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Two-photon absorption coefficient dichroism in II–VI semiconductor crystals*

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Considering two beams propagate in semiconductor crystal, this paper discusses the polarization dependence of pump beam-induced intensity attenuation of probe beam due to two-photon absorption (TPA). Numerical calculation and experimental measurement demonstrate that TPA coefficient is polarization dependent. For homogeneous materials, probe beam attenuation arises from the imaginary part of diagonal and off-diagonal components of third-order nonlinear susceptibilities.

Keywords: two-photon absorption, semiconductor crystals, nonlinear susceptibility, polarization dependence
PACC: 7865K, 4265

1. Introduction

In recent researches on semiconductor, much attentions have been focused on materials in which below band gap radiation is utilized and nonlinear absorption processes such as two-photon absorption (TPA) are the dominant sources of beam attenuation.[1−5] Considering a light pulse with photon energies fall in the range of $E_g/2 < \hbar\omega < E_g$, where E_g is the optical band gap of semiconductor, we find that the intensity attenuation of incident light mainly comes from TPA process.[6,7] In the process of TPA, two photons are simultaneously absorbed to excite a material system. As a higher order process, the absorption cross section often is many orders of magnitude smaller than that of one photon absorption. Even so, TPA is readily observable with intense lasers and has become a valuable spectroscopic technique complementary to linear absorption spectroscopy.[8−11] From the experimental point of view, a single beam z-scan technique with open aperture is often used to characterize the TPA coefficient of semiconductor crystals.[12−15] Although the technique is simple and effective, only the diagonal element, i.e. β_{xxxx}, can be obtained. In fact, TPA coefficient, β, is a fourth-rank tensor in which off-diagonal elements can be obtained by using two laser beams with different polarization. The pump–probe technique can be used to characterize the TPA by both diagonal and off-diagonal coefficient tensors.[16] It has been noted that the pump–probe signal with parallel polarization configuration is larger than that in perpendicular configuration. Coherent contribution in parallel polarization can be ignored when the intensity ratio between pump and probe beams is larger than 10. The difference of pump–probe signal in parallel and perpendicular polarization configuration originates from the different components in third-order nonlinear susceptibilities. In this article, we use the pump–probe technique to characterize the polarization dependence of TPA coefficient of some II–VI semiconductor crystals, ZnSe, CdS, CdSe and CdTe. The experimental results are consistent with the theoretical prediction.

2. Theoretical treatment

Polarization dependence of TPA process was characterized on pump–probe setup. Firstly, starting from Maxwell equations, we can derive the polarization dependence of probe beam intensity attenua-

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tion. We assume that both pump and probe beam are linearly polarized, and the polarizations are at θ degree with respect to each other. As shown in Fig.1(a), both pump field $E_1(\omega_1)$ and probe field $E_2(\omega_2)$ propagate along z direction. The polarization of $E_1(\omega_1)$ (pump field) is along x-direction, and the polarization of $E_2(\omega_2)$ (probe field) has a θ degree with that of $E_1(\omega_1)$. Without losing generality, we suppose that the angular frequencies and wave vectors for intense pump field and weak probe field are ω_1, k_1 and ω_2, k_2, respectively. By definition ,

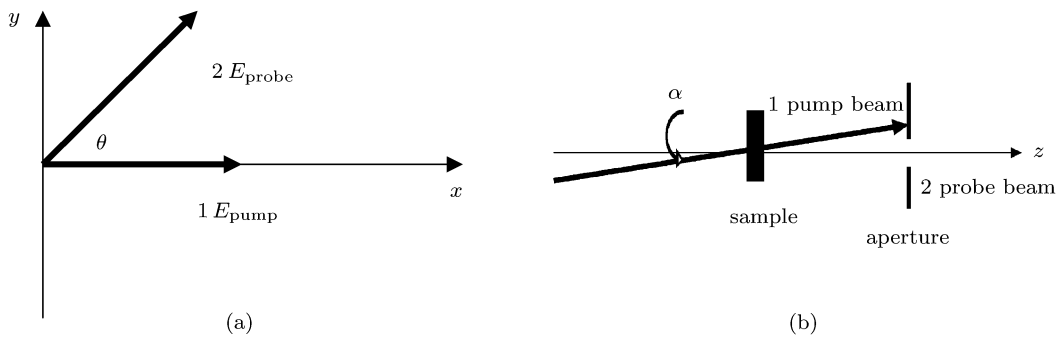


Fig.1. (a) Schematic showing the direction of pump (E_1) and probe (E_2) fields. (b) Geometrical layout of the propagation of pump and probe beams in pump–probe setup.

pump field: $E_1(z,\omega_1) = E_{1x}\boldsymbol{x} = (1/2)A_1(z)\exp[\mathrm{i}(k_1 z - \omega_1 t)] + \text{c.c.}$,
probe field: $E_2(z,\omega_2) = E_{2x}\boldsymbol{x} + E_{2y}\boldsymbol{y} = (1/2)A_2(z)\exp[\mathrm{i}(k_2 z - \omega_2 t)] + \text{c.c.}$,
where, the c.c. stands for complex conjugation, and $A_1(z) = A_{1x}(z)$, $A_2(z) = A_{2x}\boldsymbol{x} + A_{2y}\boldsymbol{y}$, with $A_{2x} = A_2(z)\cos\theta$, $A_{2y} = A_2(z)\sin\theta$. According to wave equation

$$\Big(\frac{\mathrm{d}^2}{\mathrm{d}z^2} - \frac{\varepsilon^{(1)}}{c^2}\frac{\partial^2}{\partial t^2}\Big)E_2 = \mu_0\frac{\partial^2}{\partial t^2}P^{(3)}. \tag{1}$$

Here $P^{(3)}$ is the third-order nonlinear polarization, and for simplicity, we neglect the contribution from second-order derivative. Substituting $E_2(z,\omega_2)$ into Eq.(1), we have

$$\exp(\mathrm{i}(k_2 z - \omega_2 t))\frac{\mathrm{d}A_2(z)}{\mathrm{d}z} = -\frac{\mathrm{i}\mu_0}{k_2}\frac{\partial^2}{\partial t^2}P^{(3)}. \tag{2}$$

The x- and y-component of $P^{(3)}$ can be written as

$$\begin{aligned} P_x^{(3)}(\omega_2) &= 6\frac{1}{2}\frac{1}{2}\frac{1}{2}\varepsilon_0\chi^{(3)}_{xxxx}(-\omega_2;\omega_2,\omega_1,-\omega_1)\cdot A_{2x}(\omega_2)A_1(\omega_1)A_1^*(\omega_1)\exp(\mathrm{i}(k_2 z - \omega_2 t)) \\ &= \frac{3}{4}\varepsilon_0(\chi^{(3)}_{xxyy} + \chi^{(3)}_{xyxy} + \chi^{(3)}_{xyyx})\cdot A_{2x}(\omega_2)A_1(\omega_1)A_1^*(\omega_1)\exp(\mathrm{i}(k_2 z - \omega_2 t)), \end{aligned} \tag{3a}$$

$$P_y^{(3)}(\omega_2) = \frac{3}{4}\varepsilon_0\chi^{(3)}_{yyxx}(-\omega_2;\omega_2,\omega_1,-\omega_1)\cdot A_{2y}(\omega_2)A_1(\omega_1)A_1^*(\omega_1)exp(\mathrm{i}(k_2 z - \omega_2 t)). \tag{3b}$$

Here, we use the relation for isotropic structure

$$\chi^{(3)}_{xxxx} = \chi^{(3)}_{yyyy} = \chi^{(3)}_{zzzz} = \chi^{(3)}_{xxyy} + \chi^{(3)}_{xyxy} + \chi^{(3)}_{xyyx}, \quad \chi^{(3)}_{yyxx} = \chi^{(3)}_{xxyy}.$$

It should be mentioned that all the semiconductor crystals studied here were assumed to be isotropic for simplicity. A^* stands for the complex conjugation of A. Substituting expression of $P^{(3)}$ into Eq.(2), we have

$$\exp(\mathrm{i}(k_2 z - \omega_2 t))\frac{\mathrm{d}A_{2x}(\omega_2,z)}{\mathrm{d}z} = \frac{\mathrm{i}\mu_0\omega_2^2}{k_2}\frac{3}{4}\chi^{(3)}_{xxxx}(-\omega_2;\omega_2,\omega_1,-\omega_1)A_{2x}(\omega_2)|A_1(\omega_1)|^2\exp(\mathrm{i}(k_2 z - \omega_2 t)), \tag{4a}$$

$$\exp(\mathrm{i}(k_2 z - \omega_2 t))\frac{\mathrm{d}A_{2y}(\omega_2,z)}{\mathrm{d}z} = \frac{\mathrm{i}\mu_0\omega_2^2}{k_2}\frac{3}{4}\chi^{(3)}_{yyxx}(-\omega_2;\omega_2,\omega_1,-\omega_1)A_{2y}(\omega_2)|A_1(\omega_1)|^2\exp(\mathrm{i}(k_2 z - \omega_2 t)). \tag{4b}$$

The solutions are

$$A_{2x}(z) = A_{2x}(0)\exp\Big\{\frac{\mathrm{i}\omega_2}{c}\Big[\frac{3}{4}\frac{\omega_2}{\varepsilon_0 c k_2}|A_1|^2\chi^{(3)}_{xxxx}\Big]z\Big\}, \tag{5a}$$

$$A_{2y}(z) = A_{2y}(0)\exp\Big\{\frac{\mathrm{i}\omega_2}{c}\Big[\frac{3}{4}\frac{\omega_2}{\varepsilon_0 c k_2}|A_1|^2\chi^{(3)}_{yyxx}\Big]z\Big\}. \tag{5b}$$

$\chi^{(3)}$can be divided into real and imaginary parts, and can be expressed as $\chi^{(3)} = \mathrm{Re}\chi^{(3)} + \mathrm{i}\mathrm{Im}\chi^{(3)}$, Substituting $\chi^{(3)}$ into Eqs.(5), we have

$$A_{2x}(z) = A_{2x}(0)\exp\Big\{\frac{\mathrm{i}\omega_2}{c}\Big[\frac{3}{4}\frac{\omega_2}{\varepsilon_0 c k_2}|A_1|^2(\mathrm{Re}\,\chi^{(3)}_{xxxx} + \mathrm{i}\mathrm{Im}\,\chi^{(3)}_{xxxx})\Big]z\Big\}, \tag{6a}$$

$$A_{2y}(z) = A_{2y}(0)\exp\Big\{\frac{\mathrm{i}\omega_2}{c}\Big[\frac{3}{4}\frac{\omega_2}{\varepsilon_0 c k_2}|A_1|^2(\mathrm{Re}\,\chi^{(3)}_{yyxx} + \mathrm{i}\mathrm{Im}\,\chi^{(3)}_{yyxx})\Big]z\Big\}. \tag{6b}$$

The probe beam intensity at position z is

$$\begin{aligned} I_{\mathrm{pr}}(z) &= \frac{1}{2}\varepsilon_0 c n_2\Big\{|A_{2x}(z)|^2 + |A_{2y}(z)|^2\Big\} \\ &= \frac{1}{2}\varepsilon_0 c n_2\Big\{|A_{2x}\,(0)|^2\exp\Big[-\frac{3\omega_2^2}{2c^2\varepsilon_0 k_2}|A_1|^2\mathrm{Im}\chi^{(3)}_{xxxx}z\Big] + |A_{2y}\,(0)|^2\exp\Big[-\frac{3\omega_2^2}{2c^2\varepsilon_0 k_2}|A_1|^2\mathrm{Im}\chi^{(3)}_{yyxx}z\Big]\Big\} \\ &= I_2(0)\Big\{\cos^2\theta\cdot\exp\Big[B\mathrm{Im}\chi^{(3)}_{xxxx}z\Big] + \sin^2\theta\cdot\exp\Big[B\mathrm{Im}\chi^{(3)}_{yyxx}z\Big]\Big\}, \end{aligned} \tag{7}$$

with

$$I_2(0) = \frac{1}{2}\varepsilon_0 c n_2|A_2(0)|^2,$$

$$B = -\frac{3\omega_2^2}{2c^2\varepsilon_0 k_2}|A_1|^2.$$

Suppose that the effective thickness of sample is d, then the transmission change for probe beam is

$$\begin{aligned} \Delta T/T_0 &= (I_2(0) - I_2(d))/I_2(0) \\ &= 1 - \cos^2\theta\cdot\exp[B\mathrm{Im}\,\chi^{(3)}_{xxxx}d] \\ &\quad - \sin^2\theta\cdot\exp[B\mathrm{Im}\chi^{(3)}_{yyxx}d]. \end{aligned} \tag{8}$$

In SI unit, the imaginary component of $\chi^{(3)}$ is related to the TPA coefficient β by[17]

$$\beta = \frac{3\pi}{\varepsilon_0 n_1 n_2 c\sqrt{\lambda_1\lambda_2}}\,\mathrm{Im}\chi^{(3)}. \tag{9}$$

It is seen that different elements in TPA coefficient tensor can be obtained by changing the relative polarization between pump and probe field. For parallel configuration $\theta = 0$, only the diagonal term $\chi^{(3)}_{xxxx}$ is remained, and for perpendicular configuration $\theta = \pi/2$, only the off-diagonal term $\chi^{(3)}_{xxyy}$ is retained. Both diagonal and off-diagonal terms are retained for θ taking the values between 0 and $\pi/2$.

During the measurement as shown in Fig.1(b), two beams with the same centred frequencies propagate at a small angle α ($\alpha \sim 5^\circ$) with each other. Therefore, it can be further assumed $k_1 \approx k_2 \approx k$. Applying the conditions $\omega_1 = \omega_2 = \omega$ and $k_1 \approx k_2 \approx k$ to the Eqs.(8) and (9), and substituting Eq.(9) into Eq.(8), we can rewrite the transmission change of probe beam as

$$\Delta T/T_0 = 1 - [\cos^2\theta\mathrm{e}^{-\beta_{xxxx}I_1 d} + \sin^2\theta\mathrm{e}^{-\beta_{yyxx}I_1 d}]. \tag{10}$$

Here, β, I_1 and d are in units of cm/GW, GW/cm^2 and cm respectively. In general, the terms $\beta I_1 d \ll 1$, the exponential terms on the right hand of Eq.(10) can be expanded into Taylor series, after ignoring the higher order terms, transmission change of probe beam for the cases of parallel ($\theta = 0$) and perpendicular ($\theta = \pi/2$) configuration can be written as

$$\Delta T \propto \beta I_1 I_2 d, \tag{11}$$

where, β stands for β_{xxxx} and β_{yyxx} in parallel and perpendicular configuration. Diagonal element β_{xxxx} and off-diagonal element β_{yyxx} can be independently determined through Eq.(11). Inset of Fig.2 shows the pump beam intensity dependence of transmission change in probe beam, it is seen that transmission change of probe beam is almost proportional to the pump beam intensity up to 2 GW/cm^2, which indicates that the approximation in Eq.(11) is reasonable

under pump intensity about 1 GW/cm^2.

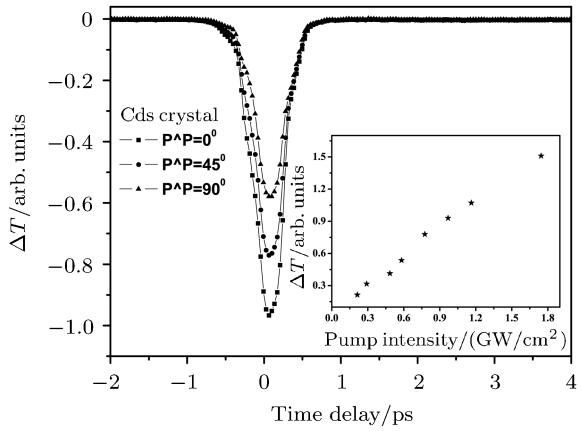


Fig.2. Transient transmission changes of probe beam with relative polarization between pump and probe field at parallel (square), 45 degree (circle) and perpendicular (triangle) configuration. The inset shows the pump density dependence of probe beam transmission changes with parallel polarization for CdS crystal.

3. Experimental results and discussions

Degenerated pump–probe experiment was employed to determine the TPA coefficient dichroism. Briefly, an ultrashort laser pulse with centred wavelength at 800 nm, pulse duration of 200 fs and repetition rate of 82 MHz was generated from a Ti: sapphire laser (Spectra-Physics, Tsunami). The laser beam was divided into pump beam and probe beam by a beam splitter, and the ratio of pump-to-probe power was set to be 20:1. The pump beam travelled through a chopper, a computer-controlled delay line, and the reflected probe beam went through a quarter-wave plate and polarizer$P1$for adjusting the polarization with respect to that of the pump beam freely. Two beams were focused by a lens of 5 cm focal length and overlapped on the same spot of the sample with a spot size about 50 μm. The transmitted light passed through a proper neutral attenuator and was detected by a photodiode connected with lock-in amplifier.[18]

Figure 2 displays the temporal evolution of transient transmission change for 0.5 mm-thickness CdS crystal under parallel, 45° and perpendicular polarization, respectively. The three curves are very similar with parallel polarization having a larger signal and perpendicular polarization having weaker signal. Around zero delay time, the signals show an abrupt decrease below baseline and followed by an abrupt rise. All signals are nearly symmetric with a peak centred at zero delay point, and the full width at half maximum (FWHM) of the peak is almost the same as that of the pulse duration, which indicates that the free carriers absorption can be neglected under the pump intensity of 1 GW/cm^2 and below. The negative change at zero delay time is identified as due to TPA since the energy of two 800 nm photons (3.1 eV) is greater than the band-gap energy of CdS (2.42 eV). The value of β_{xxxx} for the CdS crystal was reported to be 6.4 cm/GW with a 120 fs pulse at 780 nm.[19] With this reference value, the off-diagonal element value, β_{yyxx} for CdS, was measured to be 5.8 cm/GW. And also, the values of β_{xxxx} and β_{yyxx} for CdSe, ZnSe and ZnTe crystals can be determined through Eq.(11) under same experimental condition. Table 1 presents the measured values of TPA coefficients of the four crystals.

Table 1. The measured values of β_{xxxx} and β_{yyxx} for CdSe, ZnTe, CdS and ZnSe semiconductor crystals.

Material	Band gap energy (at 300K)/eV	β_{xxxx}/(cm/GW)	β_{yyxx}/(cm/GW)
CdSe	1.74	28.6	22.5
ZnTe	2.26	4.9	2.1
CdS	2.42	6.4	5.8
ZnSe	2.58	4.1	1.8

With the experimental data of β_{xxxx} and β_{yyxx}, the polarization dependence of probe beam transmission changes can be obtained from Eq.(10), and the results are shown in Fig.3. The scattering data are experimental measurement and the solid line is the theoretical prediction from Eq.(10). For comparison, all data are normalized to the value of parallel polarization configuration. It is seen that theoretical prediction agrees very well with the experimental data. It should be mentioned that diagonal component has relatively larger value than that of off-diagonal component in homogeneous materials. Therefore, the pump–

probe signal shows a stronger signal in parallel polarization configuration than that in perpendicular configuration. Both diagonal and off-diagonal elements have contributions to the pump–probe signals for polarization configuration between the 0 and 90°. For polarization angle at 45°, diagonal and off-diagonal elements contribute equally to the pump–probe signal.

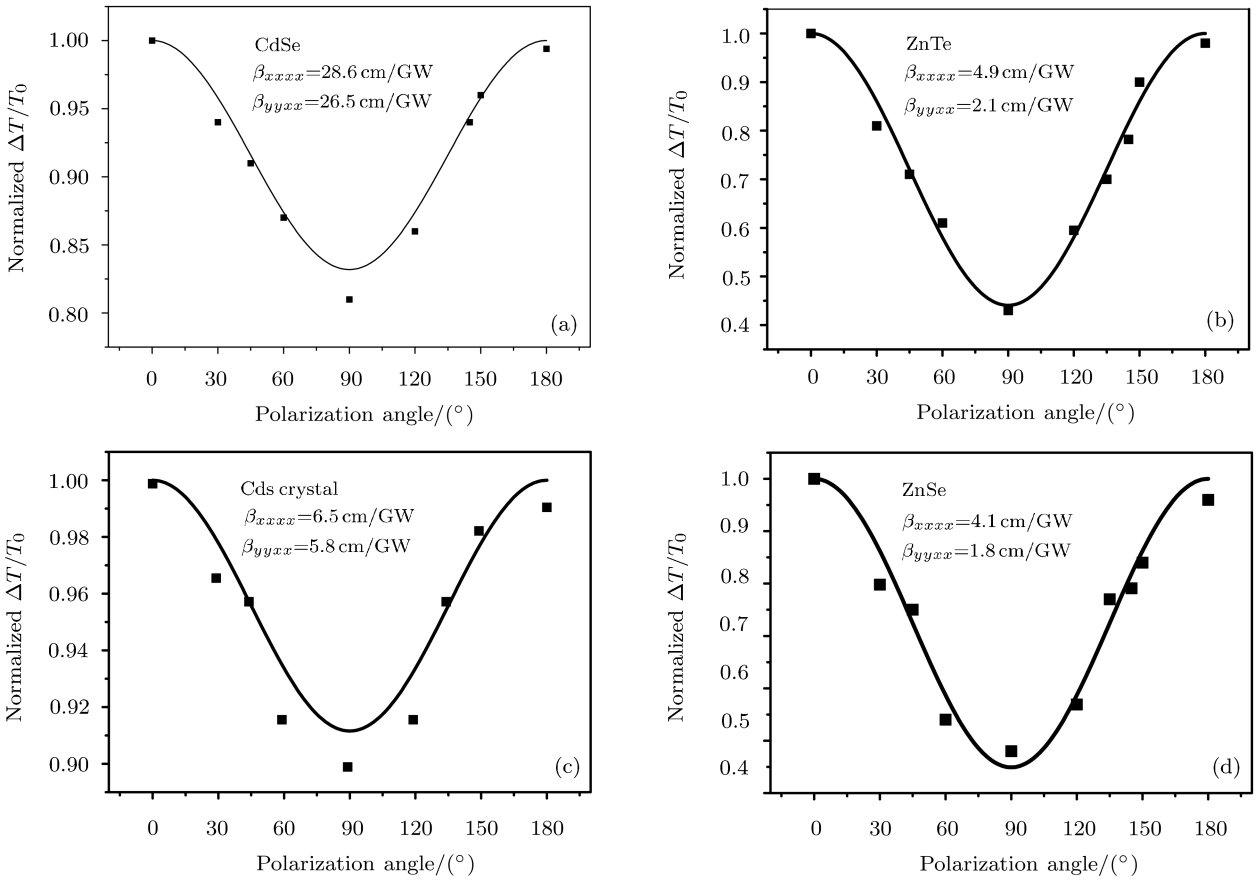


Fig.3. Polarization dependence of probe beam transmission change at zero time delay for (a) CdSe, (b) ZnTe, (c) CdS, and (d) ZnSe. The solid lines are the calculated results according to Eq.(11), the scattered dots are the measured results. All the curves are normalized to the value of parallel polarization configuration.

4. Conclusions

Starting from Maxwell equations, we derive the two beams interaction in semiconductor crystal, and a general expression for polarization dependence of probe beam attenuation due to TPA is obtained. Experimental results on CdSe, CdTe, CdS and ZnSe crystals agree very well with the theoretical prediction. It should be mentioned that the expression (8) is also applicable to any cases of nonlinear absorption, such as saturable absorption and reverse saturable absorption.

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