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A Quantitative Analysis of Two-Colour Pump and Probe Spectra from Bound Excitons in Compensated II–VI Semiconductors

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Excitonic energy transfer processes were investigated with time-resolved two-colour pump and probe spectroscopy in the ps-region. In highly compensated ZnSe epilayers, characteristic induced absorption and transmission resonances related to donor bound excitons (I_2) and acceptor bound excitons (I_1) could be observed. To explain the experimental results quantitatively a set of coupled rate equations was developed.

The interaction between acceptor and donor-bound excitons has been studied in detail in some II–VI compounds like CdS and ZnSe and has led to new insights into the excitation and emission properties of highly excited semiconductors [1].

As an example we show in Fig. 1 differential transmission (DT) spectra of a ZnSe epilayer for different time delays τ between pump and probe pulses. The probe laser is kept constant at the photon energy of the acceptor-bound exciton line I_1 while the pump energy is tuned over the whole band-edge region of the specimen. Positive DT signals are observed if the pump beam has the photon energy of I_1 of the free excitons and of the band-to-band excitation. In these cases the concentration of neutral acceptors is apparently reduced by creating additional acceptor-bound excitons, leading to an increased transmission of the probe beam. If the pump laser excites the donor-bound exciton line I_2 the DT signal becomes negative, with a decreasing tendency during the first 100 ps. Therefore, the resonant excitation of I_2 leads to an increased number of neutral acceptors.

Restricting us to the interaction between the donor and acceptor bound excitons, the dependence of the DT signal on the delay time τ is shown for a ZnSe layer up to 500 ps in Fig. 2. In both cases a negative DT signal is caused by the pump pulse within a very short time, but there is a striking difference between the two cases, pumping into I_2, probing at I_1 (Fig. 2b or vice versa Fig. 2a). In b) a fast change from negative to positive DT values is visible, whereas in a) only a slow decay of the negative signal is observed.

To perform a quantitative analysis of these spectra and all other experimental observations the following facts have to be taken into account:

1. At the beginning of the two-colour excitation by ps-laser pulses a highly compensated semiconductor contains only a small number of neutral acceptors and donors, responsible for the observed bound exciton absorption lines I_1 and I_2. During each

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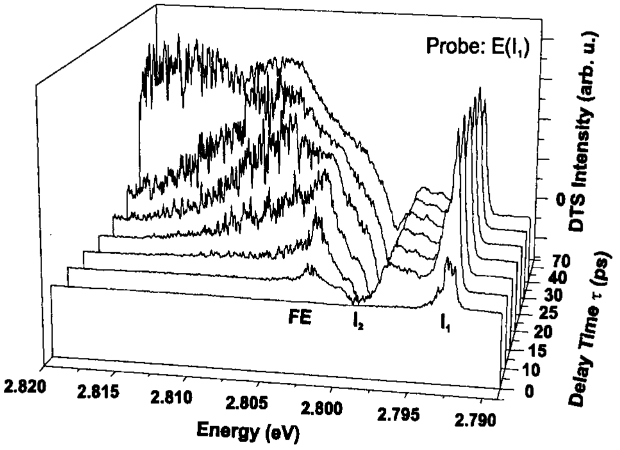

Fig. 1

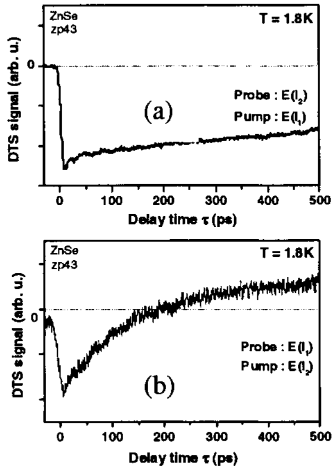

Fig. 2

Fig. 1. Excitation spectra of the differential transmission, probing at $E(I_1)$, for different delay times τ

Fig. 2. Differential transmission as a function of the delay time τ. a) Probe: $E(I_2)$, pump: $E(I_1)$; b) probe: $E(I_1)$, pump: $E(I_2)$

pump period a special recharging process creates additional neutral centers. In the time between two laser pulses (repetition rate: 3.8 MHz) their number is reduced again by different recombination processes. This leads finally to a constant equilibrium value of these centers at the beginning of each new pump pulse.

2. The mentioned recharging process must be in resonance with the bound exciton absorption and is limited to the time of the pump pulse excitation.

3. The decay of the negative DT signal pumping the I_1-resonance and probing the I_2-resonance can be explained by the usual donor–acceptor pair recombination (DAP).

4. The decay of the negative DT signal pumping the I_2-resonance and probing the I_1-resonance is governed by an energy transfer from donor-bound to acceptor-bound excitons.

5. The recharging process is assumed to be a two-step transition, exciting firstly a bound exciton at a neutral center and secondly a bound biexciton, which decays very fast into a bound exciton and a neutralized donor–acceptor pair.

6. One single pump laser pulse changes the initial concentrations of neutral donors and acceptors as well as the concentrations of bound excitons by a small amount only.

Having this in mind we have developed a system of coupled differential equations, providing a solution which explains all major observations with high accuracy. For the more complicated case of pumping into the I_2 and probing the I_1 the rate equations read

$$\frac{\mathrm{d}N_\mathrm{D}}{\mathrm{d}t} = c_\mathrm{D} I_\mathrm{p} d - (\delta_\mathrm{D} + \mu a_0)\, N_\mathrm{D}\,,$$

$$\frac{\mathrm{d}d}{\mathrm{d}t} = -c_\mathrm{D} I_\mathrm{p} d + \left(\delta_\mathrm{D} + \gamma_\mathrm{D} I_\mathrm{p} + \mu a_0\right) N_\mathrm{D} - \varepsilon d_0^2\,,$$

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \left(\gamma_\mathrm{D} I_\mathrm{p} - \mu a_0\right) N_D + \delta_\mathrm{A} N_\mathrm{A} - \varepsilon a_0^2 \tag{1}$$

by regarding the neutrality equation for a completely compensated semiconductor

$$N_A - N_D = d - a : \frac{dN_A}{dt} = \mu a_0 N_D - \delta_A N_A \,.$$

Equation (1) is a set of differential equations linear in the variables a, d, N_A and N_D, being the concentrations of acceptors, donors, acceptor-bound excitons and donor-bound excitons, respectively. The concentrations of a and d for $\tau = 0$ are identical and denoted with a_0 and d_0. The term $c_D I_p d$ is related to the excitation of donor bound excitons by the pump laser pulse with intensity I_p and an absorption factor c_D. The expressions $\delta_D N_D$ and $\delta_A N_A$ stand for the annihilation process of bound excitons at donors and acceptors, respectively. The transfer process from excitons, bound at neutral donors to neutral acceptors, is represented by $\mu a_0 N_D$. The most interesting term is represented by $\gamma_D I_p N_D$, the mentioned two-step recharging process, described in point 5 of our general discussion. The term $\varepsilon_0 d_0^2 = \varepsilon_0 a_0^2$ in the lower equations stands for the DAP recombination process. It is a very crude approximation but sufficient for the time scale of our experiments (some hundred ps). During the much longer time, given by the reciprocal repetition rate of the laser pulses (some hundred ns), the DAP-recombination brings the number of neutral acceptors and donors back to their initial values $a_0 = d_0$.

The formalism of Eq. (1) can also easily be used to describe the second case of our excitation condition when the pump beam has the photon energy of I_1. We have only to set the term $\mu a_0 = 0$ and to replace $a \leftrightarrow d$ and $N_A \leftrightarrow N_D$. The proportionality factors c_D and γ_D have now the subscripts A. As a consequence of the missing energy transfer of bound excitons the concentration of donor bound excitons N_D becomes zero and Eq. (1) is reduced to only two independent coupled differential equations.

To solve the differential Eq. (1) one has to know the time dependence of the short pump pulse $I_p(t)$. One possibility would be to assume a Gaussian pulse shape and to solve the problem numerically. Here we prefer an analytical method making the discussion of our experiments somewhat easier. We postulate a rectangular shape of the laser pulse, starting at $\tau = 0$ and ending at about $\tau_0 = 3$ ps. Then we can divide our result into two parts for $I_p \neq 0$ and $I_p = 0$. In both cases simple analytic expressions arise, containing all the above-mentioned parameters.

Combining these results and assuming that the differential transmission spectra are proportional to the concentrations of donors, respectively, acceptors (x being the thickness of the specimen)

$$\frac{T_D^\tau - T_D^{\tau=0}}{T_D^0} = -c_D x (d_\tau - d_{\tau=0}) \,, \tag{2}$$

$$\frac{T_A^\tau - T_A^{\tau=0}}{T_A^0} = -c_A x (a_\tau - a_{\tau=0}) \,, \tag{3}$$

we receive a good approximation of the following expressions for the τ dependence of the I_2 DT signals starting at the end of the 3 ps short I_1 pump pulse,

$$\frac{\Delta T_D}{T_D^0} = -c_D x d_0 (R_A - B_A \tau) \,, \tag{4}$$

$$R_A = \tfrac{1}{2}\, c_A \gamma_A I_p^2 \tau_0^2 \,,$$

$$B_A = \varepsilon a_0 = \varepsilon d_0 \,,$$

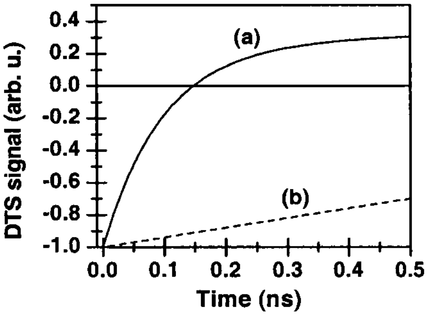

Fig. 3. Calculated differential transmission as a function of the delay time τ (in arb. units); (a) according to Eq. (5) with $c_A x d_0 = 0.25$, $B_D/R_D = 0.6$, $E/R_D = 1.3$, $\delta_A = 0.5\ \text{ns}^{-1}$, $\delta_D + \mu a_0 = 10\ \text{ns}^{-1}$; b) according to Eq. (4) with $c_D x d_0 = 0.1$, $B_A/R_A = 0.6$

and corresponding for the I_2 DT signal,

$$\frac{\Delta T_A}{T_A^0} = -c_A x a_0 (R_D - B_D \tau - E(e^{-\delta_A \tau} - e^{-(\delta_D + \mu a_0)\tau})) , \tag{5}$$

$$R_D = \frac{1}{2} c_D \gamma_D I_p^2 \tau_0^2 ,$$

$$E = \frac{\mu a_0 c_D I_p \tau_0}{\delta_D + \mu a_0 - \delta_A} ,$$

$$B_D = \varepsilon d_0 = \varepsilon a_0 .$$

Comparing experiment (Fig. 2) and calculation (Fig. 3) it is easy to perform a line shape analysis to determine the constants R_i, E, B_i and the decay constants of the bound excitons δ_A and $\delta_D + \mu a_0$, either in arbitrary units or in absolute values, if experimentally possible. To do this we must additionally obtain the absorption factors $c_D x d_0$ and $c_A x a_0$ from the linear transmission spectra of our sample. They range between 0.1 (I_1) and 0.3 (I_2). Then, knowing the concentrations d_0 and a_0 and the intensity of the pump laser I_p, the interesting parameters γ_D and γ_A (bi-exciton absorption) and μa_0 (energy transfer $N_D + a \to N_A + d$) can be determined. A full description of the dynamics of bound excitons in highly excited semiconductors becomes possible.

References

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