Observation of Interband Two-Photon Absorption Saturation in CdS

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When using 100 fs light pulses with 2 eV photon energy, the degenerate two-photon absorption process in bulk wurtzite CdS exhibits a saturation behavior with a saturation intensity of 65 GW/cm^2. This observation is possible because the optical pulse duration is shorter than the 350 fs thermalization time of the photocreated carriers in their bands that we measured. From the thermalization time an averaged carrier–LO-phonon interaction duration is deduced which is of the order of 25 fs. Examination of the band structure and the electronic state density of CdS shows that this saturation is due to the electron population rather than to the hole population. [S0031-9007(96)00934-9]

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Since its prediction by Göppert-Mayer [1] and first observation by Kaiser and Garret [2], two-photon absorption has been widely studied in a large variety of materials under a broad spectrum of physical conditions. Because of the finite number of excited states in which carriers can be promoted by the two-photon absorption process, its saturation at sufficiently high excitation intensities can easily be predicted. However, observation of this saturation has never been reported in the literature. There are at least two main reasons that explain this void in the literature. First, the saturation of the two-photon absorption can be expected to occur only for power densities larger than 10^{10} W/cm^2 in CdS [3]. At such high values of the impinging intensity, electric field induced effects take place which disturb the measurement procedure. One of these effects is self-phase modulation which, in its dynamic manifestation, broadens the spectrum of the transmitted light, while in its simultaneous Kerr lens manifestation, it modifies the optical path of the light. Another effect is simply a possible breakdown of the sample at the highest intensities. Second, a mandatory requirement must be fulfilled when trying to saturate in-band electronic states in a semiconductor: the duration needed for the creation of the photocreated carrier density must be shorter than the thermalization time of these carriers to the bottom of their bands in order to reach high values of the excited carrier density.

We present two series of experimental results: a pump and probe experiment was performed allowing the determination of the carrier thermalization time and a direct one-beam transmission measurement under degenerate two-photon excitation. Both experiments were performed at room temperature.

In these experiments we used, as a sample, bulk cadmium sulphide in the form of a high quality platelet, 130 μm in thickness, vapor grown in an argon atmosphere, in a thermal gradient furnace. During the growth process, the argon flux was kept between 0.3 to 3 l/min and the furnace maximum temperature between 1050 and 1090 °C [4]. X-ray scattering measurements showed that the sample is in the hexagonal wurtzite structure. The optical c axis lies in the plane of the platelet; its direction was determined through linear optical transmission measurement at the band gap energies [5].

Optical pulses, 100 fs in duration, at 630 nm central wavelength, were generated using a dispersion compensated CPM laser oscillator [6]. These pulses were amplified [7] with a doubled Nd:YAG laser, at 20 Hz repetition rate, up to an energy of 1 μJ, allowing focused intensities up to 150 GW/cm^2. The pump beam was focused down to an e^{-2} radius of 36 μm. In the dynamics study the probe pulses were kept down to intensities less than a few percent of the pump intensity. The pump and probe pulses were linearly cross polarized, the pump polarization being parallel to the c axis of the bulk CdS crystal in order not to induce any spurious birefringence. Scattered light from the pump was rejected by linearly analyzing parallel to the probe polarization. The time coincidence between pump and probe and the duration of the light pulses were determined by replacing the sample with a phase matched KDP crystal and recording an autocorrelation trace. No attempt was made to use a doubled 4 eV beam to probe absorption changes induced by the 2 eV pump because the penetration depth of 4 eV photons in CdS is only 16 and 20 nm for incident light beams polarized orthogonally or parallel to the c axis, respectively [8]. In the static transmission measurements the intensity of the incoming light was varied by means of thin calibrated gelatin neutral filters.

Small spectral changes in the transmitted light (self-phase modulation) were taken into account by analyzing the light using a 25 cm focal length spectrograph and an optical multichannel analyzer. The recorded spectra were then numerically integrated. The laser intensity fluctuations were estimated to be of the order of 10%. The mean value of the integrated intensity was automatically calculated over five recordings for each value of the time delay between the pump and the probe or each value of the neutral filter, in order to improve the signal to noise ratio.

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Under our excitation conditions, the fundamental photon energy (2 eV) is 80% of the value of the direct gap of CdS (2.48 eV), so that the instantaneous nonlinear index of refraction is negative [9]; therefore there is no self-focusing. In these experiments, care was taken to collect all the light coming through the sample including that experiencing defocusing. This was done by means of a $f/1.5$ lens.

For carrier densities of the order of 10^{18} cm^{-3}, band gap renormalization in CdS is overestimated to be 45 meV [10]. The fundamental 2 eV photon energy misses the equilibrium band gap energy by 480 meV, and therefore one-photon absorption can be neglected. On the other hand, two-photon excitation of the sample creates index changes at the 2 eV fundamental frequency. In a pump and probe geometry these index of refraction changes do induce defocusing of the probe ($n_2 < 0$). Recording of the index dynamics can be done by simply transforming the induced defocusing into an intensity variation by means of an aperture placed in front of the detector [11].

Figure 1 shows the variation of the probe integrated intensity versus time delay, for three pump intensities following the procedure outlined above. At zero time delay, an instantaneous index change can be observed. This has been shown in a separate experiment to be due to cross-phase modulation corresponding to a dynamic electric field induced Kerr effect. From this the value $n_2 = -5 \times 10^{-13}$ cm^2/W can be deduced [12] for the nonlinear index of refraction. The shape of the early time response is simply the autocorrelation function of the light pulses. Its width is in good agreement with that of the separately measured KDP autocorrelation functions. At this time two-photon absorption creates carrier populations with a large excess of kinetic energy; an absorption change is created 1.52 eV above the equilibrium band gap energy. The Kramers-Krönig relation is energetically resonant with the absorption change and therefore negligible change at 4 eV of the index of refraction can be expected at 2 eV arising from the carrier population. At longer time delays the carrier population thermalizes at the bottom of the conduction and valence bands having now an excess energy which is only 480 meV against the 2 eV photon energy. The thermalized carrier population induces an index change which can be seen in Fig. 1 as a signal rise following the instantaneous response. After this thermalization process has taken place, the carriers relax their potential energy and this shows up on Fig. 1 as a slow decay along the last 3 ps. The relaxation of energy has been studied in separate experiments. It was shown to be governed by a strong stimulated radiative recombination process taking place between shallow localized states in Urbach's tail. This radiative process was measured to last less than 4 ps.

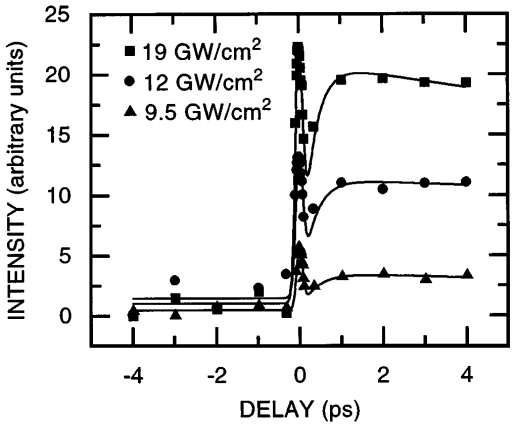

FIG. 1. Index of refraction variations versus time delay between pump and probe for three pump intensities. These curves are obtained by measuring the integrated intensity of the probe spectrum through an aperture situated in a beam region where defocusing is important: the light intensity decreases with an index increase. The background signal is subtracted and the absolute value of the signal is taken. Solid lines correspond to fits calculated with the three-level model described in the text.

The index variations results have been modeled using a set of coupled dynamic differential equations describing electronic population evolutions in a three-level system:

$$\frac{dN(t)}{dt} = \frac{n(t)}{\tau_{\text{th}}} - \frac{N(t)}{\tau_r}, \tag{1a}$$

$$\frac{dn(t)}{dt} = \Gamma^2\left(\frac{t}{t_0}\right) - \frac{n(t)}{\tau_{\text{th}}}. \tag{1b}$$

In this set of equations $N(t)$ is the thermalized population of carriers, proportional to the long lasting index change, $n(t)$ is the population of out-of-equilibrium photocreated carriers, τ_{th} is the intraband thermalization time, and τ_r is the recombination time. Finally, $\Gamma(t/t_0)$ is the pulse intensity envelope of duration t_0 which, in this simple model, has been chosen as a squared hyperbolic secant function. From this set of equations an analytical solution for $N(t)$ is derived which is proportional to the index change. To account for the instantaneous response, which is not included in Eq. (1), the intensity autocorrelation function $\Gamma'(t/t_0)$ of the pulse is added as $aN(t) + b\Gamma'(t/t_0) + c$ (the parameter c accounts for small offsets in the experimental data). A least squares fit to the experimental data following the Cholesky [13] method is then performed. The results of this calculation are shown in Fig. 1 as solid lines. From this model we deduce a thermalization time $\tau_{\text{th}} = 350$ fs, independent of the excitation intensity, and a radiative relaxation time $\tau_r = 100$ ps for the lower excitation intensities which decreases to 40 ps for the highest intensity. The observed values and the shortening of the radiative relaxation time are governed by the stimulated emission mentioned above. From this experiment, we know that the carrier thermalization time is longer by a factor of 3 than the optical pulse duration and therefore the mandatory condition for the observation of interband two-photon absorption saturation is fulfilled.

The one-beam transmission measurements were done after a series of preliminary experiments. They showed that, at the highest intensities available, the sample experiences only a shallow surface degradation of the order of 1 μm in depth, when the light beam is focused onto the entrance surface. We checked that the scattering of light induced by the surface roughness does not affect the transmission measurements within the experimental error due to laser fluctuations. This was done by observing that the output registered did not change when decreasing the intensity after having reached the peak intensity.

Figure 2 shows the superposition of a set of records where the reciprocal transmission is plotted versus the incident intensity. In a simple model, the variation of the transmitted intensity as a function of the incident intensity is given by the integration over the thickness of the sample of the following differential equation when one-photon absorption and orders higher than two are neglected:

$$dI = -\alpha_2(I) I^2 dz \,. \tag{2}$$

In this equation the two-photon absorption coefficient $\alpha_2(I)$ is supposed to depend on the intensity. A simple hyperbolic approximation is then used to model the intensity variation [14]:

$$\alpha_2(I) = \frac{\alpha_2^0}{1 + I/I_{\rm sat}} \,, \tag{3}$$

where α_2^0 is the low intensity response of the material and $I_{\rm sat}$ the saturation value of the intensity for which α_2^0 is divided by 2. Replacement in the solved differential equation of the incident intensity I_0 by $I_i = I_0(1 - R)$ and the transmitted intensity I_t by $I_t' = I_t(1 - R)$ allows

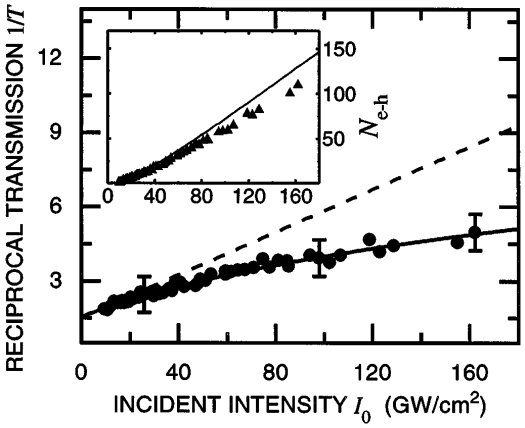

FIG. 2. The solid circles are a plot of the measured reciprocal transmission versus incident intensity. Solid line: theoretical variation for a hyperbolic intensity dependence of the two-photon absorption coefficient. Dashed line: theoretical variation for a constant two-photon absorption coefficient. In the inset is shown the density $N_{e\text{-}h}$ (in 10^{16} cm^{-3}) of photocreated electron-hole pairs versus the incident intensity I_0 (in GW/cm^2). Solid triangles: $N_{e\text{-}h}$ calculated from the experimental data. Solid line: theoretical $N_{e\text{-}h}$ for a constant two-photon absorption coefficient.

one to account for the light reflections at the entrance and exit faces of the sample with linear reflectivity coefficient R. During the two-photon absorption process, which lasts as long as the pulse duration, the nonlinear change of the index of refraction is $\Delta n = 0.005$ [12] and the corresponding relative variation of the reflection coefficient is negligible, $\Delta R/R = 4 \times 10^{-3}$. For a thickness d of the sample the formal solution of Eq. (2) then reads as

$$\frac{1}{I_0(1 - R)} - \frac{1 - R}{I_t'} + \frac{1}{I_{\rm sat}} \ln\left|\frac{I_t'}{I_0(1 - R)^2}\right| = -\alpha_2^0 d \,. \tag{4}$$

From this expression the reciprocal transmission ($1/T = I_0/I_t'$) has been numerically evaluated and used to fit the experimental data, as shown as a solid line in Fig. 2. From this fit one finds $\alpha_2^0 = \alpha_2(I \ll I_{\rm sat}) = 2.7$ cm/GW, $R = 19\%$, values which are in close agreement with the ones found in the literature [15,16]. The good agreement obtained for the linear reflectivity further confirms the harmlessness of the degradation of the sample surface already mentioned. From Eq. (4) we deduce a saturation intensity for the two-photon absorption process $I_{\rm sat} = 65$ GW/cm^2.

If the saturation effect is not taken into account, the third term on the left hand part of Eq. (4) vanishes and the variation of the reciprocal transmission versus incident intensity should be linear, as shown in Fig. 2 as a dashed line. In that approximation the calculated result strongly departs from the experimental data. We also examined the possibility for one-photon excitation of the photocreated carriers in the bands. First, the cross section of this absorption process [17] is small ($\sigma = 10^{-18}$ cm^2) so that the effect is negligible on our time scale [18]. Following Ref. [15], we made a numerical calculation of the reciprocal transmission using a model of this effect in which the two-photon absorption coefficient $\alpha_2 = \alpha_2^0$ is a constant and found no set of parameters which could account for the experimental results.

The inset in Fig. 2 shows the variation of the density of carrier pairs versus incoming intensity, calculated from the number of absorbed photons. It varies from 1.6×10^{16} cm^{-3} when $I_0 = 9.4$ GW/cm^2 (1.7×10^{10} absorbed photons) to 10^{18} cm^{-3} when $I_0 = 162$ GW/cm^2 (10^{12} absorbed photons). Again the experimental variation departs from the expected variation when no saturation is taken into account. No saturation plateau is observed due to the competition between state filling and thermalization of the carriers.

A band structure calculation of semiconductors is still underway [19] and not totally reliable for interpreting experimental results. We considered the calculation performed in Ref. [20] which gives, for hexagonal CdS, both the band structure and the associated electronic state density. Examination of the possible electronic transitions, under 4 eV two-photon excitation, which may happen in

the band structure, allows us to determine which electronic states participate in the process. The participating holes lie in a 850 meV wide band around -1 eV, when the energy is measured from the top of the valence band, while the contributing electrons are distributed in a 880 meV wide band lying 280 meV above the minimum of the conduction band. The hole band is coincident with a peak in the valence state density while the electron band lies in the slowly increasing conduction state density. The density of state available for the holes is roughly 30 times larger than the one available for the electrons; therefore the saturation of the two-photon absorption saturation is due to the electrons. The transfer of the kinetic energy of the carriers to the lattice of the crystal is efficiently done via their interactions with the polar LO phonons, whose energy is 37.8 meV. From our thermalization time measurement we deduce that the electron-phonon interaction duration should be between 11 and 50 fs. This value is about 5 times shorter than in GaAs [21] due to the more polar character of CdS when compared to GaAs.

It has been shown that, under photoexcitation of CdS with 100 fs light pulses of 2 eV photon energy, saturation of the interband two-photon absorption is observable with a characteristic saturation intensity of 65 GW/cm^2. This saturation is of great importance in the field of nonlinear optics where the conditions for its manifestation are nowadays easily fulfilled with commercially available light pulses sources. Therefore it should be taken into account in both the experimental and the formal analysis of the nonlinear response of material under resonant two-photon excitation. Our work also stresses the extreme briefness of the interaction time of highly out-of-equilibrium carries with the phonons.

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[1] M. Göppert-Mayer, Ann. Phys. (Leipzig) **9**, 273 (1931).
[2] W. Kaiser and C. G. B. Garret, Phys. Rev. Lett. **7**, 229 (1961).
[3] A. Penzkofer, W. Falkenstein, and W. Kaiser, Appl. Phys. Lett. **6**, 319 (1976).
[4] J.-I. Chikawa and T. Nakayama, J. Appl. Phys. **35**, 2493 (1964).
[5] M. Balkanski and J. des Cloizeaux, J. Phys. Rad. **21**, 825 (1960).
[6] J. A. Valdmanis, R. L. Fork, and J. P. Gordon, Opt. Lett. **10**, 131 (1985).
[7] C. Hirlimann, O. Seddiki, J.-F. Morhange, R. Mounet, and A. Goddi, Opt. Commun. **59**, 52 (1986).
[8] M. Cardona and R. Haensel, Phys. Rev. B **1**, 2605 (1970).
[9] M. Sheik-Bahae, D. C. Hutchings, D. J. Hagan, and E. W. Van Stryland, IEEE J. Quantum Electron. **27**, 1296 (1991).
[10] A. A. Said, M. Sheik-Bahae, D. J. Hagan, T. H. Wei, J. Wang, J. Young, and E. W. Van Stryland, J. Opt. Soc. Am. B **9**, 405 (1992).
[11] E. C. Fox, E. J. Canto Said, and H. M. van Driel, Appl. Phys. Lett. **59**, 1878 (1991).
[12] C. Hirlimann, E. Wassmuth, E. Kling, S. Petit, and M. Pereira dos Santos, Appl. Phys. Lett. **65**, 959 (1994).
[13] J. H. Wilkinson and C. Reinsch, in *Handbook for Automatic Computation*, Linear Algebra Vol. II (Springer-Verlag, Berlin, 1971), p. 303.
[14] A. E. Siegman, in *Lasers* (University Science Book, Mill Valley, California, 1986), p. 207.
[15] E. W. Van Stryland, M. A. Woodall, H. Vanherzeele, and M. J. Soileau, Opt. Lett. **10**, 490 (1985).
[16] M. Cardona and G. Harbeke, Phys. Rev. **137**, A1467 (1965).
[17] S. M. Oak, K. S. Brinda, R. Chari, and K. C. Rustagi, J. Opt. Soc. Am. B **10**, 613 (1993).
[18] G. P. Banfi, V. Degiorgio, M. Ghigliazza, H. M. Tan, and A. Tomaselli, Phys. Rev. B **50**, 5699 (1994).
[19] O. Zakharov, A. Rubio, X. Blase, M. L. Cohen, and S. G. Louie, Phys. Rev. B **50**, 10 780 (1994).
[20] A. I. A. Dahr and P. M. Lee, Phys. Scr. **38**, 441 (1988).
[21] J. A. Kash, J. C. Tsang, and J. M. Hvam, Phys. Rev. Lett. **54**, 2151 (1985).