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Time-resolved donor–acceptor pair recombination luminescence in highly n- and p-doped II–VI semiconductors

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Abstract

Time resolved luminescence measurements of the donor–acceptor pair (DAP) luminescence of n-doped CdS : In bulk crystals, undoped bulk ZnSe crystals grown with various VI/II ratios, and p-doped ZnSe : N epilayers in the near band gap region are presented. The decay of the donor–acceptor pair recombination luminescence is investigated for dopant concentrations below the Mott density. A discussion on the basis of a statistical theory by Thomas and Hopfield for DAP recombination yields, by knowledge of the Bohr radii of the impurities, the number of electronically active impurity centres. The reliability of this method to determine impurity concentrations is discussed.

1. Introduction

Wide band gap II–VI materials became of extreme interest since the reliable fabrication of highly p-doped epitaxial structures has been realized recently. Based on these materials new prospects are opened for technical aplications like short-wavelength lasers [1] and detectors. However, one important problem is the exact knowledge of impurity doping levels, which is required for p- or n-doped II–VI compounds. One fairly easy access is given by time-resolved measurements of the DAP luminescence, being strongly dependent on the doping concentration. Thomas et al. [2] performed time-integrated and time-resolved measurements, showing a reduction of the decay time with increasing doping concentration, and explained the development in a statistical approach by the reduction of the mean distance between donor and acceptor ions. In the present paper, the dynamics of the DAP luminescence of n-doped CdS : In, undoped bulk ZnSe grown with a large variety of VI/II ratios and p-doped ZnSe : N epilayers are presented. Time resolved measurements of DAP luminescence are introduced as a standard technique to determine the impurity concentration in II–VI semiconductors (bulk material as well as epilayers) for a wide range of concentrations below the Mott density.

2. Experimental technique

The investigated CdS crystals are grown by the Frerichs–Warminsky method from the gaseous

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phase [3]. The indium doping was achieved either during growth or subsequent by indiffusion. The ZnSe bulk material is grown by low pressure chemical vapour deposition (CVD) at $T = 675°C$ using various VI/II ratios. The ZnSe epilayers are grown by metalorganic vapour phase epitaxy (MOVPE) with DeZn and DeSe as precursors at a temperature of 480°C. The doping is carried out during growth by a nitrogen plasma. For the luminescence measurements the crystals are immersed in liquid He at 2 K. A synchronously pumped dye laser with 3 ps pulse duration and 1.9 MHz repetition rate excites the samples with an average output power of 100 mW, reduced by neutral glass filters for low excitation densities. Time resolved luminescence measurements are performed with a subtractive grating monochromator and a micro-channel-plate photo-multiplier tube (MCP–PMT) using time correlated single photon counting.

3. Experimental results

In all three systems – CdS : In, ZnSe and ZnSe : N – free excitons, bound exciton complexes and a luminescence band, several 10 meV below the band gap with strong phonon replica, are observed at liquid-helium temperatures. The broad band is attributed to donor–acceptor pair recombination [4]. Each donor–acceptor pair has a distinct separation r and a radiative recombination energy $E = E(r)$. We assume therefore exponential recombination kinetics for a single donor–acceptor pair. The superposition of a large number of exponential decays from each pair leads to the observed luminescence band. A theoretical treatment to determine the impurity concentration of the radiative dynamics is by far more reliable than line shape analyses, since in the latter case too many parameters are involved. The influence of doping on the DAP recombination dynamics is studied by time resolved measurements.

Using effective-mass theory to calculate the recombination probability $W(r)$ for a single donor–acceptor pair, where one of the impurities has a significantly larger a_0 (a_0: Bohr radius) than the other, one gets:

$$W(r) = W_{max} \exp(2r/a_0) \quad (1)$$

Eq. (1) is only valid for hydrogen-like pairs of reasonably large separation, i.e., $r \gg a_0$ [2]. Due to the fact that only the Bohr radius of the weaker bound impurity atom is used to deduce Eq. (1), the following calculations are valid with the same Bohr radius a_0 for both acceptor or donor excess.

Admitting donors or acceptors in excess, one gets for the intensity of light I emitted at time t [2]:

$$I(t) = \left\{4\pi N \int_0^\infty W(r) \exp[-W(r)t] r^2 \, dr\right\} \times \left\{\exp\left[4\pi N \int_0^\infty \{\exp[-W(r)t] - 1\} r^2 \, dr\right]\right\}. \quad (2)$$

N is the concentration of the majority constituent which should be of the order of the carrier concentration derived in Hall measurements at $T = 300$ K.

Fig. 1 shows time integrated luminescence spectra at liquid helium temperature of CdS crystals doped with indium at concentrations (N_{In}) between 10^{17} and 5×10^{18} cm^{-3}. The lowest spectrum in the inset of Fig. 1 exhibits in the near-band-gap region the DAP recombination luminescence. The energy position of the I_2 line at 2.5460 eV corresponds to a bound exciton complex formed at a substitutional indium impurity on cadmium site [5]. The energy position of the DAP luminescence confirms the incorporation of indium as a donor. The green luminescence becomes broader and the recombination dynamics faster (main part of Fig. 1) with increasing indium concentration. A good agreement between theoretical calculations using Eq. (2) and experimental transients could be established (Fig. 1). The fitting of the experimental data with $a_0 = 2.4$ nm and $W_{max} = (3 \pm 2) \times 10^8$ s^{-1} using Eq. (2) gives the concentration of donors N in the CdS : In samples (see Table 1).

The inset of Fig. 2 depicts time integrated measurements of the DAP recombination lumi-

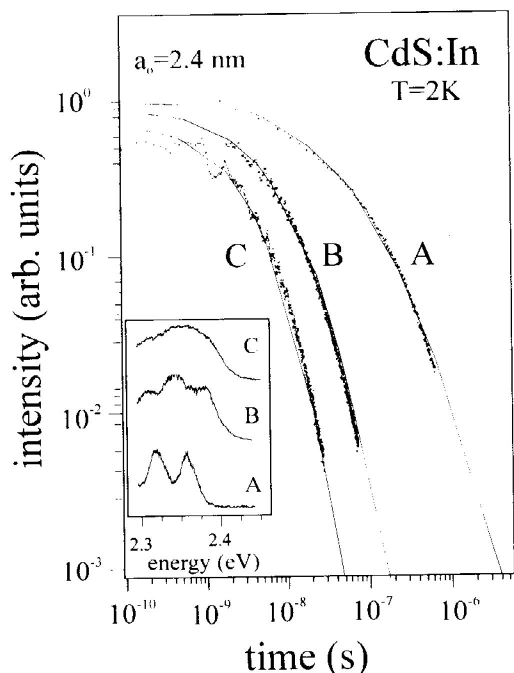

Fig. 1. Transients of the DAP luminescence of CdS with various N_{In} at low excitation densities ($I_{exc} = 10$ kW cm^{-2}). Points represents experimental data and full lines give theoretical fits using Eq. (2). In concentrations and results are given in Table 1. The corresponding luminescence is given in the inset.

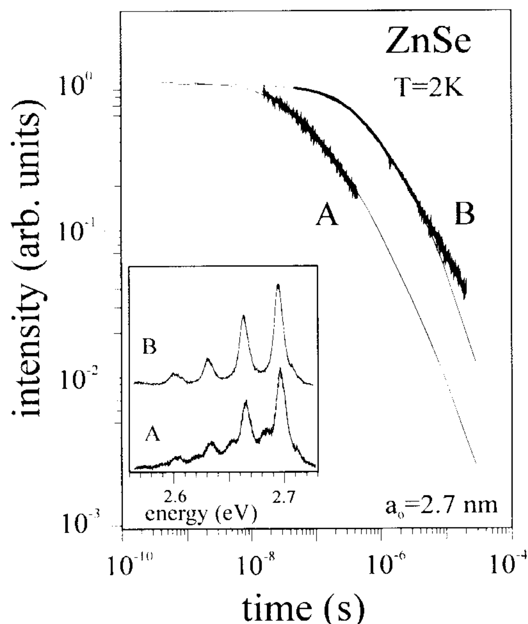

Fig. 2. Transients of the DAP luminescence of CVD-grown bulk ZnSe grown with two VI/II ratios, (A) 0.6 and (B) 0.3, during growth at low excitation densities ($I_{exc} = 10$ kW cm^{-2}). Points represents experimental data and full lines give theoretical fits using Eq. (2). Results are given in Table 1. The corresponding luminescence is given in the inset.

nescence at $T = 2$ K of bulk ZnSe crystals grown by CVD for two VI/II partial pressure ratios below one (0.6 and 0.3). The main part of Fig. 2 shows the corresponding transients taken at the maximum of the luminescence intensity. The used values of W_{max}, a_0 and N are given in Table 1. The DAP luminescence showing clearly pronounced phonon replica (curve A) decays slower than that of curve B. The VI/II ratio of the latter ones is closer to one than that of the first ones.

Table 1
Fitted values according to Eq. (2) for CdS:In, ZnSe and ZnSe:N (see Figs. 1, 2 and 3); N_{doping} gives the concentration deduced from growth conditions, and N and W_{max} give the fitted concentration and transition constant using Eq. (2), respectively

		N_{doping} (cm^{-3})	N (cm^{-3})	Impurity	W_{max} (s^{-1})
CdS:In	A	1×10^{17}	3.0×10^{17}	Donor	$(3\pm2)\times10^{8}$
	B	1×10^{18}	1.2×10^{18}	Donor	$(3\pm2)\times10^{8}$
	C	5×10^{18}	3.5×10^{18}	Donor	$(3\pm2)\times10^{8}$
ZnSe (bulk)	A	–	2.1×10^{17}	–	8×10^{6}
	B	–	6.4×10^{17}	–	1×10^{8}
ZnSe (epilayer)	A	–	1.5×10^{17}	–	8×10^{7}
	B	–	4.5×10^{17}	–	5×10^{8}
	C	–	1.7×10^{18}	–	3×10^{9}

The results of time-resolved luminescence measurements of MOVPE grown ZnSe epilayers doped in situ with nitrogen are presented in Fig. 3. The inset shows time-integrated spectra of crystals (curve A) grown with a VI/II ratio of 3.0 and a plasma power of 5.5 W as well as with a ratio of 0.8 for two plasma powers (curve B: 5.9 W; curves C: 6.5 W). The corresponding transients taken at the maximum of the DAP luminescence are given in the main part of the figure. We observe with decreasing VI/II ratio a decrease of the luminescence lifetime. The fitted

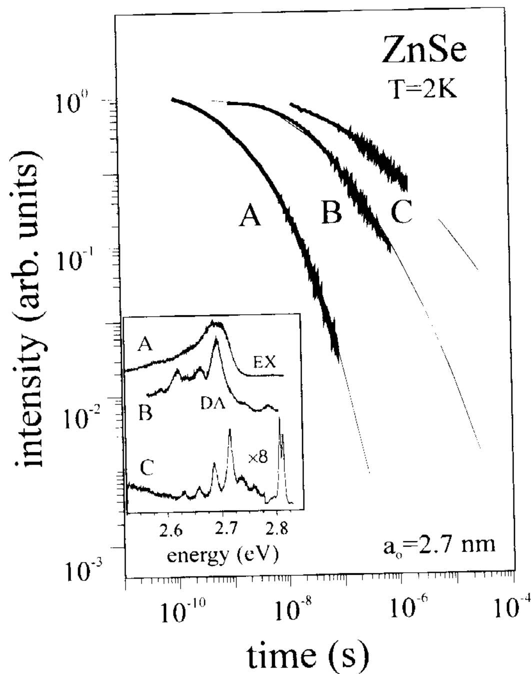

Fig. 3. Transients of the DAP luminescence of MOVPE-grown ZnSe doped with nitrogen at low excitation densities (I_{exc} = 10 kW cm^{-2}) for various VI/II ratios and nitrogen plasma powers: (A) VI/II = 3.0, P_{plasma} = 5.5 W; (B) VI/II = 0.8, P_{plasma} = 5.9 W; (C) VI/II = 0.8, P_{plasma} = 6.5 W. Points represents experimental data and full lines give theoretical fits using Eq. (2). Results are given in Table 1. The corresponding luminescence is given in the inset.

values of W_{max} and N using Eq. (2) are given in Table 1.

4. Discussion

The DAP luminescence in a semiconductor offers a unique spectroscopic access to the concentration of impurities. It is the only luminescence whose dynamics depend critically on the impurity concentration. Nevertheless, interactions with deep impurities affect the dynamics, making it complicated to obtain reliable information in a straightforward manner, as will be discussed for the three examples given above.

Under ideal conditions, i.e. the crystal contains only effective-mass-like donors and acceptors in a statistical manner, the statistical approach of Thomas and Hopfield (Eqs. (1) and (2)) is expected to be valid and an analysis of the DAP luminescence decay yields the concentration of the dominating dopant. This situation is given to a good extent for the CdS:In samples. With increasing indium concentration, the decay becomes faster. However, all transients can be fitted with one W_{max}, as expected from the theory (see Table 1). The obtained doping concentrations are in good agreement with the estimated indium concentration and $N_A - N_D$ values determined by electrical methods. It should be noted that the fit of the DAP transients gives the total acceptor or donor concentration and not only the uncompensated part. Thus, a combination of time-resolved and electrical data yields the majority constituent (N_A or N_D), its concentration, and information on the compensation.

The situation becomes more difficult if non-effective mass type defects are involved. Especially, deep defects can alter the transition probability of a DAP due to competing nonradiative recombination channels. For example, efficient excitation of 4f ions over DAPs has been attributed to a "three-centre Auger" process [6]. In this case W_{max} should increase with the deep defect concentration and N represents only an upper limit for the majority constituent (N_A or N_D). This behaviour is obvious for the CVD ZnSe samples. Both samples have been grown under the same conditions except of different VI/II ratios. The VI/II ratios critically determines the concentration of deep native defects generated during growth at 675°C. The DAP luminescence of the crystal grown with a VI/II ratio of 0.3 decays considerably faster than that of the sample with VI/II = 0.6, indicating a much higher defect concentration. However, the analysis using Eqs. (1) and (2) shows a large increase of W_{max} and only a small increase in N, see Table 1. At a VI/II ratio of 0.3, much more deeper native defects are generated, leading to an enhanced DAP recombination probability. Obviously, W_{max} is a sensitive sensor for deep defects.

The example of the MOVPE grown samples is the most complicated one. Nitrogen doping of ZnSe leads to p-conductivity in high quality MBE ZnSe epilayers. However, MOVPE-grown ZnSe

layers still suffer from the high impurity content of the available precursors, as is obvious from the high impurity concentrations determined for sample B. Upon N-doping the defect concentration increases. The simultaneous increase of the transition probability W indicates that N-doping produces not only shallow acceptors, but also deep defects. This is affirmed by electrical measurements showing that all MOVPE grown ZnSe layers are semi-insulating. Nevertheless, at high concentrations of shallow impurities energy transfer processes among DAPs can be important, too [7].

5. Conclusion

The analysis of the time behaviour of the DAP luminescence yields a fast and reliable access to impurity concentration and compensation in semiconductors. Under "ideal" conditions (deep defects can be neglected), an accuracy of about 30% can be obtained. Especially helpful is a comparison with electrical data giving the majority constituent (N_A or N_D) and the degree of compensation. In the presence of deep defects, information on the defect density can be obtained too, but a reliable determination of the shallow defect concentration becomes difficult. In general, it should be noted that the analysis of the DAP dynamics gives reliable concentrations in either p- or n-conducting samples but only qualitative arguments in case of dominating deep defects, i.e. semi-insulating samples.

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