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Citation: Applied Physics Letters **66**, 804 (1995); doi: 10.1063/1.113426
View online: http://dx.doi.org/10.1063/1.113426
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/66/7?ver=pdfcov
Published by the AIP Publishing

Nonlinear absorption and refraction of quantum confined InP nanocrystals grown in porous glass

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(Received 2 September 1994; accepted for publication 5 December 1994)

Single-beam *Z*-scan experiments have been used to measure the two-photon absorption coefficient β and bound electronic nonlinear refractive index γ of composites of InP nanocrystals grown in 40 and 150 Å Vycor porous glass. These materials were also studied with two-beam time-resolved *Z* scans to confirm that the nonlinearities are instantaneous with respect to the ~100 ps pulses used. The magnitudes of the nonlinearities in the 150 Å sample are found to be similar to those of bulk InP when scaled by the volume fraction of deposited material. For the 40 Å sample the ratio γ/β is enhanced by a factor of fourteen compared to bulk InP. © *1995 American Institute of Physics.*

There is much current interest in the nonlinear optical properties of quantum confined semiconductor nanocrystals,[1] particularly for their potential use in nonlinear photonic devices.[2] Glass is an attractive host matrix for the nanocrystals in such optical applications. Traditional glass melting/striking techniques are used in the fabrication of I–VII and II–VI semiconductor doped glasses.[3,4] The fabrication of III–V semiconductor doped glasses requires other methods such as chemical vapor deposition in the nanometer-sized channels of porous glasses. Recently,[5,6] this method has been used to deposit InP nanocrystals in porous Vycor glass. The InP-doped Vycor glasses were characterized[5] and a preliminary investigation[6] of their nonlinear optical properties was reported using single-beam *Z*-scan experiments performed at 850 nm and using ~8 ns pulses. Optical limiting due to nonlinear refraction as well as significant nonlinear absorption, most likely due to excited-state absorption exacerbated by the long pulse duration, was observed. The purpose of this work is to perform a more comprehensive investigation of the nonlinear optical properties of InP nanocrystals grown in porous Vycor glass using a laser source having a much shorter pulse duration, ~100 ps. Single-beam *Z* scans were used to measure the two-photon absorption coefficient β and bound electronic nonlinear refraction γ at 1064 nm. Two-beam time-resolved *Z*-scan experiments[7] indicate that there are no long-lived nonlinearities in these materials, i.e., that they are instantaneous relative to our 100 ps pulses.

The porous Vycor glasses (Corning, Inc.) used for these studies were of two types, standard type 7930 glass containing 40 Å diam pores, and a second glass with larger, 150 Å diam pores. The pores nominally occupy about 30% of the volume of the glass. InP nanocrystals were grown in the pores by the reaction of trimethylindium with phosphine.[5] Elemental analysis (PIXE Analytical Laboratories) of the InP-doped glass indicated the presence of indium and phosphorus in a 1:1 stoichiometric ratio and that the volume fraction of InP in the doped glass samples was ~3%. The sample lengths were 0.50 and 0.40 mm for the 40 and 150 Å InP-doped Vycor glass samples, respectively. For all samples studied the linear absorption at 1064 nm was small, $\alpha L < 0.10$. The linear absorption spectra of the 40 Å (solid line) and 150 Å (dashed line) InP-doped Vycor glasses are shown in Fig. 1. These spectra each exhibit a broad featureless absorption throughout the visible that is blue shifted with respect to the band edge (916 nm) of bulk InP.

The laser system used to study these materials consisted of a single pulse extractor used with a Q-switched/cw-mode locked Nd:YAG laser to provide single ~100 ps duration pulses at a repetition rate of 10 Hz. After spatial filtering, each pulse had a maximum energy of several microjoules and was used in the single-beam and time-resolved *Z*-scan geometry shown in Fig. 2. For single-beam experiments the probe was blocked and the sample was moved in the direction of propagation of the light. It is well known[8,9] that measurement of the normalized transmission versus sample position, for the two cases of the collecting aperture transmitting 100% and <100% of the light, allows determination of the two-photon absorption coefficient β and the bound electronic nonlinear refractive index γ. For two-beam

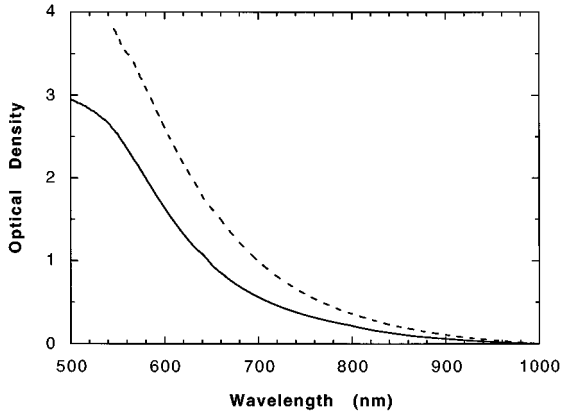

FIG. 1. Absorption spectra of InP-doped Vycor glasses. Solid line: 40 Å glass composite; dashed line: 150 Å glass composite.

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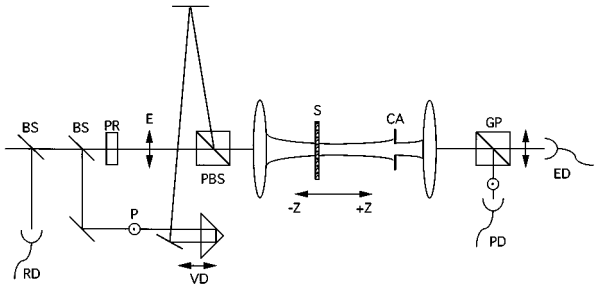

FIG. 2. Experimental geometry for single-beam and time-resolved two-beam *Z*-scans: BS=beam splitter, PR=90° polarization rotator, E=pump beam, P=probe beam, RD=reference detector, PBS=polarizing beam splitter, VD=variable delay, S=sample, CA=collecting aperture, GP=glan prism, ED=pump detector, PD=probe detector.

experiments the sample was placed in a position where there was a peak or valley[7–9] in the normalized closed-aperture transmission. The normalized probe transmission versus probe delay was then measured in order to investigate the temporal dynamics of the optical nonlinearities.

A typical single-beam *Z*-scan measurement using a 40 Å InP-doped glass sample is shown in Fig. 3. The fact that the transmission peak precedes the valley indicates that the sign of the nonlinear refraction is negative, while the symmetry in the magnitudes of $(T_{\text{peak}}-1)$ and $(1-T_{\text{valley}})$ indicates that nonlinear absorption is relatively weak. As discussed in Refs. 8 and 9, the magnitude of $\Delta T=T_{\text{peak}}-T_{\text{valley}}$ can be used to calculate the magnitude of the change in the index of refraction Δn. In order to accurately obtain the value of γ from the measured Δn, the *Z*-scan measurements must be performed at several values of I_0, the peak on-axis internal intensity, as outlined in Ref. 9. We find that, when measured at several values of I_0 between 0.05 and 0.35 GW/cm^2, the index change, when normalized by the intensity, is independent of intensity and that $\gamma=-2.1\times10^{-12}$ cm^2/W. This result indicates that there is little or no nonlinear refraction due to excited carriers, as commonly occurs in bulk semiconductors.[9] The *Z*-scan measurements were repeated at each incident intensity with the collecting aperture opened to transmit 100% of the incident light. For example, at an intensity $I_0=0.19$ GW/cm^2 the normalized nonlinear transmission at the focus was found to be ~0.97. These data, used in conjuction with the sample thickness, linear absorption coefficient, and Fig. 2 of Ref. 9 permit the calculation of the two-photon absorption coefficient, with the result $\beta\sim9$ cm/GW. (Note that there is no substantive difference between the *Z*-scan method and traditional methods[10] for measuring β.) In order to compare our measurements of γ and β for the quantum confined InP-doped glass with those of bulk InP, we recently performed similar *Z*-scan measurements[11] on a bulk, undoped InP crystal and found $\gamma=-1.5\times10^{-12}$ cm^2/W and $\beta\sim90$ cm/GW. Thus, the nonlinear index of the 40 Å InP-doped glass is approximately half-again as large as that of bulk InP while the two-photon absorption coefficient is an order of magnitude less.

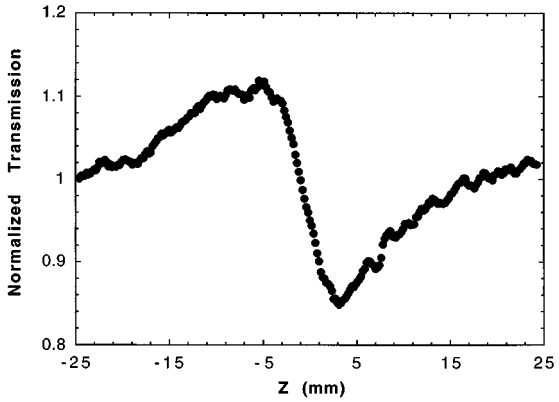

FIG. 3. Closed-aperture *Z*-scan data for the 40 Å InP-doped glass sample. For this measurement the linear transmission of the collecting aperture was $S=0.61$ and the intensity was $I_0=0.19$ GW/cm^2.

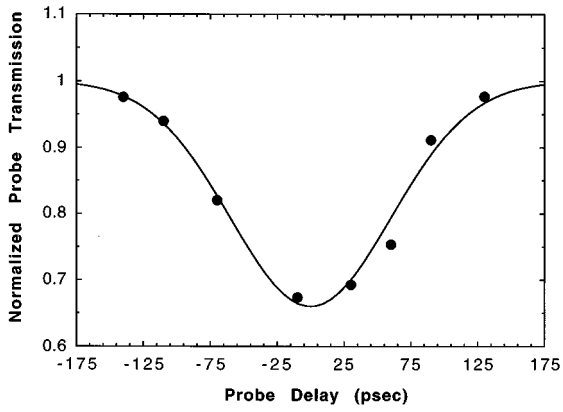

FIG. 4. Normalized probe transmission vs probe delay for 40 Å InP-doped glass. The Gaussian fit indicated by the solid line is in good agreement with an assumed instantaneous response to ~100 ps pulses. For this measurement the linear transmission of the collecting aperture was $S=0.53$ and the pump intensity was $I_0=0.47GW/\text{cm}^2$.

The volume fraction of InP in the glass can be used to scale the measured nanocrystal nonlinearities for effective comparison with the bulk values. For the nonlinear refraction this yields $\sim-7\times10^{-11}$ cm^2/W, while the scaled two-photon absorption coefficient is ~300 cm/GW. It is readily apparent that both γ and β are enhanced in the nanocrystalline doped-glass sample by factors of ~50 and ~3, respectively, when the volume fraction is considered. Note, however, that the ratio γ/β is enhanced by a factor of ~14 in the 40 Å InP-doped glass sample compared to bulk InP, without reference to the volume fraction of InP in the glass.

As previously discussed, time-resolved *Z*-scans[7] were used to study the temporal dependence of the nonlinearities. A 20:1 ratio of pump-to-probe intensity (also energy) was used to limit potential probe generated nonlinearities. The filled circles in Fig. 4 show the probe transmission versus probe delay of the 40 Å glass sample for the situation where the sample is fixed near the valley in the single-beam transmission. The solid line is a Gaussian fit whose full width at half maximum (FWHM) is $\sqrt{2}\times100$ ps. If we assume Gaussian temporal profiles of the pulses this implies, after deconvolution, that the pulses were approximately 100 ps FWHM in duration, a result which was confirmed using a fast photodiode and oscilloscope. The absence of a tail at positive

delays in Fig. 4 is an indication that the nonlinearities in these materials are instantaneous relative to the ~100 ps pulses.

Single-beam and time-resolved *Z*-scan techniques were also used to study the 150 Å InP-doped Vycor glass sample. The single-beam results indicated that the optical nonlinearities were simply those of bulk InP[11] scaled by the volume fraction. This result indicates that the nonlinear optical properties of the InP nanocrystals are highly size dependent. Time-resolved *Z*-scan measurements were also performed using the 150 Å doped-glass sample, and indicated, similar to the 40 Å glass sample, that the nonlinearities were instantaneous with respect to the laser pulse duration.

In conclusion, the two-photon absorption coefficient β and the bound electronic nonlinear refraction γ have been measured for InP nanocrystals grown in 40 and 150 Å porous glass. The 150 Å sample was found to behave like bulk InP scaled by the appropriate volume fraction. If the volume fraction is considered, both γ and β were found to be enhanced in the 40 Å doped-glass sample. The data indicate, however, that the enhancement in the nonlinear refraction is fourteen times larger than that of the nonlinear absorption. For both crystal sizes the nonlinearities have been found to be instantaneous relative to the ~100 ps pulses. The results indicate that these are promising materials for applications requiring a large ratio of nonlinear refraction to nonlinear absorption, such as nonlinear waveguide devices.

This work was partially supported by the Office of Naval Research.

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