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Laser-Induced Grating in ZnO

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Abstract—**A new simple approach for the calculation of self-diffraction in a thin combined phase and amplitude grating is presented. The third order nonlinearity, the electron-hole recombination time, and the ambipolar diffusion coefficient in a ZnO crystal is measured by means of laser-induced self-diffraction and self-defocusing. It is shown that the index of refraction changes linearly with light intensity and that the intensity dependence of the index of refraction is caused by generation of an electron-hole plasma.**

Introduction

INVESTIGATION of the nonlinear optical properties of materials is a research field in strong development. From a technical point of view, development of materials with large optical nonlinearities opens for new technical concepts with large capacity in the areas of optical signal processing, optical interconnection, and optical switching. From a scientific point of view, the optical nonlinearities are an interesting research field. The nonlinearities give new knowledge and understanding of light–matter interaction and they can be used to measure material parameters such as the electron-hole recombination time and the ambipolar diffusion coefficient.

This paper treats an experimental investigation of some of the properties of the third order optical nonlinearity of ZnO crystals. The laser-induced self-diffraction and self-defocusing techniques are used to measure the light intensity dependence in the index of refraction, the electron-hole recombination time, and the ambipolar diffusion coefficient.

Laser-induced diffraction was first used by Woerdman [1] to investigate electronic processes in Si. The phenomenon of self-focusing/self-defocusing of laser pulses in absorbing media and the ability hereby to determine the sign of the intensity dependent change in the index of refraction have been well reviewed by Shen [2]. Assuming that the laser-induced phase grating originates from electronic excitations Jarasiunas *et al.* [3] developed a method to measure the electron-hole recombination time and the ambipolar diffusion coefficient by analysis of time dependent self-diffraction of laser pulses. Recently, Weber *et al.* [4] have developed a similar method to measure the diffusion length of carriers with a CW laser. Several authors have studied self-diffraction in ZnO. Dean *et al.* [5] have studied a transient phase grating in ZnO induced by two-photon absorption. More recently, the microscopic nature of laser-induced diffraction has been investigated near the band gap at low temperature in ZnO by Kalt *et al.* [6] and in CdSe by Dörnfeld and Hvam [7]. This paper reports the behavior of the electronic optical nonlinearity in ZnO near the band gap at room temperature and therefore constitute a supplement to the beautiful work already published.

The structure of this paper is as follows. First the basic behavior of diffraction in a thin combined phase and amplitude grating is discussed. Subsequently, the phenomenon of self-focusing/self-defocusing in the near-field behind a nonlinear crystal is recapitulated. Thereafter, we present the connection between the time dependence of self-diffraction of laser pulses and the values of the electron-hole recombination time and the ambipolar diffusion coefficient. Finally, follows the experimental work done on ZnO and a discussion of the results.

Basic Concepts

Diffraction in grating structures has been treated extensively in the literature. In [8], [9] excellent reviews are given of the different theories. Unfortunately, these theories do not fully cover the case of interest here where the energy of the exciting laser light is just below the band-gap energy. The absorption of light in the crystal cannot be neglected. Further, in order to evaluate the kind of grating induced by the light in the crystal, i.e., phase, amplitude, or a combination of both from measurement of the diffraction efficiencies, it is necessary to include the possibility of both kinds of gratings in the theoretical diffraction analysis. Therefore an analysis of laser-induced diffraction in a thin grating based on the boundary value method [8] follows. The analysis gives good predictions in the low excitation regime whereas a much more comprehensive analysis is necessary in the highly excited regime [8].

Fig. 1 shows the experimental situation. The two laser beams of equal intensity interfere in the crystal. If it is assumed that the intensity is not affected by the optical nonlinearity, the intensity in the crystal can be written as

$$I = 2TI_i \exp(-\alpha z)(1 + \cos(2\pi x/\Lambda)). \quad (1)$$

T is the intensity transmission coefficient of an air–crystal boundary, I_i is the intensity of the pump laser beams, α is the absorption coefficient at low intensity, and $\Lambda \simeq \lambda/(2\theta)$ is the period length of the optical grating in the crystal. λ is the vacuum wavelength of the laser light.

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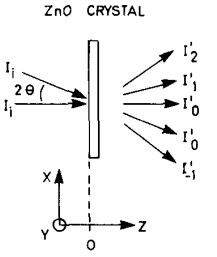


Fig. 1. Laser-induced diffraction in a thin ZnO crystal.

Equation (1) is true when $2\theta << 1$ in agreement with most experimental situations. The pump beams may give rise to a change in the index of refraction and the absorption coefficient proportional to the local intensity. Therefore the index of refraction and the absorption coefficient in the crystal can be written as

$$n(x, z) = n + \frac{\Delta n(z)}{2}(1 + \cos(2\pi x/\Lambda)) \quad (2a)$$

$$\alpha(x, z) = \alpha + \frac{\Delta\alpha(z)}{2}(1 + \cos(2\pi x/\Lambda)). \quad (2b)$$

n is the value of the index of refraction at low intensity, $\Delta\alpha(z)$ and $\Delta n(z)$ are the modulation (peak–peak) of n and α. Since the angle 2θ is small, the diffraction can be calculated as if both pump beams have normal incidence on the crystal surface. When multiple reflections are neglected the geometrical optics gives a simple expression for the amplitude transmission coefficient of the crystal

$$t(x) = T\exp\left(i\int_0^d k\,dz\right) \quad (3a)$$

$$\text{Re}(k) = 2\pi n/\lambda \quad \text{and Im}(k) = \alpha/2. \quad (3b)$$

k is the complex wavenumber in the crystal and d is the thickness of the crystal. In (3a) the light propagation is approximated by a straight line parallel to the z axis which is correct when $\Delta n(z) << n$ and $2\theta << 1$. In complex notation the electric field of each pump beam can be expressed as

$$E_i = \tfrac{1}{2}E_i^k \exp(i(kz - \omega t)) + \text{c.c.} \quad (4)$$

E_i^k is the complex amplitude of the electric field. After transmission the electric field of each pump beam will be

$$E(d < z) = t(x)E_i. \quad (5)$$

$t(x)$ is a periodic function $t(x) = t(x + \Lambda)$ which can be expressed as a complex Fourier series

$$t(x) = \sum_{m=-\infty}^{\infty}\left[\frac{1}{\Lambda}\int_{-\Lambda/2}^{\Lambda/2} t(x')\exp(-i\cdot m2\pi x/\Lambda)\,dx'\right] \cdot \exp(i\cdot m2\pi x/\Lambda). \quad (6)$$

Inserting (4) and (6) into (5) shows that the field transmitted consists of a sum of waves propagating in different directions and the field in the mth order will be

$$E_m^k = \frac{E_i^k}{\Lambda}\int_{-\Lambda/2}^{\Lambda/2} t(x)\exp(-im2\pi x/\Lambda)\,dx \quad (7a)$$

$$\sin\theta_m = \frac{k_m}{k} = m\frac{\lambda}{\Lambda}$$

where

$$k_m = 2\pi\frac{m}{\Lambda}. \quad (7b)$$

θ_m is the angle between the propagation direction of the mth order wave and the pump wave. By using (7a), (3a), (3b), (2a), and (2b), the intensity I_m diffracted in mth order can be calculated. The result is

$$I_m = T_{cr}I_i\exp(-B)\left|J_m\left(\frac{\phi}{2}\right)\right|^2 \quad (8a)$$

where

$$T_{cr} = T^2\exp(-\alpha d) \quad (8b)$$

$$\phi = A + iB \quad (8c)$$

$$A = \frac{2\pi}{\lambda}\int_0^d \Delta n(z)\,dz \quad (8d)$$

$$B = \frac{1}{2}\int_0^d \Delta\alpha(z)\,dz. \quad (8e)$$

T_{cr} is the transmission coefficient of the crystal when the intensity is low, J_m is the Bessel function of order m, and A and B measure the strengths of the phase grating and the amplitude grating in the crystal. Equation (8a) expresses diffraction of one pump beam. From Fig. 1 it is seen that the self-diffracted intensity in a particular order has two contributions, one from each pump beam. The total self-diffraction efficiency in the mth order is thus

$$\eta'_m = \frac{I'_m}{T_{cr}I_i} = \exp(-B)\left[\left|J_m\left(\frac{\phi}{2}\right)\right|^2 + \left|J_{m+1}\left(\frac{\phi}{2}\right)\right|^2\right]. \quad (9)$$

Fig. 2 shows η'_1 for different ratios of $B/|A|$. The phase grating and the amplitude grating clearly influence the diffraction efficiency. When $B/|A|$ increases η'_1 decreases. This is true because a positive amplitude grating causes higher attenuation of the light in the crystal. On the other hand a negative value of $B/|A|$ means that the crystal is bleached and the diffraction efficiency increases more quickly when $|A|$ increases. Note that the diffraction efficiency is independent of the sign of A.

The best way to determine whether the change in the refractive index is positive or negative is self-focusing/self-defocusing [10]. It should be noticed that it is only in the near field close to the sample that self-focusing/self-defocusing can be observed. In the far-field, the beam will defocus for both positive and negative changes in the index of refraction. If the sample is placed at the beam waist a practical guide will be to observe self-focusing/self-de-

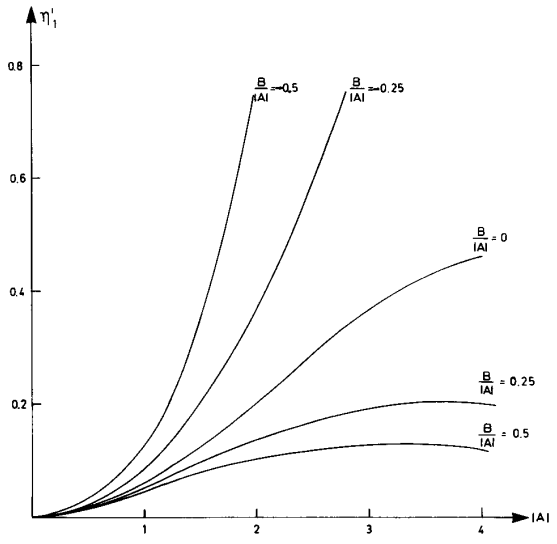


Fig. 2. First order diffraction efficiency in a combined phase and amplitude grating. $B/|A| = 0$ corresponds to a pure phase grating. The light bleaches the crystal when $B < 0$.

focusing about 1/2 to 1 times the Rayleigh length from the sample.

When the photon energy of the exciting light is just below the band gap of an optical allowed transition the two major contributions to the intensity dependence in the index of refraction are from electronic excitation and thermal heating. The contribution to the change in the index of refraction from generation of an electron-hole plasma can be calculated from quantum theory [11]

$$\Delta n = \frac{-Ne^2}{2n\epsilon_o m_{nh}}\left[\frac{1}{\omega_g^2 - \omega^2} + \frac{1}{\omega^2}\right]. \tag{10}$$

N is the concentration of electron-hole pairs, ϵ_o is the vacuum permittivity, m_{nh} is the reduced electron-hole mass, and $\omega_g = E_g/\hbar$ is the band-gap frequency. Equation (10) can be interpreted classically as the change in the index of refraction due to loss of a density of N bound electron-hole oscillators and generation of a density of N free-electron-hole pairs. Equation (10) can also be calculated from the classical Drude and Lorentz models. The result (10) uses the assumption of low excitation, i.e., low density of electron-hole pairs compared to the density of atoms in the crystal. This implies that many body effects such as band-gap renormalization and Coulomb screening are not taken into account.

The connection between N and the intensity I is found as the steady-state solution to the diffusion equation when diffusion can be neglected $N = \eta\alpha\tau_r I/(\hbar\omega)$. η is the quantum efficiency and τ_r is the electron-hole recombination time. The index of refraction can now be written as

$$n(I) = n + n_2 I \tag{11a}$$

$$n_2 = \frac{-\eta\alpha e^2\tau_r\omega_g^2}{2nm_{nh}\epsilon_o\hbar\omega^3(\omega_g^2 - \omega^2)}. \tag{11b}$$

When the photon energy is below the band gap the electronic contribution to the change in the index of refraction is negative whereas thermal heating gives a positive change in n. The thermal change in the index of refraction is difficult to calculate because it depends upon how much of the absorbed light that is converted to heat.

In case the electronic nonlinearity is dominating, the electron-hole recombination time and the ambipolar diffusion coefficient can be calculated from time resolved measurements of laser pulse diffraction [3]. The experimental setup is shown in Fig. 3. The two pump pulses I_A and I_B of equal intensity excite the crystal, and the probe beam $I_i \ll I_A$ is diffracted by the crystal. By moving the mirrors M_1 and M_2 the optical grating period $\Lambda \simeq \lambda/(2\theta)$ can be changed. The purpose is to find an expression for the first order diffracted intensity $I_1(t)$. The concentration of electron-hole pairs is governed by the diffusion equation

$$\frac{\partial N}{\partial t} = \frac{\eta\alpha I}{\hbar\omega} - \frac{N}{\tau_r} + D_a\nabla^2 N \tag{12a}$$

$$D_a = \frac{2D_nD_h}{D_n + D_h}. \tag{12b}$$

D_a is the ambipolar diffusion coefficient and D_n and D_h are the diffusion coefficients of electrons and holes. Calculation of N from (12a) is relieved by using an analytical expression for the laser pulse. $I_A(t) = I_A \cdot (t/\tau_1)^n \exp(-n(t/\tau_1 - 1))$. n is a real number, τ_1 is a time constant, and both parameters are chosen to fit the actual laser pulse. The general solution of (12a) is very complicated. However here it turns out that two important simplifications can be made. The absorption coefficient α is assumed to be small. This assumption leads to neglection of the diffusion of carriers in the z direction compared to diffusion in the x direction and the recombination of carriers in the calculation of N. Furthermore, the influence of surface recombination is not taken into account. This is justified if the period length of the electron-hole plasma is small compared to the crystal thickness when the diffusion of carriers in the x direction involves an equal contribution as the recombination to the destruction of the electron-hole plasma grating. With these assumptions only the recombination and the diffusion of carriers in the x direction is taken into account in the calculation of the time evolution of N. The density of carriers can be expressed as

$$N = \sum_{i=0}^{2} N_i(t)\exp(-\alpha z)\cos(i2\pi x/\Lambda). \tag{13}$$

The excitation intensity is of the form

$$I = 2TI_A(t)\exp(-\alpha z)(1 + \cos(2\pi x/\Lambda)). \tag{14}$$

Now (13) and (14) are inserted in (12a) and the resulting expression have to be fulfilled for all values of t and x. Therefore, the coefficients to cos $(i2\pi x/\Lambda)$ $(i = 0, 1)$ on each side of the sign of the equation must be equal. The diffusion equation can be seperated in two equations,

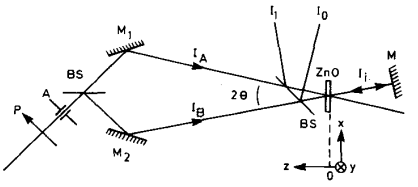


Fig. 3. Experimental setup for time resolved measurements of laser-induced diffraction. *P*: polarizer, *A*: aperture, *BS*: beamsplitter, and *M*: mirror.

one for $N_0(t)$ and one for $N_1(t)$. It is only $N_1(t)$, i.e., the strength of the electron-hole plasma grating that results in the phase grating. The equation for $N_1(t)$ is

$$\frac{dN_1}{dt} = \frac{N_1}{\tau_e} + \frac{2\eta\alpha T I_1(t)}{\hbar\omega} \tag{15a}$$

$$\tau_e^{-1} = \tau_r^{-1} + \frac{4\pi^2 D}{\Lambda^2}. \tag{15b}$$

Equation (15a) and the condition $N_1(t = 0) = 0$ leads to

$$N_1(t) = \frac{2\eta\alpha T}{\hbar\omega} \exp\left(\frac{-t}{\tau_1}\right) \int_0^t I_A(t') \exp\left(\frac{t'}{\tau_e}\right) dt'. \tag{16}$$

In case of a pure phase grating, the diffracted intensity $I_1(t)$ is found from (8a) with $B = 0$. When the phase grating is small ($A < 1$) it is allowed to Taylor expand (8a) to only one term proportional to $A^2(t)$. From (8d) and (10) it is seen that $A(t)$ is proportional to $N_1(t)$. These considerations shows that $I_1(t)$ can be written as

$$I_1(t) = \text{const} \cdot I_i(t) N_1^2(t) \quad \text{when } I_1(t) \ll I_0(t). \tag{17}$$

Fig. 4 shows courses of $I_1(t)$ calculated from (16) and (17) for different values of τ_e. The first order diffraction depends on the value of the effective time constant τ_e given in (15b). When τ_e is small, the first order diffraction $I_1(t)$ is small also. This result can be interpreted in a simple way. When the period length of the electron-hole plasma is made smaller by increasing the angle 2θ in Fig. 3, it follows from (15b) that the effective time constant τ_e decreases below τ_r. τ_e decreases because the diffusion of carriers begins to take a bigger part in the wash-out of the optically induced electron-hole plasma grating. The strength of the induced phase grating becomes smaller and consequently the first order diffraction decreases.

The insert in Fig. 4 of the time delay $\Delta t(I_{i,m}, I_{1,m})$ between the maximum in $I_1(t)$ relative to the maximum in $I_i(t)$ as a function of τ_e. There is an unambiguous connection between the time delay $\Delta t(I_{i,m}, I_{1,m})$ and τ_e.

In the light of the discussed behavior of $I_1(t)$ when the electron-hole plasma grating period is changed, the recombination time and the ambipolar diffusion coefficient are measured easily. For a large grating period (15b) shows that $\tau_e \simeq \tau_r$. $I_i(t)$ and $I_1(t)$ are measured by a sam-

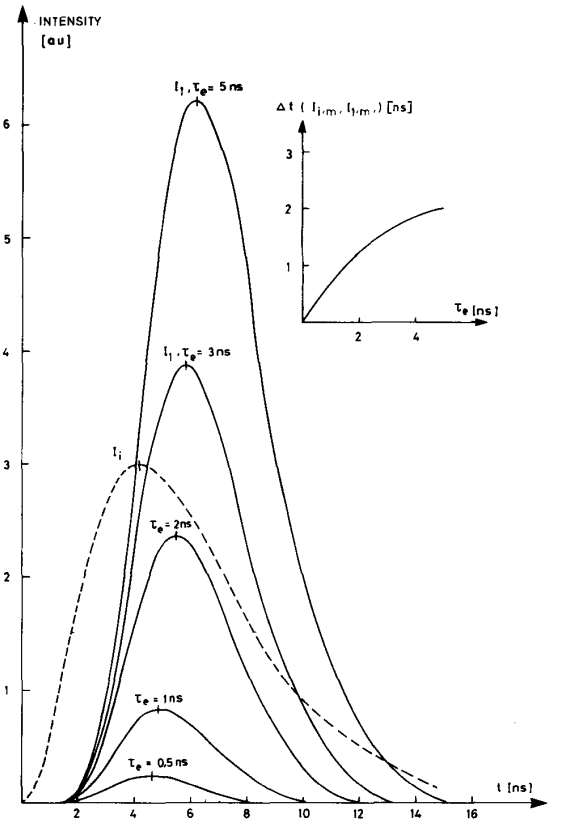


Fig. 4. Courses of $I_1(t)$ for different values of τ_e. $I_i(t)$ is the probe pulse. $\Delta t(I_{i,m}, I_{1,m})$ is the time delay between the moment for maximum in $I_1(t)$ relative to the moment for maximum in $I_i(t)$. Insert shows $\Delta t(I_{i,m}, I_{1,m})$ as function of τ_e.

ple oscolloscope, the time delay $\Delta t(I_{i,m}, I_{1,m})$ is determined and translated to τ_r from the insert in Fig. 4. Next, the maximum value of $I_1(t)$, $I_{1,m}$, is measured for different values of the grating period. From different guesses of D_a and the measured value of τ_r, $I_{1,m}(\Lambda^{-2})$ can be calculated by using (17) and (16). D_a is chosen from the best fit between measured and calculated values of $I_{1,m}(\Lambda^{-2})$.

Experiments

For the experiments, a Lambda Physik EMG 50 excimer laser (XeCl, 308 nm) was used as pump source to a Lambda Physik FL 3002 E dye laser. BBQ diluted in ethanol and toluene [12] was used as dye. Hereby the wavelength could be changed continuously between 380 and 398 nm ($1/e$ power limits). The laser coherence length was 2.5 cm and the pulsewidth was 6.5 ns (FWHM). The diffracted light was measured with reverse biased fast p–i–n photo diodes, Hewlett-Pachard 4220 (response time less than 1 ns). The used ZnO crystal was grown at our laboratory by the vapor phase reaction method [13] and polished to a thickness of 33 μm. The

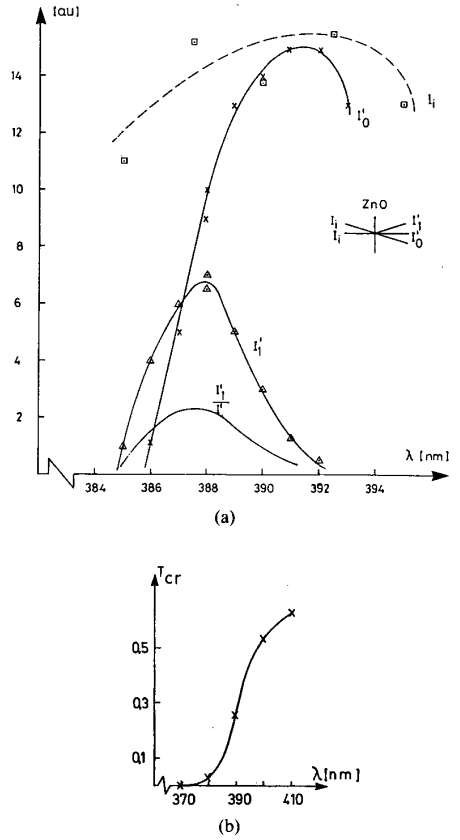


Fig. 5. (a) Spectral dependence of excitation intensity, zero, and first order diffraction intensity in a self-diffraction experiment shown in insert. The grating period was 8.3 μm. I_i, I_0', and I_1' is depicted for different units of the ordinate. The temperature of the crystal was 23°C. (b) Transmission spectrum of the ZnO crystal. $T_{cr} = T^2 \exp(-\alpha d)$.

crystal was n-type and had a free-electron density of 10^{16} cm^{-3}. During the diffraction measurements, the electric field of the laser pulses were perpendicular to the crystal c axis, i.e., $\bar{E} \perp c$ axis. All measurements are made at room temperature.

Fig. 5(a) shows the measured zero and first order self-diffraction intensities as function of the wavelength and Fig. 5(b) shows the low intensity transmission spectrum of the ZnO crystal. First order diffraction was seen from 385 to 392 nm. In this wavelength range the ZnO crystal clearly absorbs the light. The transmission coefficient is $\simeq 10\%$ at 385 nm and it increases to $\simeq 40\%$ at 392 nm. It is noticed that the first order self-diffraction I_1' has maximum value about 388 nm. Above 388 nm I_1' decreases rapidly in spite of the excitation intensity I only changes slightly. What we see is the tail of a resonant behavior of the optical nonlinearity in the crystal. The decrease in I_1' below 388 nm is probably due to the absorption that increases immensely in this wavelength range. The maximum in I_1' at 388 nm is a result of the compromise between large optical nonlinearity and small absorption

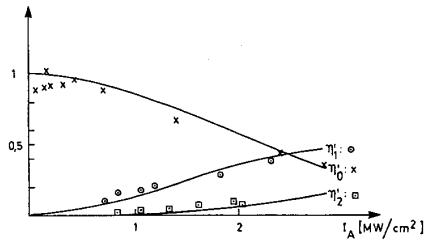


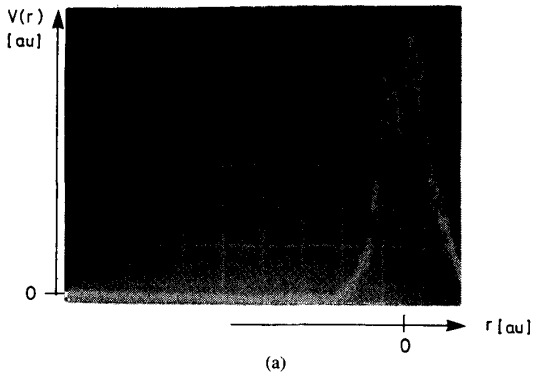
Fig. 6. Measurements of zero, first, and second order diffraction efficiencies as function of the intensity of one of the pump beams. The grating thickness parameter $Q = 2\pi\lambda d/(\Lambda^2 n) = 0.49$. The curves are the theoretical diffraction efficiencies (9) for a pure phase grating when it is assumed that the index of refraction follows (11a) with $|n_2| = 1.7 \cdot 10^{-9}$ cm^2/W.

coefficient. This happens when the crystal thickness $D \simeq \alpha^{-1}$.

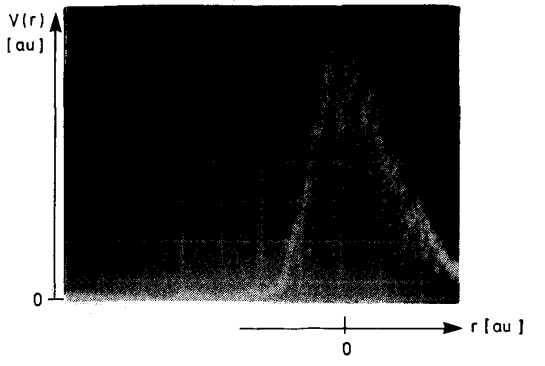
We now turn to a more detailed investigation of the optical nonlinearity at 388 nm. Fig. 6 shows the measured self-diffraction efficiencies as a function of the intensity of one of the pump beams. It is seen that when the pump intensity increases, more and more of the light is diffracted into higher orders. The strength of the grating, i.e., the optical nonlinearity, clearly depends on the intensity of the pump beams. In Fig. 6 the theoretical self-diffraction efficiencies for a pure thin phase grating is shown. The index of refraction is assumed to depend linearly on the intensity as in (11a) with $|n_2| = 1.7 \cdot 10^{-9}$ cm^2/W. The good agreement between the measured and calculated diffraction efficiencies strongly indicates that ZnO is a Kerr medium. The index of refraction changes linearly with intensity. The laser-induced amplitude grating is very small and can be neglected. It is also seen that the change in the index of refraction is very small. For $I = 9$ MW/cm^2 $\Delta n = 1.5 \cdot 10^{-2}$ and $\Delta n/n = 6 \cdot 10^{-3}$. Nevertheless this corresponds to that half of the light is diffracted from zero order to higher orders.

As mentioned previously, self-diffraction only gives information of the numerical change in the index of refraction. The sign of the change is established by self-focusing/self-defocusing. Fig. 7 shows the measured integrated laser pulse profile for low and high peak intensity of the pulse. These measurements were made with a Gaussian beam (beam waist diameter 1 mm, $\lambda = 388$ nm, and Rayleigh length 2.0 m) 0.58 times the Rayleigh length away from the ZnO crystal. The crystal obviously defocuses the laser pulse when the intensity is high. Theoretical calculation of the beam profile of a CW beam behind a nonlinear crystal has been carried out from Fresnel diffraction integral. With use of the experimental beam parameters and distance from the crystal it is only possible to get defocusing at the high intensity when the experimental n_2 value is assumed to be negative. On this basis it is concluded than $n_2 = -1.7 \cdot 10^{-9}$ cm^2/W in ZnO at 388 nm.

A theoretical value of n_2 from generation of an electron-hole plasma can be calculated from (11b). If we use



(a)



(b)

Fig. 7. Integrated laser pulse profile $0.50 \cdot b$ behind the crystal for (a) $I = 0.32$ MW/cm^2, (b) $I = 7.2$ MW/cm^2 in the center of the pulse. Here, I means the maximum intensity of the laser pulse.

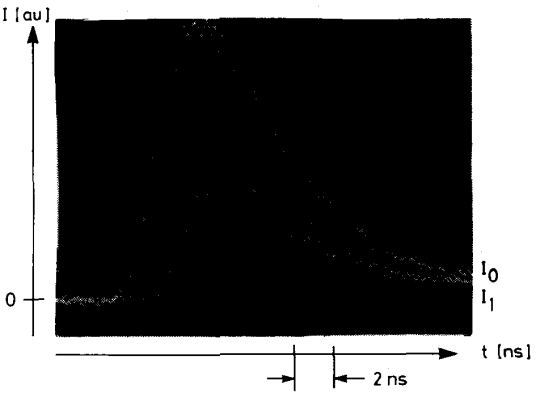


Fig. 8. Measurements of $I_i(t)$ and $I_1(t)$ in Fig. 3 for $\Lambda = 23$ μm. The noise is due to fluctuations in the laser pulse energy.

the ZnO parameter values: $\eta \simeq 1$, $\alpha = 4.2 \cdot 10^4$ m^{-1}, $\tau_r = 1.2$ ns, $\lambda_g = 370$ nm (300 K), $n = 2.4$, $m_{nh} = 0.19$ m_e, we get $n_2 = -1.8 \cdot 10^{-9}$ cm^2/W at 388 nm. From this (surprisingly) good agreement with the measured n_2 it is concluded that the observed self-diffraction in ZnO is caused by generation of an electron-hole plasma in the crystal. Hence, thermal effects are considered to be unimportant.

Knowing that the light-induced phase grating in the ZnO crystal originates from an electron-hole plasma grating, the electron-hole recombination time and the ambipolar diffusion coefficient can be measured with the setup shown in Fig. 3. In Fig. 8 the probe pulse $I_i(t)$ and the diffracted pulse $I_1(t)$ are shown when the grating period is large ($\Lambda = 23$ μm). The pulses are not very well resolved because of pulse to pulse fluctuations in the laser pulse energy. Still we observe a time delay of 0.8 ± 0.8 ns between the maximum values of the two pulses. From the insert in Fig. 4 the recombination time is determined to $1.2\ \text{ns}\ {}^{+1.2\text{ns}}_{-0.6\text{ns}}$.

Fig. 9 shows the measured maximum intensity diffracted in first order $I_{1,m}$ as a function of Λ^{-2}. As expected the first order diffraction decreases when the grating period becomes smaller. In the figure is also shown the theoretical curves of $I_{1,m}$ calculated from (16) and (17). For $\tau_r = 1.2$ ns and $D_a = 1.4$ cm^2/s there are good agreement between theory and all the measured values of $I_{1,m}$ except one. The measured value of $I_{1,m}$ for $\Lambda = 1.7$ μm is most probably wrong because of missing optimal alignment of the pump beams I_A and I_B in Fig. 3. The experiment demands very high stability of the optical components during measurements. The results in Fig. 9 are the best of a series of measurements. The uncertainty in τ_r infects the determination of D_a. For both a higher and a lower value of τ_r it is possible to adapt the calculated values of $I_{1,m}$ to the experimental values for certain values of D_a. The ambipolar diffusion coefficient in ZnO is determined to 1.4 cm^2/s $\,{}^{+1.0}_{-0.5}$ cm^2/s. This value is comparable to what has been measured in other similar semiconductors [3], [4] at room temperature. Measurement of D_a in ZnO by means of laser-induced diffraction is a unique possibility to determine the diffusion coefficient of the holes that can not be measured in any other way.

Laser-induced diffraction is a powerful tool to study intensity dependent changes in the optical properties of materials, to measure the electron-hole recombination time, and the ambipolar diffusion coefficient.

In order to evaluate the third order nonlinearity of a particular semiconductor it is common to introduce a figure of merit given by $n_2/(\alpha\tau_r)$ [14]. The figure of merit of the nonlinearity in ZnO studied here is about 100 times smaller than the figure of merit of the nonlinearity in GaAlAs–MQW's at 848 nm [15]. The nonlinearity in GaAlAs–MQW's is also compatible with a diode laser wavelength whereas there doesn't exist cheap and compact lasers emitting at 388 nm. The technical potential of GaAlAs–MQW's is considered to be much higher than the potential of ZnO. From a scientific point of view it is important to get knowledge of the nonlinear properties of different semiconductors.

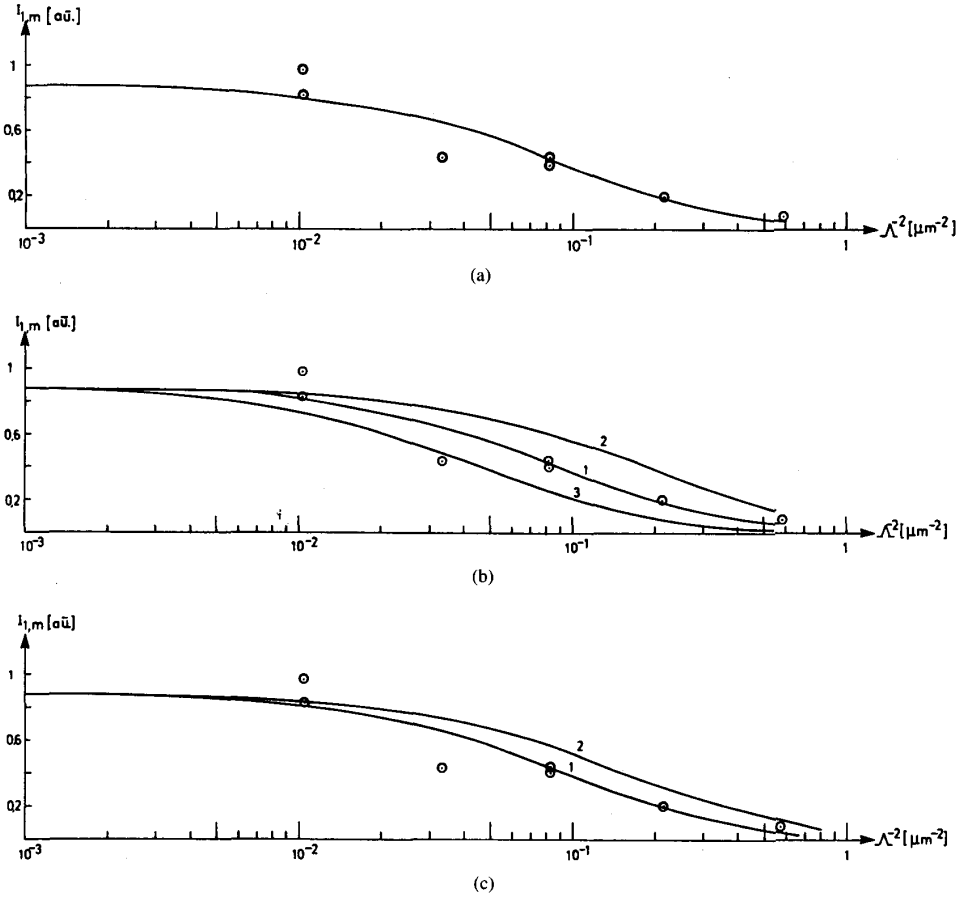


Fig. 9. Measurements of maximum intensity diffracted in first order as function of Λ^{-2}. The curves are theoretical calculations from (17) and (16). (a) $\tau_r = 2.4$ ns and $D_a = 0.9$ cm^2/s. (b) 1: $\tau_r = 1.2$ ns and $D_a = 1.4$ cm^2/s. 2: $\tau_r = 1.2$ ns and $D_a = 0.7$ cm^2/s. 3: $\tau_r = 1.2$ ns and $D_a = 2.8$ cm^2/s. (c) 1: $\tau_r = 0.6$ ns and $D_a = 2.4$ cm^2/s. 2: $\tau_r = 0.6$ ns and $D_a = 1.4$ cm^2/s.

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REFERENCES

[1] J. P. Woerdman, "Some optical and electrical properties of a laser-generated free-carrier plasma in Si," *Philips Res. Rep. Suppl.*, 1971.

[2] Y. R. Shen, "Self-focusing experimental," in *Prog. Quantum Electron.* New York: Pergamon, 1975, vol. 4, pp. 1–34.

[3] K. Jarasiunas and H. J. Gerritsen, "Ambipolar diffusion measurements in semiconductors using nonlinear transient gratings," *Appl. Phys. Lett.*, vol. 33, no. 2, pp. 190–193, 1978.
K. Jarasiunas, S. Stronys, and E. Sirmulis, "Transient grating in InSb at two-photon excitation," *IEEE J. Quantum Electron.*, vol. QE-22, pp. 1341–1343, Aug. 1986.

[4] C. Weber, V. Becker, R. Renner, and C. Klingshirn, "Measurement of the diffusion-length of carriers and excitons in CdS using laser-induced transient gratings," *Z. Phys. B-Condensed Matter*, vol. 72, pp. 379–384, 1988.

[5] D. R. Dean and R. J. Collins, "Transient phase gratings in ZnO induced by two-photon absorption," *J. Appl. Phys.*, vol. 44, p. 5455, 1973.

[6] H. Kalt, R. Renner, and C. Klingshirn, "Resonant self-diffraction from dynamic laser-induced gratings in II/VI compounds," *IEEE J. Quantum Electron.*, vol. 22, p. 1312, 1986.

[7] C. Dörnfeld and H. M. Hvam, "Optical nonlinearities and phase coherence in CdSe studied by transient four wave mixing," *IEEE J. Quantum Electron.*, vol. 25, p. 904, 1989.

[8] H. F. Eichler, P. Günter, and D. W. Pohl, *Laser induced dynamic gratings*, Springer Ser. Opt. Sci. New York: Springer-Verlag, 1986, vol. 50.
A. Miller, D. A. B. Miller, and S. Desmond Smith, "Dynamic nonlinear optical processes in semiconductors," *Adv. Phys.*, vol. 70, no. 6, pp. 697–800, 1981.
C. Klingshirn and H. Haug, "Optical properties of highly excited direct gap semiconductors," *Phys. Rep.* (Review Section of Phys. Lett.) vol. 70, no. 5, pp. 315–398, 1981.
D. Richardson, E. M. Wright, and S. W. Koch, "Raman–Nath theory of degenerate four-wave mixing in semiconductors," *Phys. Rev. A*, vol. 41, p. 1620, 1990.

[9] V. L. Vinetskii, N. V. Kukjtarev, S. G. Odulov, and M. S. Soskin, "Dynamic self-diffraction of coherent light beams," *Sov. Phys. Usp.*, vol. 22, p. 742, Sept. 1979.

[10] E. Van Stryland, H. Vanherzeele, H. Woodall, M. Soileau, A. L.

Smirl, S. Guha, and T. Boggess, "Two photon absorption, nonlinear refraction, and optical limiting in semiconductors," *Opt. Eng.*, vol. 24, pp. 613–623, 1985.

[11] R. K. Jain and M. B. Klein, "Degenerate four-wave mixing in semiconductors," in *Optical Phase Conjugation*, R. A. Fisher, Ed. New York: 1983, pp. 307–415.

[12] F. Bos, "Optimation of spectral coverage in an eight-cell oscillator-amplifier dye laser pumped at 308 nm," *Appl. Opt.*, vol. 20, no. 20, pp. 3553–3556, 1981.
H. Telle, W. Hüffer, and D. Basting, "The XeCl excimer laser: A powerful and efficient uv pumping source for tunable dye lasers," *Opt. Commun.*, vol. 38, no. 5–6, pp. 402–406, 1981.

[13] K. F. Nielsen, "Growth of ZnO single crystals by the vapor phase reaction method," *J. Cryst. Growth*, vol. 3, no. 4, pp. 141–145, 1968.

[14] D. H. Auston *et al.*, "Research on nonlinear optical materials: an assessment," *Appl. Opt.*, vol. 26, no. 2, p. 211, 1987.

[15] D. A. B. Miller, D. S. Chemla, D. H. Eilenberger, and P. W. Smith, "Large roomtemperature optical nonlinearity in $GaAs/Ga_{1-x}Al_xAs$ multiple quantum well structures," *Appl. Phys. Lett.*, vol. 41, no. 8, pp. 679–681, 1982.

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