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Characterization of ZnSe epitaxial layers by four-wave mixing experiments

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Abstract. Four-wave mixing experiments in two- and in three–beam configurations have been performed at room temperature on ZnSe layers grown by two different techniques: high quality ZnSe layers grown on a GaAs (001) substrate by low-pressure metal-organic vapour phase epitaxy and pulsed laser deposited ZnSe layers on GaAs (001). The GaAs substrates were first removed by polishing and chemical etching. The linear optical properties of the ZnSe epilayers have been studied by photoluminescence, reflection and transmission measurements, in order to analyse the quality of the samples. The third-order nonlinear susceptibility $\chi^{(3)}$ has been measured by degenerate four-wave mixing in the two-beam configuration near the absorption edge at room temperature. $\chi^{(3)}$ values of 3.4×10^{-4} and 1.8×10^{-4} esu respectively have been obtained at about 2.7 eV close to the band edge of the two types of samples.

The dynamics of photocreated free carriers has also been studied in the same samples by four-wave mixing experiments in the three-beam configuration at room temperature. A lifetime $T_1 = 720 \pm 20$ ps and an ambipolar diffusion coefficient $D_a = 5.0 \pm 0.3$ cm^2 s^{-1} have been obtained for metal-organic vapour phase epilayers and compared with previously published results. The carrier recombination in the laser-deposited samples has been shown to be much faster, probably due to their higher concentration of crystalline defects. For all the samples studied, the homogeneous dephasing time T_2 was found to be shorter (< 2 ps) than the temporal resolution of our experimental set-up.

1. Introduction

Wide-bandgap II–VI semiconductors are promising materials for visible-light-emitting diodes, lasers or for optoelectronic devices. In particular, ZnSe, a semiconductor with a direct bandgap of 2.7 eV at room temperature (RT), is intensively studied as a material for blue light-emitting diodes and lasers (see, for instance, [1, 2]). Therefore, all information about its energy levels, its carrier dynamics and other optical characteristics are very valuable in this context.

In this work, we have performed four-wave mixing (FWM) experiments in two different experimental configurations on ZnSe layers grown by low-pressure metal-organic vapour phase epitaxy (MOVPE) and by pulsed laser deposition (PLD). We first describe, in section 2, the sample preparations and the study of their linear optical properties. The FWM experimental set-ups are sketched in section 3 and, finally, the experimental results are presented, compared with previous measurements and discussed in the last two sections.

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2. Sample preparation and optical characterization

The MOVPE samples as ZnSe epilayers grown on GaAs substrates employing ASM-France OMR 12 equipment [3]. H_2Se (5% in H_2) and triethylamine-dimethylzinc ($Me_2Zn{:}NEt_3$) were used as the Se and Zn precursors respectively [3, 4]. The substrates were (100)-oriented GaAs monocrystalline platelets. The temperature of growth was at about 300 °C, the VI/II ratio was 5 and the pressure 40 Torr. The thickness of the deposited layers was around 3 μm. A detailed analysis of the growth conditions of these samples is given in [3].

The PLD layer has been grown in a vacuum of about 10^{-6} Torr on GaAs substrates at 450 °C using an excimer

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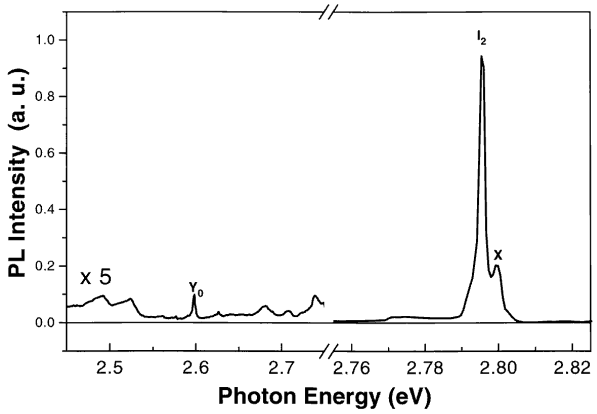

Figure 1. Typical photoluminescence spectrum of an MOVPE ZnSe epilayer grown on a GaAs substrate. The sample cooled down to T = 2 K was excited by the 365 nm UV emission line of a mercury lamp: X is the free-exciton line, I_2 is the recombination of an exciton bound to a neutral donor.

laser (XeCl, 308 nm) as the ablation light source and a Morton International ZnSe target as the matter source. The growth conditions and the detailed characteristics of the samples are given in [5].

Every sample was divided into two parts: one was left as-grown on its GaAs substrate, the second one was completely released from its GaAs substrate. This was necessary since in the transient FWM experiments presented, the samples have been studied in a transmission configuration and the GaAs substrates (0.5 mm thickness) had to be removed. They were mechanically polished down to 0.1 mm, and then totally taken away by chemical etching with a NH_4OH:H_2O_2 (1:20) solution [4]. The ZnSe layer itself was slightly etched by the same chemical procedure. The final thickness of the samples was about 2.4 and 1.4 μm.

The optical quality of the layers was investigated at pumped liquid helium temperature (2 K) by photoluminescence (PL) and reflection (R) measurements. Moreover, the transmission (T) spectra were recorded for the samples released from their substrates.

Figure 1 shows the PL spectrum at 2 K of a characteristic MOVPE sample. The near-bandgap emission (NBE) lines corresponding to the free and bound excitons (on shallow traps) are more intense than those due to deep-level centres. In contrast, no NBE luminescence was observed for the PLD samples. The transmission, reflection and PL spectra at 2 K of the MOVPE sample presented here can be found in a previous paper (they correspond to the sample 5 of [4]). The absorption spectrum at room temperature of the PLD sample is given in [5].

No excitonic structures were observed in the transmission spectra at room temperature since these quasi-particles strongly interact with phonons in II–VI compounds.

3. Experimental set-up

In the FWM experiments at room temperature, we used a pair of dye lasers with Coumarin 47 in ethanol (0.3 g l^{-1}) as the active medium, synchronously pumped by the third harmonics of a train of infrared pulses emitted by an active/passive mode-locked Nd:YAG laser. A single infrared pulse was selected from the train of pulses through a Pockels cell and amplified. The third harmonics of this single pulse was then used to pump dye amplifiers for the two dye lasers. Pulses of 15 ps duration (FWHM) with a repetition rate of 5 Hz were generated. They could be tuned from 2.6 to 2.75 eV (around the absorption edge of ZnSe).

The output beam of one dye laser was sent through a variable neutral density filter and then split into two beams of equal intensity (these intensities could therefore be changed simultaneously). These two beams, called 'pump' beams, were focused onto the surface of a sample. Their spot size was about 100 μm and their maximum pump density was about 100 kW cm^{-2}. They created a light induced grating (LIG).

In FWM experiments with a two-beam configuration, the signal of first-order self-diffraction on the LIG was measured as a function of the pump intensity and of the time delay between the two pump pulses. An optical multichannel analyser (ARP) was used to detect the intensity of one of the incident pulses, of one of the transmitted ones and of the signal diffracted into the first order.

For FWM experiments in a three-beam configuration, the pulses of the two pump beams were sent in temporal and spatial coincidence onto the sample. The pulses from the second dye laser attenuated to very low levels of intensity were used to test the LIG. The decay of the first-order of diffraction of these 'probe' pulses on the LIG was measured after spatial filtering by varying the delay τ between the pump and probe pulses. This was performed for four different spatial periods Λ of the grating ranging from 3 to 15 μm. They were obtained by changing the angle between the two incident pump beams on the sample.

4. FWM in a two-beam configuration

4.1. Theoretical background

Four-wave mixing is a well-known phenomenon which has been described in detail in several articles and reviews (for instance in [6–8]). We will briefly recall here its main mechanisms and precisley define the physical parameters it gives to characterize our samples. The third-order nonlinear polarization P, induced by the periodic spatial modulation of the electron and hole density created by the interference of two pump laser beams (characterized by their (same) photon energy ($h\nu$), their respective wavevectors K_{1P} and K_{2P} and their electric fields E_{1P} and E_{2P}) reads [6]

$$P = A[E_{1P}(t)E^*_{2P}(t+\tau)]E_{1P}(t) + B(E_{1P}(t)E_{1P}(t))E^*_{2P}(t+\tau) \quad (1)$$

where A and B are linear combinations of the third-order susceptibility tensor elements and τ is the temporal delay between the two laser pulses.

The first and the second terms of equation (1) represent two different processes [7]:

(1) the creation by the two laser beams of a grating of real and/or virtually generated quasi-particles on which each of the two waves is self-diffracted in a background-free direction;

(2) the two-photon absorption of one of the two laser beams and the emission simultaneously induced by the other laser beam in the same direction as the preceding self-diffracted signal.

The periodic spatial modulation of the electron and hole density induces a nonlinear spatial variation of the real index of refraction Δn and of the absorption coefficient $\Delta\alpha$. Near the fundamental absorption edge, the main third-order polarization process is due to the generation of a transient induced grating. The corresponding diffracted signal intensity I_s is given as a function of the incident beam intensity I_p, for a 'thin' grating [7], by the following expression [9, 10]

$$\frac{I_s}{I_p} = \left(\frac{\pi\Delta n}{\lambda} + \mathrm{i}\frac{\Delta\alpha}{4}\right)^2 d_\alpha^2 \exp(-\alpha d) \tag{2}$$

where α is the absorption coefficient of the sample for an incident light beam of wavelength λ, d is the sample thickness and d_α the effective absorption thickness defined as [10]

$$d_\alpha = \frac{1-\exp(-\alpha d)}{\alpha}. \tag{3}$$

For excitation intensities low enough to have only third-order nonlinear effects, we have shown from equation (2) that the induced grating is essentially due to a refractive effect, the contribution of the absorptive one being less than 1%.

Therefore, the variation Δn of the index of refraction can be approximately determined from the diffraction measured efficiency (equation (2)). Furthermore, the nonlinear susceptibility $\chi^{(3)}$ can then be deduced from

$$\Delta n(\mathrm{cm}^{-3}) = \frac{4\pi}{9\times10^4}\frac{1}{n^2\varepsilon_0 c}\chi^{(3)}(\mathrm{esu})I_p(\mathrm{W\ cm}^{-2}). \tag{4}$$

The Kerr index of refraction n_2 is defined as a function of Δn as follows:

$$\Delta n = 4n_2 I_p. \tag{5}$$

Finally, the change of index of refraction n_{eh} per electron–hole (eh) pair and per unit volume of the medium characterizes the nonlinear efficiency of each photon absorbed, independently of the specific character of each sample such as its absorption and the decay time of its nonlinearity [11]:

$$n_{\mathrm{eh}} = \Delta n / N_{\mathrm{eh}} \tag{6}$$

where N_{eh} (cm^{-3}) is the number of eh pairs created per unit volume of sample.

If we now consider the correlation trace $I_S(\tau)$ representing the diffracted signal intensity as a function of the time delay τ between the two incident pump pulses, this trace depends on the coherence time of the laser T_L and on the dephasing time of the material T_2 (sometimes called transverse relaxation time [12]). The final correlation trace is a convolution of the two effects.

4.2. Experimental results

We first studied the dependence of the first-order self-diffracted signal on the pump intensity in order to determine the saturation threshold. In figure 2, we show a typical cubic dependence of the FWM signal I_S on the pump intensity I_P up to 50 kW cm^{-2}, when we excite a typical MOVPE sample of thickness 2.4 μm in its band edge at a photon energy of 2.7 eV at room temperature. At higher pump intensities, the effect saturates. The value of $\chi^{(3)}$ of 3.4×10^{-4} esu has been evaluated according to equation (4) in the region of cubic dependence of the diffracted efficiency for this sample. Its Kerr nonlinear index of refraction n_2 is then equal to 2.1×10^{-6} cm^2 W^{-1}. A number of eh pairs, 1.5×10^{16} cm^{-3}, has been created, well below the Mott density ($\sim 10^{17}$ cm^{-3} as approximated in [13]). Therefore, the change of the refraction index per eh pair and per unit volume n_{eh} for this MOVPE sample is equal to 2.9×10^{-18} cm^3.

The value of $\chi^{(3)}$ of PLD-grown epilayers of ZnSe, measured at a photon energy of 2.7 eV, is considerably smaller (five times less) than those of MOVPE samples. This is certainly due to the poorer quality of these samples.

The values of $\chi^{(3)}$ of the MOVPE samples we have studied are quite high but still smaller than some of the values found in the literature. Indeed, a value of $\chi^{(3)}$ of 6×10^{-2} esu has been measured by a reflection-type polarization spectroscopy performed at 8 K for a 2.4 μm thick MOVPE-grown sample of ZnSe (GaAs) [14]. A value of 3×10^{-6} esu at 77 K in a 0.5 mm thick single crystal has been given in [15]. However, it is difficult to compare these $\chi^{(3)}$ with our results since they were measured under very different conditions. We could have compared the corresponding values of n_{eh} if they had been given in [14, 15].

We have plotted in figure 3 the diffraction efficiency measured as a function of the photon energy of the pump beams for the same MOVPE and PLD samples. We observe a strong maximum of the efficiency at 2.7 eV, when we excite band edge states resonantly. After a low-energy peak at 2.687 eV, not yet explained, a second strong maximum appears about 30 meV below the bandgap. One possible explanation of this low-energy peak is an excitation of electrons to the conduction band with annihilation of LO phonons. The electron–phonon interaction is strong at room temperature. We note an absence of this peak at low temperatures.

We have also measured the diffracted signal intensity from the MOVPE and PLD ZnSe samples as functions of the time delay τ between the two pump pulses (the so-called correlation traces) at a pump density below saturation. A decay time of about 6 ps was obtained for both samples by fitting their correlation traces with a single exponential. But a nearly similar correlation trace and an equal decay time were obtained when replacing the ZnSe samples by a thin cell with rhodamine B dye (see figure 4). As the dephasing time T_2 for rhodamine B is very short (a few hundreds of fs [16]), we could conclude that all the traces measured did in fact correspond to the autocorrelation of pump-laser pulses and that the same decay times measured were simply the coherence time of the dye laser (about 6 ps). We could also

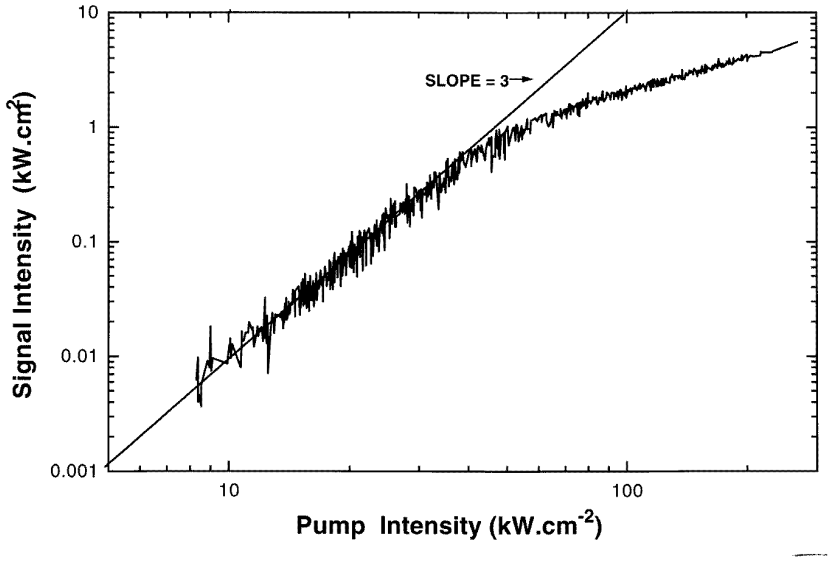

Figure 2. Log–log plot of the intensity of the first-order self-diffracted signal as a function of the pump intensity for the same MOVPE sample at room temperature. The photon energy of the pump laser beams is 2.7 eV.

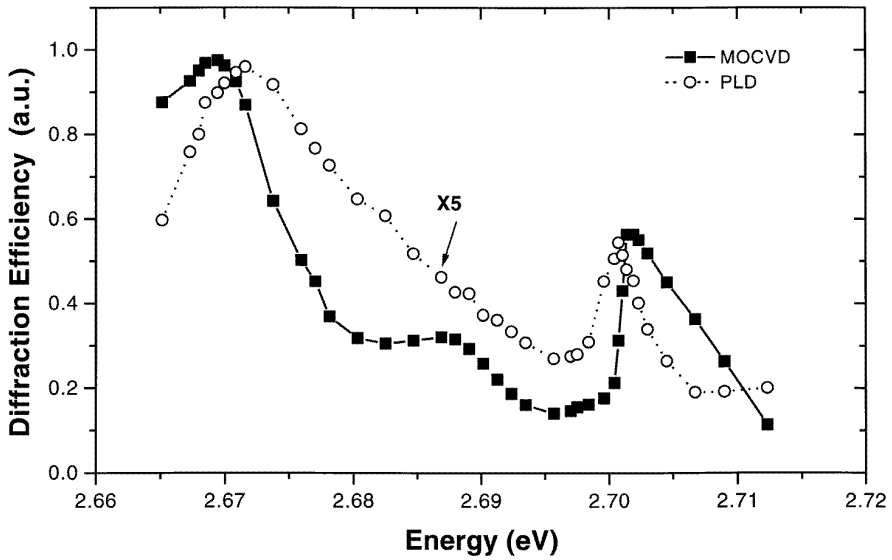

Figure 3. Self-diffraction efficiency plotted as a function of the photon energy of the dye laser for the MOVPE and PLD samples.

note that the dephasing times T_2 of the two ZnSe samples were less than the coherence time T_L of the laser (6 ps) and could therefore not be obtained with our set-up.

5. FWM in a three-beam configuration

5.1. Theoretical background

When two 'pump' beams of photon energy 3 eV (above the bandgap of ZnSe) are sent simultaneously into the same spot of the sample surface, at room temperature, they generate in the sample a spatially periodic modulation of intensity and therefore of free carrier density [17], giving rise to a transient grating, the period Λ of which is determined by the angle θ between the two pump beams

$$\Lambda = \lambda/[2\sin(\theta/2)] \tag{7}$$

where λ is the wavelength of the exciting light.

A pulsed 'probe' beam (emitted by the second dye laser) was directed on the light induced grating (LIG) with a delay time τ. Its photon energy was taken below the gap (2.5 eV) to avoid absorption. The first-order diffracted signal of the 'probe' beam was measured as a function of τ up to 3 ns. As the LIG disappears due to the finite lifetime of the elementary excitations created by the pump pulses and due to their diffusion, the FWM experiments in three-beam configurations reveal the temporal evolution of carrier distributions in semiconductors.

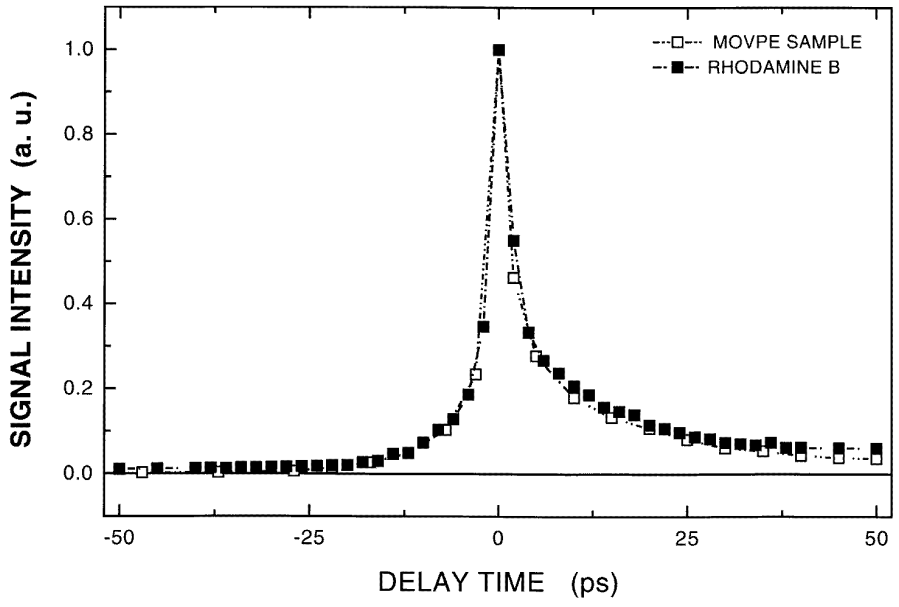

Figure 4. Correlation trace of the self-diffraction signal of the MOVPE sample compared with that of rhodamine B.

The density of carriers created by the optical excitation being much higher than that due to unintentional doping of the sample, we can assume that the local densities of electrons and holes are equal and that the common diffusion of electrons and holes can be described by an ambipolar diffusion coefficient D_a, written as follows [18]

$$D_a = D_e D_h/(D_e + D_h) \tag{8}$$

with D_e the electron and D_h the hole diffusion. For Boltzmann-like carrier distributions, these diffusion constants D_i are directly connected to the carrier mobility μ_i through the Einstein relation

$$D_i = \mu_i k_B T/e \tag{9}$$

where T is the crystal temperature, k_B is the Boltzmann constant and e the elementary electrical charge.

In a simple Drude model, the mobility μ_i depends on the effective electron and hole masses

$$\mu_i = e\tau_{coll}/m_i^* \tag{10}$$

τ_{coll} being the time between two successive collisions of quasi-particles. If we assume an exponential decay of the carrier density described by T_1 and a constant diffusion coefficient D_a, the diffraction efficiency also decreases exponentially. If one takes into account that the diffraction efficiency follows the temporal evolution of the squared carrier density, the inverse of its decay time is given by [11, 19]

$$1/\tau = 2(1/T_1 + 4\pi^2 D_a/\Lambda^2). \tag{11}$$

From the measurement of τ for different grating periods, both T_1 and D_a can be determined.

5.2. Experimental results

In figure 5 we show the exponential decays obtained for the following four periods of the LIG: 25 μm, 16 μm, 10 μm and 5 μm, for the MOVPE and the PLD ZnSe samples. The decay times measured are respectively 365 ps, 330 ps, 315 ps and 230 ps for the first sample and an ultrafast decay time of about 20 ps for the second sample for all four periods of the LIG. We plot in figure 6 the values of $1/2\tau$ against $4\pi^2/\Lambda^2$ for the four different periods Λ of the LIG, for a MOVPE sample.

The ambipolar diffusion coefficient D_a obtained from the slope of the curve in figure 6 is equal to 5.0 ± 0.3 cm^2 s^{-1}. The carrier lifetime T_1 deduced from the extrapolation of the curve of figure 6 to $4\pi^2/\Lambda^2 = 0$ is $720 + 20$ ps.

We can compare our results with previously published ones. For instance, Jarasiunas and Gerritsen [19] have investigated a polycrystalline ZnSe sample about 2.8 mm thick. They measured the self-diffracted signal in a two-beam configuration too. They used a single-mode Q-switched ruby laser ($h\nu = 1.786$ eV, $T_L = 20$ ns) as pump beam to generate transient free-carrier gratings by two-photon absorption. They measured an ambipolar diffusion coefficient value of 2.5 cm^2 s^{-1}, twice as low as our result.

Bolger *et al* [20] have also investigated the carrier recombination processes in a 2 μm thick expitaxial ZnSe layer grown by molecular beam epitaxy (MBE) using the transient-grating technique. They observed that the decay time of the grating was independent of its period and had a constant value of about 500 ps. They could conclude that the diffusion of the free carriers did not contribute efficiently to the erasure of the grating, but that only free carrier recombinations were involved. This means that the erasure time corresponding to the diffusion was small

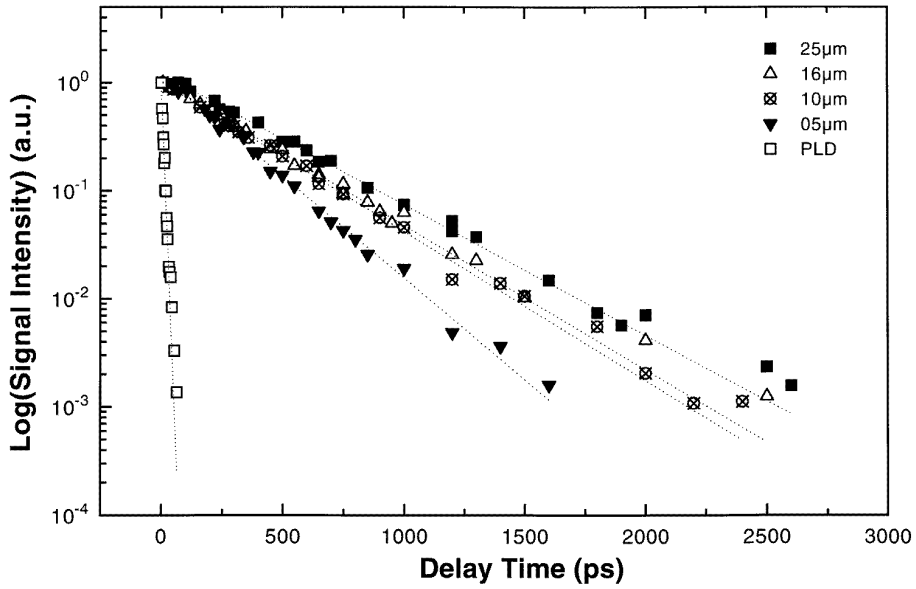

Figure 5. Intensities of the signal of diffraction of a probe beam on gratings of different periods (four for the MOVPE sample, only one for the PLD one as the decay is very fast for these samples).

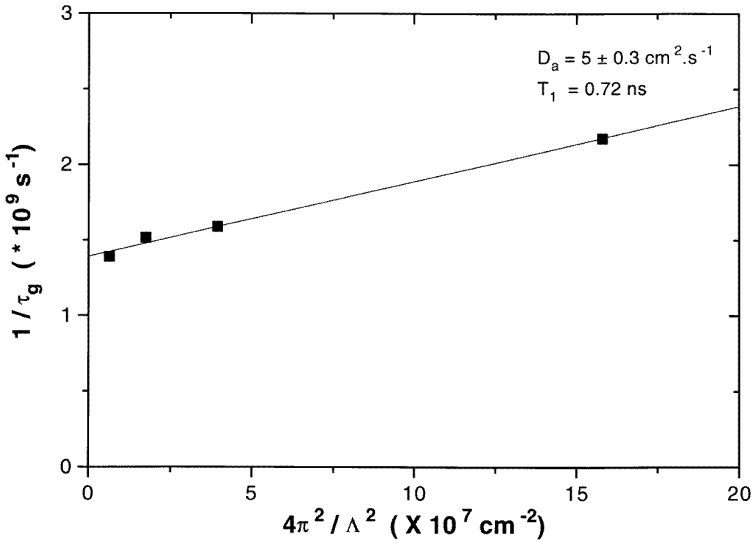

Figure 6. Inverse of the decay times of gratings of different periods plotted as a function of $4\pi^2/\Lambda$ (where Λ is the LIG period). The carrier lifetime T_1 and the ambipolar diffusion coefficient D_a deduced from these curves are indicated on the figure.

compared with the free carrier lifetime in their sample. In our experiments, laser ablated samples behave similarly but have an even smaller carrier lifetime. On the contrary, an equal efficiency has been found for both processes in MOVPE samples. Both parameters T_1 and D_a could be measured precisely.

The comparison of our results with those of other authors emphasizes the role of the sample quality on the carrier dynamics. The free carrier lifetime T_1 and the erasure time corresponding to the diffusion coefficient D_a shortens as the quality of the sample becomes poorer. The MOVPE crystals, which are the purest of the samples we studied, have the higher T_1 and D_a.

It is also interesting to compare the value of the mobility obtained by our method to that determined by Hall and transport measurements for the same MOVPE samples. The electronic mobility μ_b, deduced from the ambipolar coefficient D_a, using Einstein's relation (equation (7)), is of the order of 200 $cm^2\ V^{-1}\ s^{-1}$ for MOVPE samples, when a population of e–h pairs of $1,5 \times 10^{16}\ cm^{-3}$ is photogenerated. The same value of μ_b has been measured by Hall experiments performed on the same MOVPE samples for the same number of carriers [21].

6. Conclusions

We have characterized MOVPE- and LPD-grown samples of ZnSe by four-wave mixing experiments performed in two- and three-beam configuration at room temperature.

In a two-beam configuration, we could determine the third-order nonlinear susceptibility around the band edge absorption. We obtained the susceptibility per e–h pair for different ZnSe layers and compared them.

In a three-beam configuration, we generated gratings of different periods by the excitation of e–h pairs at the resonance. By measuring the temporal evolution of the third-order diffracted signal of these induced gratings, we could determine both the carrier ambipolar diffusion constant and the lifetime of the carriers. We could compare these results with those given by other authors on different samples with the same method. We showed that the mobility of the carriers is 200 $cm^2\ V^{-1}\ s^{-1}$ for a photogenerated population of carriers of $1.5 \times 10^{16}\ cm^{-3}$. This mobility is equal to that measured by Hall experiments on similar MOVPE samples.

Acknowledgments

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References

[1] Nurmikko A V and Gunshor R L 1993 *Physica* B **185** 16
[2] Jeon H, Hagerott M, Ding J, Nurmikko A V, Grillo D C, Xie W, Kobayashi M and Gunshor R L 1993 *Opt. Lett.* **18** 125
[3] Cloitre T, Briot N, Briot O, Gil B and Aulombard R L 1993 *Mater. Sci. Eng.* B **21** 169
[4] Chergui A, Valenta J, Loison J L, Robino M, Pelant I, Grun J B, Levy R, Briot O and Aulombard R L 1994 *Semicond. Sci. Technol.* **9** 2073
[5] Deiss J L, Chergui A, Koutti L, Loison J L, Robino M and Grun J B 1995 *Appl. Surf. Sci.* **86** 149
[6] Bloembergen N 1965 *Nonlinear Optics* (New York: Benjamin) p 13
[7] Eichler H J, Günter P and Pohl D W 1986 *Laser Induced Dynamic Gratings* (Springer Series in Optical Sciences 50) (Berlin: Springer)
[8] Maruani A and Chemla D 1981 *Phys. Rev.* B **23** 841
[9] Miller A, Manning R J, Milson P K, Hutchings D C, Crust D W and Woodbridge K 1989 *J. Opt. Soc. Am.* B **6** 567
Gibbs H M 1985 *Optical Bistability: Controlling Light with Light* (Orlando, FL: Academic) p 137
[10] Chemla D S, Miller D A B, Smith P W, Gossard A C and Wiegmann W 1984 *IEEE J. Quantum Electron.* **20** 265
[11] Othmani A, Plenet J C, Berstein E, Bovier C, Dumas J, Riblet P, Gilliot P, Lévy R and Grun J B 1994 *J. Crystal Growth* **144** 141
[12] Yajima T and Souma H 1978 *Phys. Rev.* B **17** 309
[13] Zimmermann R 1988 *Phys. Status Solidi* b **146** 371
[14] Saiki T, Takeuchi K, Kuwata-Gonokami M, Mutsuyu T and Ohkawa K 1992 *Appl. Phys. Lett.* **60** 192
[15] Ding Y J, Guo C L, Swartzlander G A Jr, Khurgin J B and Kaplan A E 1990 *Opt. Lett.* **15** 143
[16] Sperber P, Weidner M and Penzkofer A 1986 *Ultrafast Phenomena V* (Springer Series in Chemical Physics 46) (Berlin: Springer) p 469
[17] Auston D H, McAfee S, Shank C V, Ippen E P and Teschke O 1978 *Solid-State Electron.* **21** 47
[18] Kippelen B, Grun J B, Hönerlage B and Levy R 1991 *J. Opt. Soc. Am.* B 8 2363
[19] Jarasiunas K and Gerritsen H J 1978 *Appl. Phys. Lett.* **33** 190
[20] Bolger A, Kar A K, Wherrett B S, Prior K A, Simpson J, Wang S Y and Cavenett B C 1993 *Appl. Phys. Lett.* **63** 571
[21] Briot O, Briot N, Cloitre T, Sauvezon R and Aulombard R L 1991 *Semicond. Sci. Technol.* **6** A24