Photoluminescence decay measurements of *n*- and *p*-type doped ZnSe grown by molecular beam epitaxy

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Time-resolved photoluminescence has been used to study carrier recombination in *n*- and *p*-type doped ZnSe at room temperature. A band-edge photoluminescence decay time of ~240 ps has been measured for heavily doped *n*-type material together with a relaxation time of a few microseconds for the associated deep-level emission. The band-edge photoluminescence decay time for *p*-type doped material was ≤11 ps and is indicative of a high level of nonradiative Shockley–Read recombination.

In recent years there has been considerable interest in developing a compact low-power source of radiation in the blue/blue-green spectral region. One of the most promising technologies is based on the II-VI wide-gap semiconductor ZnSe which has recently been used to fabricate light emitting diodes and laser diodes[1–3] capable of emitting in this spectral region. At present, the material quality limits the performance of these devices. An important parameter that indicates the quality of the material and determines the laser threshold condition is the carrier lifetime. Both time-resolved photoluminescence (TRPL)[4,5] and pump-probe[6] techniques have been used to measure the carrier lifetime in ZnSe grown by various methods. In this letter, we report photon-counting TRPL measurements over several decades of excess carrier density, from ZnSe grown by molecular beam epitaxy (MBE), with various levels of both *n*- and *p*-type doping.

The measurements were performed using a microscope-based instrument[7,8] (a derivative of an Edinburgh Instruments Life-Map) with the sample excitation at 415 nm, provided by a commercial frequency-doubled picosecond GaAs/AlGaAs laser diode (pulse duration ~20 ps). The detector was an actively quenched silicon single-photon avalanche diode (SPAD)[9] with an active area ≤7 μm diameter. TRPL measurements with a spatial resolution of <5 μm[10] were obtained by using a microscope system, with appropriate optical routing to split off the collected luminescence. The instrument used the time-correlated single photon counting technique,[11] and had an instrumental full width at half-maximum (FWHM) of 50–60 ps.

In this investigation, all four samples consisted of MBE-grown ZnSe layers of 2-μm thickness on a GaAs substrate [100] orientation. The first sample was nominally undoped, with an uncompensated donor concentration, N_D-N_A, of $<10^{16}$ cm^{-3}, where N_D is the donor concentration and N_A the acceptor concentration. The second and third samples were iodine doped, with N_D-N_A of 1.3×10^{17} cm^{-3} and 1.5×10^{18} cm^{-3}. The fourth sample was *p*-type doped with nitrogen, N_A-N_D of 4×10^{17} cm^{-3}. N_D-N_A was measured by electrochemical capacitance-voltage profiling,[12] and was found to be uniform in the direction of growth.

The band-edge photoluminescence (PL) decays from the undoped and the two iodine-doped samples, at room temperature, are shown in Fig. 1. In these measurements the laser excitation was focused to a spot of area ~40 μm^2 on the sample surface, the peak excitation power was 1.2 mW and the laser pulse length was ~20 ps. Assuming an absorption coefficient[13] of 10^5 cm^{-1} (i.e., an absorption length of ~0.1 μm), this corresponds to a peak photogenerated carrier density of ~10^{16} cm^{-3}. Spectral discrimination of the luminescence was provided by multiple-cavity bandpass filters, in this case centered at 460 nm with a bandpass of ~10 nm (FWHM). The iodine-doped material showed single exponential PL decays corresponding to a monomolecular recombination process over the first two decades of PL intensity. The best-fit exponential time constants were 335 ps and 240 ps for the 1.3×10^{17} cm^{-3} and 1.5×10^{18} cm^{-3} *n*-type doped samples, respectively.

In both the *n*-type (iodine-doped) samples additional broad-band visible luminescence was observed, consistent with recombination via long-lived states deep in the band gap. Room-temperature PL spectra from these samples show

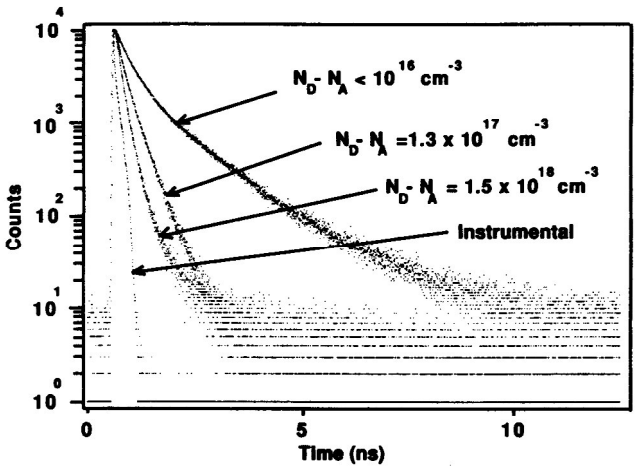

FIG. 1. PL decays from MBE-grown iodine-doped ZnSe with N_D-N_A~1.3×10^{17} cm^{-3} and 1.5×10^{18} cm^{-3} and from nominally undoped material, N_D-N_A<10^{16} cm^{-3}. An instrumental response is also shown for comparison. Sample excitation was at a wavelength of 415 nm and PL detection was over the spectral region 455–465 nm. The peak photogenerated carrier density in each case was ~10^{16} cm^{-3}.

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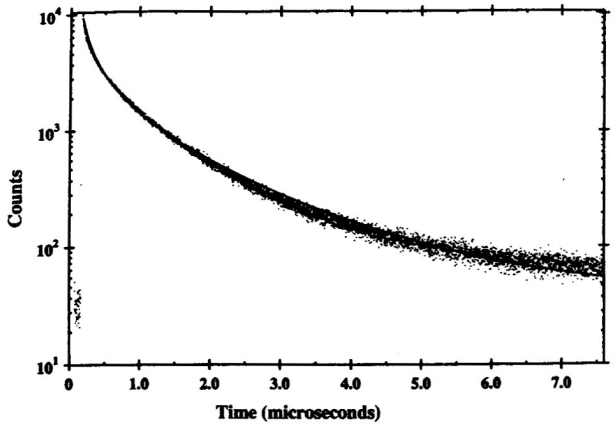

FIG. 2. PL decay of the deep-level emission from iodine-doped ZnSe with N_D-N_A~1.5×10^{18} cm^{-3}. Sample excitation was at a wavelength of 415 nm and the luminescence was detected at 510–650 nm. The initial photogenerated carrier density was ~10^{16} cm^{-3}. Also shown is the fit obtained with the donor–acceptor recombination model.

a broad emission band within the spectral region 510–650 nm. Figure 2 shows the integrated TRPL decay for this spectral region from a sample with N_D-N_A=1.5×10^{18} cm^{-3}. It can be seen that this luminescence decays on a much longer, microsecond, time scale.

Figure 3 shows the PL decay for the nitrogen-doped, p-type material with an uncompensated acceptor concentration N_A-N_D of ~4×10^{17} cm^{-3}, together with the instrumental response of the measurement system for comparison. The PL was detected over the spectral region 440–470 nm, and under the same excitation conditions as the previous measurements. The decay fitted well to a two-exponential function with time constants of ~11 ps(97%) and ~512 ps(3%), respectively, and is approaching the lower temporal resolution of the system. This very rapid PL decay is evidence of a high concentration of Shockley–Read[14] nonradiative recombination centers, possibly as a result of the self-compensation process[15] which occurs during the growth of p-type ZnSe.

The time dependence of the luminescence signal from n-type material, can be explained if it is assumed that minority carrier trapping via deep acceptor levels in the dominant recombination pathway. For a simple three-level system consisting of the conduction band, valence band, and a single acceptor level, the rate equations for the electron concentration n, hole concentration p, and trapped hole concentration p_1 are

$$\frac{dn}{dt}=-Bnp-bp_1n, \tag{1}$$

$$\frac{dp}{dt}=-Bnp-s(\bar{p}_1-p_1)p, \tag{2}$$

$$\frac{dp_1}{dt}=s(\bar{p}_1-p_1)p-bp_1n, \tag{3}$$

where B is the radiative coefficient for band-edge recombination, s is the rate of capture of holes by traps, $\bar{p}_1$ is the trap concentration, and b is the recombination rate for trapped holes. The associated band-to-band PL intensity is given by $I_B=Bnp$ and the deep-level PL intensity by $I_t=bnp_1$.

For heavily doped n-type material at low excitation densities (i.e., $n\gg p$ and $\bar{p}_1\gg p$), n is effectively constant in time and the band-edge luminescence decay can be described by a single exponential of time constant $\tau_B=1/(Bn+s\bar{p}_1)$. In this case we can neglect any effects due to carrier diffusion out of the detector field of view, since the diffusion length for free carriers on the subnanosecond time scale is <1 μm (assuming an ambipolar diffusion coefficient[16] of ~2.5 cm^2 s^{-1}). The band edge decays in Fig. 1 have time constants of 335 ps and 240 ps for the 1.3×10^{17} cm^{-3} and 1.5×10^{18} cm^{-3} doped samples, respectively. This small change implies that the decay is dominated by the trap capture term, $s\bar{p}_1$ since the decay rate does not increase proportionately with doping level. These results would also seem to indicate an upper limit on the value of B of ~2.5×10^{-9} cm^{-3}. However, the short absorption lengths in this material mean that photon recycling effects will be significant, and therefore, could indicate a higher value for B than the above estimate.

The nominally undoped material has a PL decay rate which decreases with time and is characteristic of carrier diffusion. The solution of the carrier diffusion equation in an infinite m-dimensional system (where m=1,2,3) with a linear recombination rate of $1/\tau$ gives a decay of the PL intensity I_{PL} of the form

$$I_{PL}\propto\left(\frac{1}{t}\right)^{m/2}\exp-\left(\frac{2t}{\tau}\right), \tag{4}$$

where, as a first approximation, we have ignored the presence of the upper ZnSe/air interface. In our measurements the excitation spot is larger than the detection region, and so we would expect to be able to neglect transverse diffusion. This was confirmed by fitting the PL decay with Eq. (4), using reconvolution analysis, and this yielded best-fit parameters of m=1.2 and τ=1.7 ns.

The nonexponential nature of the deep-level emission cannot be modeled by assuming linear recombination, via a single deep level, which would be necessary for a sample with such a high donor density. Figure 1 indicates that for times of greater than a few ns, all the holes will be in traps

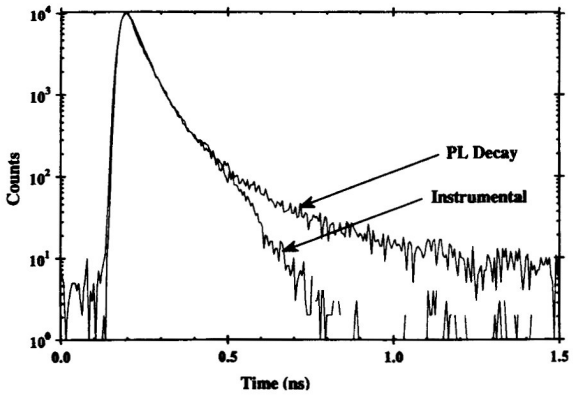

FIG. 3. PL decay from p-type, nitrogen-doped ZnSe with N_A-N_D~4×10^{17} cm^{-3} together with an instrumental response. Sample excitation was at a wavelength of 415 nm, with a peak photogenerated carrier density of ~10^{16} cm^{-3}, and PL detection at 440–470 nm.

and thus for a single midgap level, the deep-level emission should also have a single exponential decay with a time constant $\tau_T = 1/bn$. If however we assume that this emission is due to donor–acceptor (DA) recombination then the overlap of the donor and acceptor wave functions gives a transition probability $R(r)$ which varies with the separation r, of the donor and acceptor pair, as[17]

$$R(r) = K \exp\left(-\frac{r}{a}\right), \tag{5}$$

where K is the transition probability for zero separation and a is a scaling factor related to the Bohr radii of the donors and acceptors involved. Assuming the number of nonionized donors is constant and integrating spatially over the number density of DA pairs, then

$$I_T(t) \propto N_D N_A \int_{r_1}^{r_2} r^2 \exp\left\{-\left[\frac{r}{a} + \alpha K t \exp\left(-\frac{r}{a}\right)\right]\right\} dr, \tag{6}$$

where α is a constant dependent on N_D. Since the Coulomb energy of the DA pair varies with separation, the emission is red-shifted with increasing separation, and the limits r_1 and r_2 are thus dependent on the spectral measurement bandwidth.

The decay of the deep-level emission from the 1.5×10^{18} cm^{-3} doped sample (shown in Fig. 2), and the similar deep-level emission from the 1.3×10^{17} cm^{-3} doped sample were fitted numerically to the integral in Eq. (6) with values for αK of 0.046 and 0.012 ns^{-1}, respectively. Such long decays are typical of deep-level recombination processes and they provide additional evidence of spatial localization of charge carriers, since on this time scale almost all of the carriers would otherwise have diffused out of the 5-μm-diam spatial detection region. The higher radiative efficiency for the more heavily doped n-type material is illustrated by the higher intensity and more rapid decay of the band-edge PL.

In conclusion, we have studied recombination in n- and p-type doped ZnSe using time-resolved photoluminescence. Iodine-doped n-type material shows a very rapid decay ($\tau\sim250$ ps) of the near band-edge PL emission and a much longer decay ($\tau>1$ μs) corresponding to deep-level emission. We conclude that carrier recombination in this material is dominated by minority carrier trapping by deep-level acceptors, followed by radiative donor–acceptor recombination. We also measured the "band-edge" PL decay from nitrogen doped p-type ZnSe, this showed a very rapid decay ($\tau<20$ ps) and is characteristic of a high density of nonradiative recombination centers. The results appear generally consistent with the carrier dynamics deduced from independent pump-probe four-wave mixing experiments on similar material.[18]

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