Two-photon absorption in semiconductors with picosecond laser pulses*

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Single pulses from a well-calibrated mode-locked YAlG:Nd laser have been used to measure the two-photon absorption coefficient at 1.064 μm in several semiconductors. The materials studied are four direct-gap semiconductors, GaAs, CdTe, ZnTe, and CdSe, and one indirect-gap semiconductor, GaP. The results for the direct-gap semiconductors are interpreted with respect to the imaginary part of the third-order nonlinear susceptibility $\chi^{(3)}_{1111}(-\omega,\omega,\omega,-\omega)$. An anisotropy of the two-photon absorption coefficient is observed in GaAs.

I. INTRODUCTION

With the development of quantum mechanics in the late nineteen-twenties it became clear that when electromagnetic radiation interacts with matter, processes involving more than one photon can occur. One such interaction is two-photon absorption (TPA) and the basic theory for this process was formulated by Maria Goppert-Mayer in 1931.[1] The experimental observation of two-photon absorption had to await the development of the laser, however, and the first experimental observation was reported by Kaiser and Garrett in 1961.[2]

Several techniques are used to study two-photon absorption. One technique involves measuring the transmission of the two-photon absorbing material for different incident irradiances. Another involves measuring the luminescence from a material pumped by two-photon excitation, and a third involves measuring the change in the conductivity of a material under two-photon excitation.

There are several reasons for studying two-photon absorption in various materials. Not only can two-photon absorption measurements yield new information on the electronic states in a solid, but also TPA can provide a novel method of exciting large volumes in semiconducting and insulating materials. Such excitation has been used previously to pump semiconductor lasers.[3] Moreover, two-photon absorption can provide a damaging mechanism in materials that are nearly transparent to low-intensity radiation. This will constitute a very serious materials problem to the development of high-power ultraviolet lasers. Finally, two-photon absorption techniques in both liquids and solids have provided useful tools in ultrashort-pulse laser diagnostics.[4]

For comprehensive reviews involving many aspects of two-photon absorption and spectroscopy we refer the reader to Refs. 5 and 6.

There have been several previous studies of TPA in semiconductors, but there are very large differences in the measured values of the TPA coefficients. For example, in GaAs the measured values range from 0.02–5.6 cm/MW at a laser wavelength of 1.06 μm. Values of the TPA coefficient will be presented here for GaAs, CdTe, ZnTe, CdSe, and GaP.

Since two-photon absorption is a nonlinear optical phenomenon, the TPA coefficient can be expressed in terms of nonlinear optical susceptibilities. In Sec. II we outline a theory of TPA and relate this theory to nonlinear optics. In Sec. III the experimental apparatus and procedure are discussed. In Sec. IV the results of the TPA measurements are presented. Finally in Sec. V we discuss the results of our experiments and their relation to other experiments and theory.

II. THEORY

In semiconductors it is possible to have TPA from a single light pulse with angular frequency ω if twice the photon energy, $2\hbar\omega$, exceeds the semiconductor energy gap E_g. The number of two-photon transitions per unit volume per unit time $W^{(2)}$ is given by second-order perturbation theory as

$$W^{(2)} = \frac{(2\pi)^3}{n^2 c^2 \hbar^2}\left(\frac{I}{\hbar}\right)^2 \sum_f |M_{fg}|^2 \,\delta(\omega_{fg} - 2\omega)\,, \qquad (1)$$

where

$$M_{fg} = \frac{e^2}{m^2\omega^2}\sum_i \frac{\vec{p}_{fi}\cdot\hat{a}\,\vec{p}_{ig}\cdot\hat{a}}{\omega_{ig}-\omega}\,.$$

Here n is the index of refraction of the semiconductor, c is the vacuum speed of light, m is the electron mass, e is the electron charge, $\hbar$ is Planck's constant divided by 2π, and I is the power per unit area of the laser radiation. The sums are to be extended over all final states (or bands) denoted by the index f and all intermediate states denoted by the index i. The ground state is denoted by the subscript g, and the transition rate should be averaged over this index if there is more than one possible initial state.

The unit vector $\hat{a}$ is directed along the electric field of the laser, and $\vec{p}_{fi}$ and $\vec{p}_{ig}$ are matrix elements of the momentum operator between respectively the final state and the intermediate state,

and the intermediate state and the ground state. The angular frequencies ω_{fg} and ω_{ig} correspond to the angular frequency differences between the final and ground states and the intermediate and ground states, respectively. These differences, in general, depend on the wave vector $\vec{k}$. If we express the transition rate in terms of the peak electric field amplitude E instead of the irradiance I the transition rate per unit volume becomes

$$W^{(2)} = \frac{2\pi}{\hbar}\left(\frac{eE}{2m\omega}\right)^4 \times \sum_f \left| \sum_i \frac{\vec{p}_{fi}\cdot\hat{a}\,\vec{p}_{ig}\cdot\hat{a}}{\hbar\omega_{ig}-\hbar\omega} \right|^2 \delta(\hbar\omega_{fg}-2\hbar\omega) \ . \quad (2)$$

In addition to the perturbation-theory calculations of $W^{(2)}$ that involve matrix elements between the initial and final unperturbed states, it is also possible to calculate the transition rate by a method that includes the effect of the electromagnetic field on the Bloch wave functions at the beginning of the calculation. Such a theory has been described by Keldysh.[7] In this model the band distortion due to the electromagnetic field is included and the results are applicable to both the optical and the dc limits. Moreover, for higher-order multiple-photon processes the Keldysh model offers both a simple and convenient method of estimating transition rates.

One method of measuring TPA in semiconductors is to measure the attenuation of a beam or pulse propagating through a two-photon absorbing medium. If the pulse irradiance is I, then the pulse is attenuated according to the expression

$$\frac{dI}{dz} = -\alpha I - \beta I^2 \ . \quad (3)$$

Here α is the one-photon absorption coefficient and β is the two-photon absorption coefficient. If we neglect multiple reflections within the medium, the transmitted irradiance is given by the expression

$$I(r, l, t) = \frac{(1-R)^2 I(r, 0, t) e^{-\alpha l}}{1+\beta(1-R) I(r, 0, t)(1-e^{-\alpha l})/\alpha} \ . \quad (4)$$

Here l is the thickness and R is the reflectivity of the medium.

The TPA coefficient β is related to the two-photon transition rate per unit volume by the expression

$$\beta = 2\hbar\omega W^{(2)}/I^2 \ . \quad (5)$$

An alternative formulation of the TPA problem is to start with Maxwell's wave equation and treat TPA as a nonlinear source polarization. For a monochromatic beam the electric field amplitude $\vec{E}(\vec{r}, \omega)$ is determined by the solution to this wave equation given by

$$\nabla\times\nabla\times\vec{E}(\vec{r}, \omega) - (\omega^2/c^2)\,\vec{\epsilon}\cdot\vec{E}(\vec{r}, \omega) = (4\pi\omega^2/c^2)\,\vec{P}^{\rm nls}(\vec{r}, \omega) \ . \quad (6)$$

Here $\vec{\epsilon}$ is the linear dielectric tensor and $\vec{P}^{\rm nls}(\vec{r}, \omega)$ is the nonlinear source dipole moment per unit volume.

For TPA the relevant nonlinear source polarization term is cubic in the electric field and is purely imaginary in character. In centrosymmetric media the relation is

$$P_i^{\rm nls}(\vec{r}, \omega) = i\chi_{ijkl}^{(3)\prime\prime}(-\omega, \omega, \omega, -\omega) \times E_j(\vec{r}, \omega) E_k(\vec{r}, \omega) E_l^*(\vec{r}, \omega) \ . \quad (7)$$

Here $\chi_{ijkl}^{(3)\prime\prime}(-\omega, \omega, \omega-\omega)$ is the imaginary part of the complex third-order nonlinear susceptibility. In non-centro-symmetric media for electric field directions such that second-harmonic generation is not symmetry forbidden there are contributions to $P^{\rm nls}$ not only from the imaginary part of $\chi^{(3)}(-\omega, \omega, \omega, -\omega)$ but also from terms proportional to $\chi^{(2)}(-\omega, 2\omega, \omega)\chi^{(2)}(-2\omega, \omega, \omega)$. For a detailed discussion of these effects see Ref. 8.

We will be interested in determining the TPA coefficient β for laser electric field directions that preclude the generation of second-harmonic radiation. In this case the total nonlinear source polarization is given by Eq. (7). By using the slowly varying amplitude approximation to solve Eq. (6) we can express β in terms of $\chi_{ijkl}^{(3)\prime\prime}(-\omega, \omega, \omega, -\omega)$. The explicit relation between β and $\chi_{ijkl}^{(3)\prime\prime}(-\omega, \omega, \omega-\omega)$ depends both on the crystal class and the laser electric field direction. For example, in a crystal of $\bar{4}3m$ symmetry (e.g., GaAs, CdTe, or ZnTe) with the laser electric field polarized along the [001] direction we find

$$\beta = (32\pi^2\omega/n^2c^2)[3\chi_{1111}^{(3)\prime\prime}(-\omega, \omega, \omega, -\omega)] \ . \quad (8)$$

Here ω is the laser angular frequency, c is the vacuum speed of light, and n is the index of refraction at the laser frequency. Note that we are using the Maker and Terhune[9] convention for the third-order nonlinear susceptibility. In this convention the effective nonlinear susceptibility is $3\chi_{1111}^{(3)\prime\prime}(-\omega;\omega, \omega, -\omega)$ because there are three distinct permutations of the positive and negative frequency arguments. This is the same convention that has recently been used by Levenson and Bloembergen[10] in their study of the resonant behavior of third-order nonlinear susceptibilities by three-wave mixing.

The results that we have heretofore discussed are for pure two-photon transitions. These theoretical results are appropriate for the interpretation of data for which the direct energy gap of the semiconductor is less than the combined energy of two photons. It is also possible to have TPA in an indirect gap semiconductor by the simultaneous emission or absorption of a phonon. Although we

report here TPA from GaP, an indirect gap material, we shall not attempt to present here the theory associated with this third-order process. For a discussion of the theoretical aspects of TPA from indirect gap materials the reader is referred to Refs. 11 and 12.

There are, however, several theoretical aspects of TPA from indirect gap materials that are noteworthy. Firstly, the TPA coefficient β is expected to be a strong function of the temperature because of the phonon participation in the TPA process. Secondly, for the laser intensities and frequency used in this experiment the TPA in indirect gap materials is less than that in direct gap materials.

Until now we have tacitly assumed that absorption by two-photon created excess carriers is negligible. This assumption is not always valid. Usually the dominant absorption by excess carriers comes from free holes; therefore, we can write by analogy with Eq. (3)

$$\frac{dI(\vec{r}, t)}{dz} = -\alpha I(\vec{r}, t) - \beta I^2(\vec{r}, t) - n(\vec{r}, t)\,\sigma_h I(\vec{r}, t) \quad , \qquad (9)$$

where $n(\vec{r}, t)$ is the number of two-photon excited free holes per unit volume, and σ_h is the free hole absorption cross section. The excess hole density $n(\vec{r}, t)$ is determined by the relation

$$\frac{\partial n(\vec{r}, t)}{\partial t} = D_h \nabla^2 n(\vec{r}, t) - \frac{n(\vec{r}, t)}{t_h} + \frac{\beta I^2(\vec{r}, t)}{2\hbar\omega} \quad , \qquad (10)$$

where D_h is the hole diffusion coefficient and t_h is the hole recombination lifetime. In general, one must solve the coupled Eqs. (9) and (10). For picosecond pulses both diffusion and recombination may be neglected; therefore, the hole density is expressed by the relation

$$n(\vec{r}, t) = \int_{-\infty}^{t} (\beta/2\hbar\omega)\, I^2(\vec{r}, t')\, dt' \quad . \qquad (11)$$

Note also that we can solve Eq. (9) for the picosecond laser pulse if we assume that all absorption mechanisms are small. In this case the perturbation solution for the irradiance is given by the expression

$$I(r, z, t) = (1 - R)\Big(I_0(r, 0, t) - \alpha z I_0(r, 0, t) - \beta z I_0^2(r, 0, t) \times (1 - R) - \frac{\sigma_h \beta z I_0(r, 0, t)(1 - R)^2}{2\hbar\omega} \times \int_{-\infty}^{t} I_0^2(r, 0, t')\, dt'\Big). \qquad (12)$$

We have assumed that the incident irradiance is $I_0(r, 0, t)$ and that the irradiated medium occupies the half-space $z \geq 0$.

Finally we note that for picosecond pulses the attenuation due to the excited hole absorption is comparable to the direct two-photon absorption if the irradiance is equal to a critical irradiance I_{cr} given by the expression

$$I_{cr} = 2\hbar\omega/\sigma_h \tau(1 - R) \quad ,$$

where τ is the $1/e$ pulse intensity half duration. The corresponding expression for pulses longer than the hole lifetime is given by a similar expression in which the pulse duration is replaced by the hole lifetime. We conclude, therefore, that in order to obtain pulse attenuation due to pure two-photon absorption one should use the shortest possible pulse duration.

III. EXPERIMENTAL APPARATUS AND TECHNIQUES

A. Laser system

A passively mode-locked YAlG: Nd (neodymium-doped yttrium aluminum garnet) laser system produced the picosecond pulses used in these experiments. A schematic diagram of the experimental apparatus is exhibited in Fig. 1. The laser oscillator is a xenon flashlamp pumped 6-mm-diameter by 7.62-cm-long YAlG: Nd rod in the Brewster-Brewster configuration. The oscillator is simultaneously Q-switched and mode-locked by a flowing saturable absorber (Kodak 9860) in contact with the high reflectivity mirror of the oscillator cavity. The output of the oscillator is restricted to the TEM_{00} mode by a 2 mm diameter aperture. The output of the oscillator consists of a train of picosecond pulses separated by approximately 8 nsec. From this train of pulses a single pulse is selected by a cylindrical-ring electrode potassium-dideuterium-phosphate Pockels cell. This Pockels cell is positioned between crossed Glan prisms, and is activated by a laser-triggered spark gap. The selected laser pulse is subsequently amplified by two YAlG: Nd laser amplifiers.

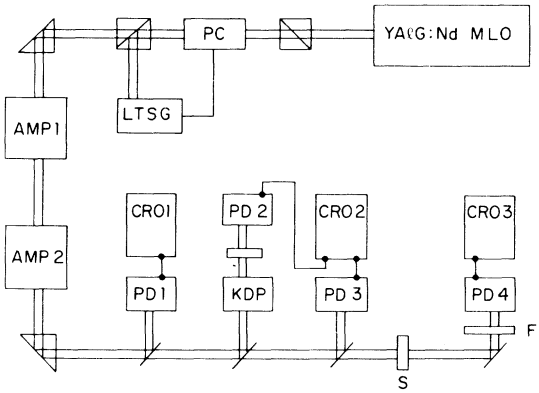

FIG. 1. Schematic diagram of the experimental apparatus. YAlG: Nd MLO, neodymium doped YAlG mode-locked laser; PC, Pockels cell; LTSG, laser triggered spark gap; AMP, neodymium doped YAlG laser amplifier; PD, photodiode; CRO, oscilloscope, F, filter; KDP, second-harmonic generation crystal; S, sample.

A high speed biplanar photodiode PD-1 (ITT F4000) is used in conjunction with CRO-1, a Tektronix 519 oscilloscope, to insure that only a single pulse is selected from the oscillator train of pulses. The calibrated photodiode PD-3 (S-1 response) measures the energy incident on the two-photon absorbing medium, and photodiode PD-4 (S-1 response) measures the energy transmission of this medium. A phase matched KDP (potassium dihydrogen phosphate) second-harmonic generation crystal and photodiode PD-2 (S-20 response) are used together with PD-3 to measure the individual pulse maximum irradiance. This technique is discussed below.

B. Pulse characteristics

For an accurate quantitative measurement of many nonlinear optical properties of materials it is necessary to know the spatial and the temporal form of the pulse incident on the material being studied. The spatial profile of the laser pulse at the site of the two-photon absorbing medium was determined by several independent techniques. In one experiment we employed transverse scans of a 50 μm diameter pinhole coupled to a photodiode. The results of one of these scans are shown in Fig. 2. In another experiment we directly monitored with an oscilloscope the output of a linear array of 256 silicon photodiodes that were irradiated by an attenuated laser pulse. The results of each of these experiments indicated that the spatial form of the incident irradiance was Gaussian, and that the $1/e$ intensity radius was 1.1 ± 0.1 mm.

In order to determine the temporal pulse width two techniques were utilized—a second-harmonic autocorrelation (SHAC) method and two-photon fluorescence (TPF) photography.[13] In the TPF technique the initial pulse is split into two pulses by a beamsplitter, and these pulses are redirected by mirrors to overlap within a two-photon absorbing material such as Rhodamine 6G. The dye fluorescence is photographed, and the pulse duration is determined by the spatial distribution of the exposure produced by the fluorescence track. In the second-harmonic autocorrelation method the pulse is split into two pulses by a Michelson interferometer. These two pulses are collinearly recombined after one pulse has been delayed by a variable amount. The recombined pulses are subsequently directed through a phase matched second-harmonic generation crystal. One plots the second-harmonic output as a function of the delay, and the result of such a plot is exhibited in Fig. 3. The curve is a four parameter least-squares fit to the function, $K_1 + K_2 \exp[-2(z - z_0/2)^2/c^2\tau^2]$. This curve gives a contrast ratio, $(K_1 + K_2)/K_1$, of 2.7 to 1. The results of both the TPF photography and the SHAC method give the average temporal duration full width at half maximum of 30 ± 6 psec, implying an average $1/e$ halfwidth $\langle\tau\rangle$ of 18 ± 3.6 psec.

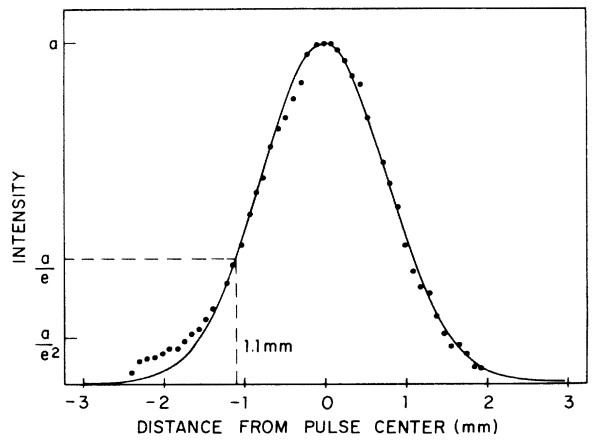

FIG. 2. Irradiance distribution at the sample. Solid line is a Gaussian fit to the data yielding a $1/e$ irradiance radius of 1.1 mm.

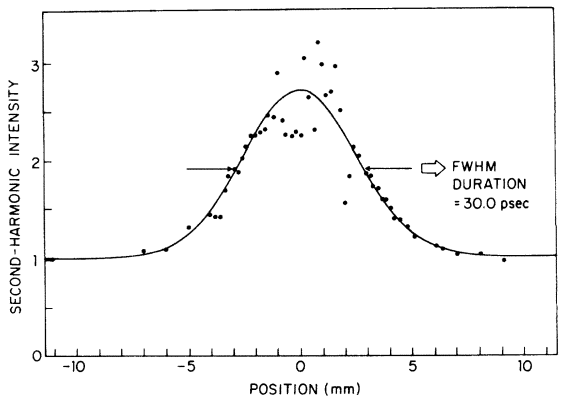

FIG. 3. Results of measurement of the average temporal duration of the laser pulse using a second-harmonic autocorrelation technique. Solid curve is a least-squares fit to the data yielding a FWHM duration of 30 psec and a contrast ratio of 2.7 to 1.

Although single-pulse TPF photographs are possible, the SHAC method is based on using many laser shots. We have found, however, that there are pulse-to-pulse fluctuations in the pulse duration.[14] A convenient way to measure the pulse duration, and thus the pulse irradiance for individual pulses, is to employ a nonlinear technique.[15] This method was first suggested by Glenn and Brienza[16] and involves measuring both the incident pulse energy $\mathcal{E}_f$ at the fundamental frequency and the total energy $\mathcal{E}_{sh}$ created at the second-harmonic frequency from a portion of the incident pulse. For small second-harmonic conversion efficiencies in the phase matched second-harmonic generation

crystal the relation $\mathcal{E}_f^2/\mathcal{E}_{sh}$ is proportional to the product of the incident pulse duration and the incident pulse area. If in an experiment a sufficiently large number of data points are taken so that the ratio $\mathcal{E}_f^2/\mathcal{E}_{sh}$ is meaningful, then this average value can be equated to the product of the known values of the average pulse duration and the average pulse area. Thus we can measure the individual pulse maximum irradiance on a shot-to-shot basis.

C. Procedure

The technique of obtaining the two-photon absorption coefficient β is to measure for each laser pulse the incident pulse energy, the transmitted pulse energy, and the pulse energy created at the second-harmonic frequency. The measurement of the pulse energy at the laser frequency in conjunction with the pulse energy at the second-harmonic frequency allows us to know the maximum pulse irradiance for each laser pulse as described in the previous section. The reciprocal of the energy transmission is then plotted versus the maximum incident irradiance. The incident irradiance was changed by either changing the gain of the amplifiers or by changing the position of the pulse selected from the oscillator train.

IV. EXPERIMENTAL RESULTS

In order to determine β, the two-photon absorption coefficient, we measured the energy transmission for different irradiances. The irradiance exiting a sample of thickness l for a spatially and temporally Gaussian laser pulse is given by the expression

$$I(r,l,t) = \frac{I_m e^{-(r/d)^2} e^{-(t/\tau)^2}(1-R)^2 e^{-\alpha l}}{1+\beta I_m (1-R) e^{-(r/d)^2} e^{-(t/\tau)^2}(1-e^{-\alpha l})/\alpha} \quad . \tag{13}$$

The energy transmission coefficient T is thus

$$T = \frac{\mathcal{E}^{\text{out}}}{\mathcal{E}^{\text{in}}} = \frac{2\pi \int_0^\infty r\,dr \int_{-\infty}^{\infty} I_m(r,l,t)\,dt}{I_m \pi d^2 \pi^{1/2} \tau}$$

$$= 2\frac{\alpha}{\beta}\frac{e^{-\alpha l}}{I_m \pi^{1/2}}\frac{1-R}{1-e^{-\alpha l}} \times \int_0^\infty \ln\left(1+\frac{\beta}{\alpha} I_m (1-R)(1-e^{-\alpha l}) e^{-x^2}\right) dx \quad . \tag{14}$$

Expression (14) represents the basic equation used to derive β from the experimental measurement of T (or T^{-1}) vs I_m. Of course Eq. (14) is only appropriate when the absorption by two-photon excited free holes in negligible. The limitations thus required will be considered separately for each of the materials studied.

The TPA coefficient β was measured for three samples of single-crystal n-type GaAs with the laser electric field along the [001] direction of this zinc-blende material. In all experiments unless otherwise indicated the samples were irradiated at normal incidence along the [110] direction. Sample 1 was Te doped with a carrier concentration of 2×10^{18} cm^{-3}; the thickness was 0.09 cm. The experimental results indicate that $\beta = 0.030 \pm 0.005$ cm/MW with a one-photon absorption coefficient $\alpha = 8.0$ cm^{-1}. Samples 2 and 3 were both cut from the same boule and both had a carrier concentration of 5×10^{16} cm^{-3}. Sample 2 had a length of 0.22 cm, and β was measured to be 0.030 ± 0.005 cm/MW with $\alpha = 0.7$ cm^{-1}. The results for this sample are plotted in Fig. 4. From this figure we note that for incident irradiances above 300 MW/cm^2 there is a small but significant departure of the experimental data points from the theoretical curve. Similar effects were observed in other samples. This departure can be attributed to the free hole absorption, and thus there is an enhanced attenuation of the pulse at high intensities. Another possible explanation is beam distortion due to the real part of the third-order nonlinear susceptibility. This will be considered in Sec. V.

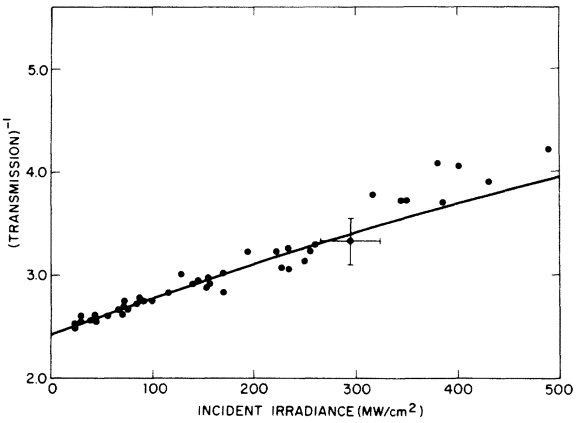

FIG. 4. Plot of reciprocal energy transmission coefficient vs maximum incident irradiance for GaAs. Sample thickness is 0.22 cm, and the laser electric field was polarized along the [001] direction. Theoretical curve is given by Eq. (14) with $\alpha = 0.7$ cm^{-1} and $\beta = 0.03$ cm/MW.

Sample 3 had a length of 1.29 cm; the one-photon absorption coefficient was the same as Sample 2, but the TPA coefficient was found to be 0.023 ± 0.005 cm/MW. The reason that the measured value of β is smaller for the longer sample probably results from the reflection at the exit surface. The reflected wave suffers a π phase change that enhances the total irradiance at and near the exit surface. Since the model that we are using doesn't include the effects of multiple reflections, we can expect the effective TPA coefficients to be slightly smaller for longer crystals.[17]

TABLE I. Various experimental values of the two-photon absorption coefficient β, the linear absorption coefficient α, and the optical electric field direction in GaAs at 1.06 μm and at room temperature.

	β (cm/MW)	α (cm^{-1})	Electric field
Present work	0.023–0.030	0.7–8.0	[001]
Bepko[a]	0.085	···	[001]
Lee and Fan[b]	0.23–0.36	4.0	···
Kleinman *et al.*[c]	0.019–0.045	0.05–4.0	···
Jayaraman and Lee[d]	5.6	3–4	···
Oksman *et al.*[e]	0.2	···	···
Ralston and Chang[f]	0.02	···	···
Arsen'ev *et al.*[g]	0.8	4.0	···
Basov *et al.*[h]	5.0	···	···

[a]Reference 18.
[b]Reference 20.
[c]Reference 21.
[d]Reference 22.
[e]Reference 23.
[f]Reference 24.
[g]Reference 25.
[h]Reference 26.

Finally we observed a small anisotropy of the TPA coefficient in Sample 3. For the laser field along the [110] direction we find that β is approximately 20% larger than when the laser field is along the [001] direction. A similar anisotropy was recently observed in Ref. 18.

A single crystal of high-resistivity ($\rho > 10^8$ Ω cm) n-type CdTe was examined for TPA. The crystal was 0.49 cm in length and was irradiated along the [110] direction with the electric field polarized along the [001] axis. The best fit to the experimental data gives $\alpha = 0.45$ cm^{-1} and $\beta = 0.025 \pm 0.005$ cm/MW.

A sample of 0.10-cm-thick p-type ZnTe was irradiated along the [110] direction with the laser electric field along the [001] direction. The best fit to the data gives $\alpha = 8$ cm^{-1} and $\beta = 0.008 \pm 0.004$ cm/MW.

In addition to the zinc-blende crystals described above we have also measured the TPA properties of CdSe, a wurtzite structure. The sample was 0.385 cm thick, and the incident laser irradiance was directed along the c axis of this hexagonal crystal. The data indicate that $\alpha = 0.2$ cm^{-1} and $\beta = 0.030 \pm 0.005$ cm/MW.

Of the materials considered in this experiment GaP is unique for two reasons. Firstly, at the laser energy of 1.165 eV per photon, GaP does not exhibit a direct-gap two-photon absorption. Instead the transition needs a phonon to participate in the absorption process. Secondly, the only crystal that we had available to us had an orientation such that the laser electric field could not be polarized along the [001] direction. We found that the two-photon absorption coefficient is much smaller in this material than in any of the other materials that we studied. The sample that we used was 4 mm thick with the [111] direction normal to the optically polished surfaces. For our experiment data were taken with the laser electric field along the [110] direction.

In order to measure any change in the transmission coefficient it was necessary to use incident irradiances in excess of 1 GW/cm^2. Since this irradiance is comparable to the critical irradiance I_{cr} for GaP then the effect of free hole absorption must be considered. This was considered in our interpretation of the data, and the TPA coefficient β was determined by comparing the experimental energy transmission coefficient to the theoretical coefficient obtained by integrating Eq. (12) over the spatial and temporal profile of the laser pulse. The free hole absorption cross section was assumed to be 2×10^{-17} cm^2.[19] From our data we find that $\alpha = 0.5$ cm^{-1} and $\beta = 0.0002 \pm 0.0001$ cm/MW.

V. DISCUSSION AND SUMMARY

There are very large discrepancies among the various measurements of the two-photon absorption coefficient β in GaAs as can be seen from Table I.[18,20–26] Our measurements seem to be in closest agreement with those of Ref. 21. It is noteworthy that any spatial or temporal fluctuations in the laser pulses used for the TPA measurements can lead to larger TPA. Thus if the lasers used in some of these other experiments did not produce smooth reproducible pulses, the inferred value of the two-photon absorption coefficient would be larger than the true value.

In Sec. II we discussed the importance of free hole absorption and noted that picosecond pulses are favored over nanosecond pulses for an accurate measurement of the TPA coefficient. The cross sections for free hole absorption were estimated from the one-photon absorption measurements in p-type materials. The results are as follows: 1×10^{-17} cm^2 (GaAs),[27] 4×10^{-17} cm^2 (CdTe),[28] 3×10^{-17} cm^2 (ZnTe),[29] and 2×10^{-17} cm^2 (GaP).[19] There is no known measurement for CdSe. From these values the critical irradiance, I_{cr}, was calculated and except for GaP, as noted above, only data points less than I_{cr} were used to infer the TPA coefficient. If we compare our experiments with others as in Tables I and II we find that our experimental results for the TPA coefficients are among the smallest reported values. Our results for the direct-gap semiconductors are typically within a factor of 2 of the theoretical results obtained using the Keldysh model to calculate the TPA coefficient.

Our experimental results as well as the results based on several theoretical calculations are presented in Table III. For the direct-gap semiconductors the TPA coefficient was measured with the laser electric field polarized along the [001] direction; thus, second-harmonic generation was pro-

TABLE II. Experimental values of the two-photon absorption coefficient β in CdTe, CdSe, ZnTe, and GaP at room temperature. The units are cm/MW.

	CdTe	CdSe	ZnTe	GaP
Present work	0.025	0.03	0.008	2×10^{-4}
Bepko[a]	0.17			
Ralston and Chang[b]	0.2	0.2		
Basov *et al.*[c]		0.95		
Lee and Fan[d]			0.04	
Yee and Chau[e]				1.7×10^{-3}
Bryukner *et al*[f]		0.14		

[a]Reference 18.
[b]Reference 24.
[c]Reference 26.
[d]Reference 20.
[e]Reference 30.
[f]F. Bryukner, V. S. Dneprovskii, and V. U. Khattatov, Kvant. Electron. 1, 1360 (1974); [Sov. J. Quantum Electron. 4, 749 (1974)].

hibited for these materials, and the imaginary part of the third-order optical nonlinear susceptibility $\chi^{(3)}_{1111}(-\omega, \omega, \omega, -\omega)$ at the laser frequency may be inferred from the TPA coefficient.

In GaP several different attenuation mechanisms are possible. In addition to indirect TPA and free hole absorption it is also possible to have second-harmonic generation followed by one-photon absorption for the laser electric field polarized along the [110] direction. Finally since the observed attenuation was very small three-photon absorption was also considered. To predict the amount of three-photon absorption a simple calculation using the Keldysh model shows that three-photon absorption is negligible compared to the other attenuation mechanisms at the irradiances used in this experiment. Moreover, we can calculate the effective TPA coefficient due entirely to second harmonic generation followed by one-photon absorption. We find for GaP at 1.064 μm that $\beta_{SHG}\approx10^{-6}$ cm/MW. This is approximately two orders of magnitude less than the experimental value that we obtain. We conclude, therefore, that the attenuation mechanism is a combination of two-photon absorption across the indirect gap plus linear absorption by the resulting free holes. If the value of the free hole absorption cross section is known, then we may infer the TPA coefficient β from the measured transmission change. This value is reported also in Table III. Our experimental value compares very favorably with the theoretical value given in Ref. 30, but is approximately an order of magnitude less than the experimental value reported in this same reference.

In Sec. IV we noted that at high irradiances there is a departure of the experimental data from the theoretical curve obtained from the lower irradiance data. We noted that one possible explanation for this departure would be beam deformation due to the self-focusing aspect of the real part of the third-order nonlinear susceptibility. In order to estimate this effect we have calculated the beam intensity radius $a(l)$ at the exit surface of the crystal for an input radius a_0. The relation between these radii is given by the following approximation[31]

$$\frac{a(l)^2}{a_0^2}\approx\left[1+\left(1-\frac{P}{P_{cr}}\right)\frac{l^2}{k_0^2a_0^4}\right]. \tag{15}$$

The length of the crystal is l, P is the maximum laser power, and k_0 is the laser wave vector in vacuum. The parameter P_{cr} is the critical power for self-focusing and is given by

$$P_{cr}=c^3/8\omega^2n_2\ . \tag{16}$$

Here c is the vacuum speed of light, ω is the laser

TABLE III. Summary of the experimental results obtained in this work, and the results of several theoretical models.

Material	Index of refraction	β (cm/MW)[a]	$\chi^{(3)\prime\prime}_{1111}(-\omega\,\omega, \omega, -\omega)$ (cm^3/erg)	β (cm/MW), Theory 1[b]	2[c]	3[d]	4[e]
GaAs	3.475	$(2.8\pm0.5)\times10^{-2}$	1.8×10^{-11}	1.7×10^{-2}	3.1×10^{-2}	6.2×10^{-2}	
CdTe	2.818	$(2.5\pm0.5)\times10^{-2}$	1.1×10^{-11}	2.1×10^{-2}			
CdSe	2.539	$(3.0\pm0.5)\times10^{-2}$	1.0×10^{-11}	1.9×10^{-2}			
ZnTe	2.777	$(8.0\pm4.0)\times10^{-3}$	3.3×10^{-12}	3.8×10^{-3}	2.5×10^{-3}	3.2×10^{-2}	
GaP	3.106	$(2\pm1)\times10^{-4}$					1.9×10^{-4}

[a]If more than one sample was measured, the average value is given.
[b]Calculated from Eq. (41) of Ref. 7.
[c]Reference 20, degenerate valance band, no exciton.
[d]Reference 20, degenerate valance band, with exciton.
[e]Reference 30.

angular frequency, and n_2 is the intensity dependent nonlinear index of refraction. For self-focusing produced by an electronic nonlinearity, the intensity-dependent nonlinear index of refraction may be estimated by Wang's rule.[32] This is the contribution due to the bound electrons, and as an example, for GaAs we estimate that $n_2 \approx 1.6 \times 10^{-10}$ esu and $P_{cr} \approx 670$ W. Additional contributions to n_2 may come from the nonparabolicity of the conduction band and the number of conduction-band electrons.[33,34] However, for the intensities at which these effects become important, there is a decrease in the *linear* index of refraction that is linear in the number of excited free electrons. The net result would be a defocusing of the beam. Using the maximum possible values of the effective n_2 and Eqs. (15) and (16) we find that the area of the laser pulse at the exit surface is less than 10% smaller than at the incident surface. This is true even for the longest sample at the highest power. Moreover, we have estimated the effects of thermal self-focusing due to the temperature dependence of the linear index of refraction. We find that these effects are also small. Finally, the beam size was observed using an infrared-absorbing-visible-emitting phosphor. At no time was there a discernible change in the beam size at either high or low powers. We conclude, therefore, that pulse deformation due to self-focusing effects was not a serious problem in the interpretation of any of the experiments reported here.

In conclusion, we have measured the TPA coefficient for four direct gap and one indirect gap semiconductors. Our experimentally measured values of the TPA coefficient are significantly less than most previous measurements, but in reasonable agreement with several theoretical models. For the direct gap semiconductors we have related our measurement of the TPA coefficient to the imaginary part of the third-order nonlinear susceptibility of the material.

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