cd_{0.25}Se/ZnSe$ SQW structures with 30 and 70 Å wells. The PL was detected over the whole PL band for each well.

nent was reduced compared to the main decay. For the heavily doped material, $N_D - N_A > 10^{19}$ cm^{-3}, and the lightly doped material, $N_D - N_A < 10^{16}$ cm^{-3}, the luminescence efficiency was too low to identify a longer component above the background noise level. The temperature dependence of the PL decay, under low injection level conditions, can be explained [6] by the trapping, thermal emission, and subsequent radiative decay of minority carriers. The time constant τ, of the temperature dependent tail is determined by the thermal emission process and is given by

$$\tau = (N_B v \sigma)^{-1} \exp(\Delta E/kT), \quad (1)$$

where ΔE and σ are the activation energy and cross section of the trap. N_B and v are respectively, the effective density of states of the band from which the carriers are trapped, and their corresponding thermal velocity. These are given by $N_B = (2\pi m^* kT/h^2)^{3/2}$ and $v = (3kT/m^*)^{1/2}$ with $m^* = 0.6\ m_0$. The minority carrier dynamics in this material are governed by two coupled rate equations:

$$\frac{dp}{dt} = \frac{m}{\tau} - (Bn + b + \sigma v N_T)\, p, \quad (2)$$

$$\frac{dm}{dt} = \sigma v N_T p - \frac{m}{\tau}, \quad (3)$$

where the electron concentration n is effectively constant, and m and p are the trapped and free hole concentrations, respectively. N_T is the trap density, B is the radiative recombination coefficient and b is the rate at which carriers are trapped by other levels not involved in the recombination process. Eqs. (2) and (3) were solved numerically and fitted to the PL decays using reconvolution analysis to obtain values for τ and $\sigma v N_T$ at each temperature [6]. Fig. 3 shows the Arrhenius plots for the 1.5×10^{18} cm^{-3} doped sample and Table 1 gives the trap parameters for this sample and the 1.3×10^{17} cm^{-3} doped sample, obtained by fitting the data in Fig. 3 with Eq. (1). The density of the acceptor levels at 80 and

Table 1
Trap parameters for the three acceptor levels A_1, A_2, and A_3, observed in iodine-doped ZnSe

	ΔE.(eV)	$\sigma(\times 10^{-15}$ cm$^2)$	N_T (cm^{-3})	
			Sample: $N_D - N_A \approx 1.3 \times 10^{17}$ cm^{-3}	Sample: $N_D - N_A \approx 1.5 \times 10^{18}$ cm^{-3}
A_1	0.08	9.5	2.1×10^{15}	3.2×10^{16}
A_2	0.12	4.6	6.9×10^{14}	7.2×10^{15}
A_3	0.35	8.6	4.9×10^{15}	1.4×10^{16}

120 meV increases proportionately with doping density and thus they are probably due to the presence of impurities or defects related to the dopant. The density of the acceptor level at 350 meV shows a sub-linear increase with doping density and thus it is probably due to a lattice defect such as a zinc vacancy or an associated complex.

The PL decays from $Zn_{0.75}Cd_{0.25}Se/ZnSe$ SQW structures have a predominantly single exponential form in the temperature range 60–300 K, but show evidence of re-emission processes with an intensity ~ 4 decades lower than the main decay. Fig. 4 shows a plot of the PL decay time [7] from the 30 and 70 Å SQW structures. In the temperature range ~ 60–120 K the PL decay time follows the linear dependence on temperature derived by Feldmann et al. [8], and this indicates the dominance of radiative excitonic recombination processes. As the temperature is further increased the PL decay time reaches a peak, at a different temperature for each sample, and then both the PL intensity and decay time decrease to different limiting values. These observations are in contrast to the behaviour of undoped bulk ZnSe (Fig. 1) and provide evidence to indicate that the non-radiative processes are associated with the well-barrier interfaces.

Acknowledgements

The authors acknowledge the support of the Royal Society Paul Instrument Fund and the Engineering and Physical Sciences Research Council (EPSRC). The actively quenched SPADs were developed by Sergio Cova and co-workers, Polytechnico di Milano, Italy.

References

[1] G.S. Buller, J.S. Massa and A.C. Walker, Rev. Sci. Instrum. 63 (1992) 2994.
[2] A. Lacaita, M. Ghioni and S. Cova, Electron. Lett. 25 (1989) 841.
[3] J.S. Massa, G.S. Buller, A.C. Walker, J.L. Oudar, E.V.K. Rao, B.G. Sfez and R. Kuselewicz, Appl. Phys. Lett. 61 (1992) 2205.
[4] D.V. O'Connor and D. Phillips, Time-Correlated Single Photon Counting (Academic Press, New York, 1983).
[5] J.S. Massa, G.S. Buller, A.C. Walker, J. Simpson, K.A. Prior and B.C. Cavenett, Appl. Phys. Lett. 64 (1994) 589.
[6] J.S. Massa, G.S. Buller, A.C. Walker, J. Simpson, K.A. Prior and B.C. Cavenett, Appl. Phys. Lett. 67 (1995) 61.
[7] J.S. Massa, G.S. Buller, A.C. Walker, G. Horsburgh, J.T. Mullins, K.A. Prior and B.C. Cavenett, Appl. Phys. Lett. 66 (1995) 1346.
[8] J. Feldmann, G. Peter, E.O. Göbel, P. Dawson, K. Moore, C. Foxon and R.J. Elliott, Phys. Rev. Lett. 59 (1987) 2337.