INFLUENCE OF FREE CARRIER CONCENTRATION ON NONLINEAR ABSORPTION OF n-TYPE ZnSe CRYSTALS

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The dependence of nonlinear absorption at 532 nm of n-type ZnSe crystals upon annealing temperature and free carrier concentration is reported. The nonlinear optical absorption as well as the efficiency of degenerate four wave mixing of ZnSe are investigated. It is found that the magnitude of the nonlinear absorption decreases with an increase in the electron concentration. The nonlinear refractive index change is estimated.

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1. Introduction

Wide-gap semiconducting materials are being widely studied as potential components of various optical systems, especially for light-emitting diodes and lasers which operate in the blue-green region of the spectrum, and nonlinear optical devices [1–5]. Knowledge of the absorption coefficients and refractive indexes of crystals under high excitation is especially important in the design and analysis of laser structures and waveguiding devices using these semiconductors in the visible and infrared range. Although the optical properties of ZnSe crystals have been well established recently, little is known about their nonlinear properties versus concentration of free carriers. The nonlinear optical properties of ZnSe crystals with different free carrier concentrations are studied here using picosecond pulses from a mode locked Quantel YAG laser operating at 532 nm. The pulses are nearly Fourier transform limited and the laser operates at the 1 Hz repetition rate.

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2. Preparation of the samples

Intentionally undoped zinc selenide (ZnSe) crystals were grown from the melt by the modified high-pressure Bridgman method under argon over pressure of 11 MPa using ZnSe powder (6N Koch-Light) as a starting material. The crystals were cut into 1 mm thick plates parallel to (111) crystallographic plane and annealed in liquid zinc at different temperatures in the range 750–950°C. After this process, the samples are mechanically polished and chemically etched in the mixture of K_2CrO_7:H_2SO_4:H_2O in proportion 3:2:1, followed by a treatment in CS_2 and boiling 14 n NaOH solution. The final thickness of ZnSe crystals in the measurement is 0.73 mm. The measurements of the resistivity, Hall mobility and carrier concentration were performed by the Van der Pauw method using indium dots as contacts. The influence of annealing temperature on the electron concentration was presented in paper [6] and is displayed in Table.

TABLE

The values of linear and nonlinear absorption coefficients α and β in ZnSe for different annealing temperatures T and free carriers concentration n.

Ref. crystals	T [°C]	n [cm^{-3}]	α [cm^{-1}]	β [cm GW^{-1}]
1	760	1.5×10^{15}	15	27
2	780	3.2×10^{15}	13.2	24.6
3	830	1.5×10^{16}	9.3	17.3
4	870	7.4×10^{16}	5	14.9
5	890	1.3×10^{17}	3.3	13.7
6	920	2.9×10^{17}	2.1	12.3

3. Results and discussion

The following experiments have been performed:

- Pump transmission versus pump fluence: in this case only one beam is sent in the medium.

- Degenerate four wave mixing measurements (DFWM): the signal beam intensity is measured as a function of the exciting beam intensities.

3.1. Nonlinear transmission

The absorption is characterized by the transmission of ZnSe as a function of input intensity. In ZnSe, two-photon absorption is observed at 532 nm as the incident photon energy is lower than the direct band gap energy E_g but greater than $E_g/2$ [7]. The linear absorption is due, among other reasons, to the impurity levels in the band gap. If the beam (1) is sent alone in the medium, its transmission can be expressed as follows:

$$T = \frac{I_1(l)}{I_1(0)} = \frac{\alpha \exp(-\alpha l)}{\alpha + \beta I_1(0)[1 - \exp(-\alpha l)]}, \tag{1}$$

where l is the sample length.

To deduce the absorption coefficients α and β, we perform for all crystals studied the best fit of the experimental data (Fig. 1) using Eq. (1). The obtained results show that the magnitude of the nonlinear absorption decreases with an increase in the electron concentration (Table). Coming out from the first-order perturbation approach which takes into account electron–phonon interaction, an increase in free electron concentration should lead to decrease in corresponding nonlinear optical absorption response.
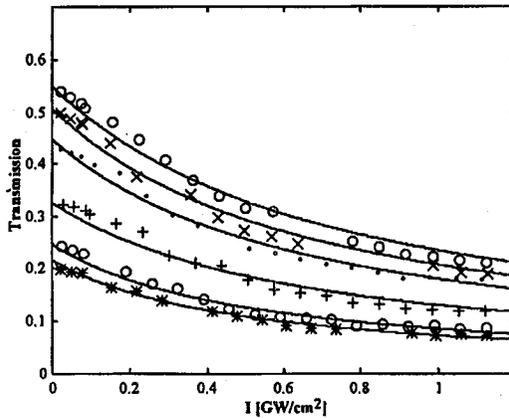
Fig. 1. The nonlinear transmission as a function of the incident beam intensity I_1 in ZnSe for different annealing temperatures (* 760°C, o 780°C, + 830°C, ● 870°C, × 890°C, and o 920°C). All samples reveal a strong nonlinear (two-photon) absorption of light. For all sets of the experimental data we perform the best fit of the data using Eq. (1) to extract the α and β values.

3.2. DFWM

The DFWM experiment with the basic geometry illustrated in Fig. 2 is used to measure the DFWM efficiency of ZnSe crystals. The incident wave intensities verify the relations: $I_1(z = 0) = I_2(z = l)$ and $I_3 = 10^{-2}I_1$. The angle θ between
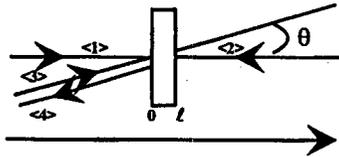
Fig. 2. Geometry of degenerate four wave mixing experiment.
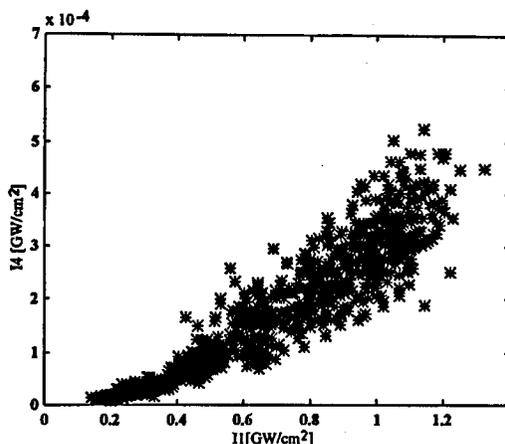
Fig. 3. The fourth beam intensity $I^{(4)}$ with respect to the pump intensity $I^{(1)}$ for ZnSe. * represent the experimental data for n-type ZnSe annealed at the temperature 870°C.

the beams $\langle 1 \rangle$ and $\langle 3 \rangle$ in air is 12°. The beam $\langle 4 \rangle$ intensity is measured as a function of the exciting beam intensity for all crystals studied. As an example we present in Fig. 3 the experimental data for ZnSe crystal annealed at 870°C. The phase conjugation efficiency R is calculated from the propagation equations [8] of the four beams in interaction, using the slowly varying amplitude approximation and taking in account linear and nonlinear absorption and the transformation from the crystallographic axis to laboratory axis. The phase conjugation efficiency R can be expressed as follows:

$$R = \frac{I_4(0)}{I_3(0)} = \frac{K^2}{[q\coth(ql) - \Psi/2]^2}, \tag{2}$$

where

$$q^2 = (\Psi/2)^2 - K^2, \quad K^2 = \left(\frac{4\pi H}{nc}\right)(\chi'^2 + \chi''^2)I_1 I_2,$$

$$H = \frac{12\pi^2}{n\lambda} \quad \text{and} \quad \Psi = -\alpha - 2\beta(I_1 + I_2).$$

χ' and χ'' are the real and imaginary parts of the sum of the four independent non-zero components of the susceptibility tensor $\chi_{xxxx} + \chi_{xxyy} + \chi_{xyxy} + \chi_{xyyx}$. All crystals studied display relatively strong absorption which means $\Psi^2 - 4K^2 > 0$. The value of χ'' is deduced from β, and thus χ can be extracted from the measured values of R compared to formula (2). The estimated value of the real part of $\chi^{(3)}$ for ZnSe annealed at 870°C is $(5.7 \pm 1) \times 10^{-12}$ (e.s.u. system) (nearly 3 times the CS_2 value). The value χ of increases with n. To deduce the sign of real part of $\chi^{(3)}$ we have performed supplementary tests concerning self-defocusing of a single beam travelling through ZnSe [9, 10]. We have found that for ZnSe the sign of real part of $\chi^{(3)}$ is negative.

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Acknowledgment

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