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Nonlinear optical response of silicon nanocrystals

E. Koudoumas [a,*], O. Kokkinaki [b], M. Konstantaki [b], N. Kornilios [a], S. Couris [c], S. Korovin [d], V. Pustovoi [d], V.E. Ogluzdin [d]

[a] Electrical Engineering Department, TEI of Crete, 71004 Heraklion, Greece
[b] Foundation for Research and Technology-Hellas (FORTH), IESL, P.O. Box 1527, 71110 Heraklion, Greece
[c] Physics Department, University of Patras, 26500 Patras, Greece
[d] Natural Science Center, General Physics Institute, Moscow, Russia

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Abstract

Experimental results are presented related to the nonlinear optical response of silicon nanocrystals under visible nsec laser excitation. The nanocrystals were examined in water and glycerol suspensions and as was shown, they exhibit saturable absorption and negative nonlinear refraction. Finally, in the case of the glycerol suspensions and under sufficiently high incident intensity, the formation of bubbles was found to cause a serious modification of the sample's transmission.

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The optical nonlinearities of nanometer scale particles have received a lot of interest the last few years and there are several reports in the literature concerning the response of various metal and semiconductor nanocomposites [1–10]. In these small sized particles, the quantum confinement of the electron wavefunction leads both to a modification of the electron band structures and the dipole transition matrix elements and to less effective screening of the electrons [11]. In addition, for a very low volume fraction of spherical crystallites embedded in a transparent dielectric, an effective dielectric constant should be applied [12,13] leading to the possibility of the so-called plasmon resonances. As a result, the small size can in general induce a significant enhancement of the nonlinear optical response of various nanostructures with respect to that of the bulk material.

It has been shown that silicon nanoparticles in various forms and embedded in different matrices exhibit considerable optical nonlinearites. There are several reports in the literature concerning the nonlinear optical response of silicon nanoparticles in suspensions [7,14–16], deposited on quartz substrates [16–18] or embedded in silica matrix [19,20] and porous silicon [21,22]. In the present work we report on initial experimental results concerning the nonlinear optical response of nanometer size silicon crystals in suspensions and in particular of the nonlinear absorption and refraction exhibited by these nanostructures when excited by visible nanosecond laser radiation. As it is shown, the observed nonlinear optical response can be explained in terms of their transient nonlinear optical response in combination with thermal effects taking place under the currently used excitation wavelengths and pulse duration.

The silicon nanocrystals were prepared through the dissociation of SiH_4 with a CO_2 laser. As was verified by X-ray diffraction (XRD) and atomic force microscopy (AFM) measurements, the produced powder consisted of

* Corresponding author. Tel.: +30 2810 379887; fax: +30 2810 260752.
E-mail address: koudoum@stef.teiher.gr (E. Koudoumas).

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silicon nanocrystals with diameters in the range 12–40 nm, covered with a thin layer of silicon oxide. The nanocrystal powder was used to prepare suspensions in water and glycerol with a concentration of 0.75 mg/ml. The suspensions were then introduced between two glass slices, resulting in sandwiched-like films of about 120 μm thickness. The absorption spectra of the suspensions, recorded with a Varian Cary 50 spectrophotometer (having a resolution of 1.5 nm), are presented in Fig. 1. As shown, the Si suspensions present an absorption band centered near 400 nm, a value in good agreement with previously reported results [14,16].

The nonlinear optical response of the silicon nanocrystals suspensions was studied using the *z*-scan technique [23]. The experimental setup of the *z*-scan and the procedure for the determination of the corresponding nonlinear parameters has been already described in details elsewhere [24]. Briefly, a sample is moving along the direction of propagation of a focused Gaussian beam (z) and its transmission is recorded for various z positions. The recording of all the light transmitted through the sample reveals information about the nonlinear absorption of the sample while the nonlinear refraction can be deduced if only the light transmitted through a pinhole placed in front of the detector is recorded. The samples were irradiated with the second harmonic of the Nd:YAG laser (532 nm) operating at 5 Hz, with a pulse duration of 10 ns. The laser beam was focused to about 80 μm diameter with a 15 cm focal length lens and the nonlinear absorption and the nonlinear refraction were examined simultaneously by splitting the beam after the sample into two equal parts by a large area beam splitter.

First we examined the nonlinear absorption of the Si–glycerol suspensions. For intensities of about 1 MW/cm^2, the suspensions were found to exhibit nonlinear optical response. Fig. 2 presents open aperture *z*-scan curves recorded at three values of the incident intensity. As can

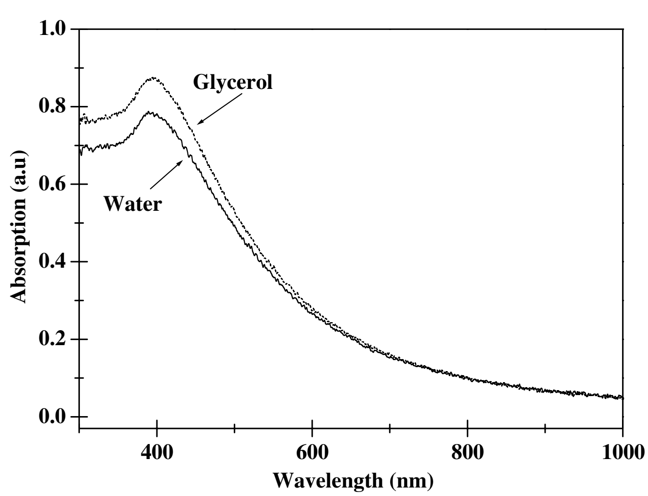

Fig. 1. Absorption spectra of water and glycerol Si nanocrystals suspensions. The concentration of the suspensions was 0.75 mg/ml.

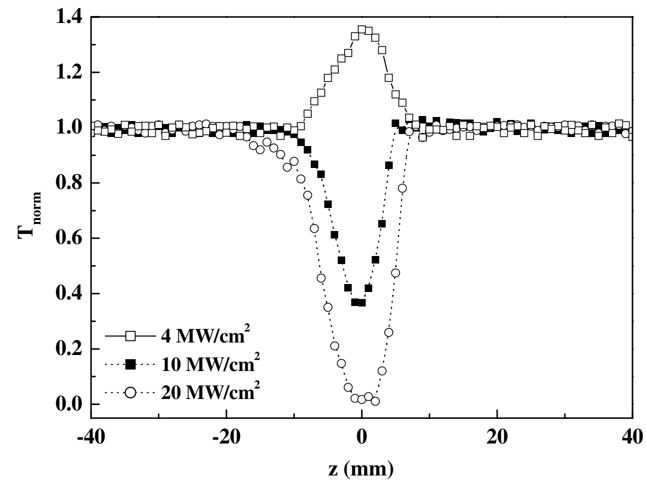

Fig. 2. Open aperture *z*-scans of the Si nanocrystal glycerol suspensions recorded for three different values of the incident laser intensity.

be seen, for incident intensity of about 4 MW/cm^2 the suspensions exhibit saturable absorption (SA), the response coming from the Si nanocrystals only since no effect was observed for a pure glycerol sample. The normalized transmission at focus was found to increase by almost 40%, the increase depending on the incident intensity. Conversely, for incident intensity above an intensity threshold I_{th} of approximately 6–10 MW/cm^2 (the value depended on the concentration of the suspensions), the transmission of the suspensions was significantly reduced, the samples simultaneously presenting strong scattering. The decrease in the transmission is quite strong and for an intensity of about 20 MW/cm^2, the transmission becomes almost zero. This decrease in the transmission can be seen as a strong reverse saturable absorption similar to that reported in a previous work [14]. However, if a sample was irradiated with intensity higher than I_{th}, then, the reverse saturable absorption was present for a time period (10–20 min depending on the irradiation conditions and the concentration) even for *z*-scans performed with a low incident intensity for which the sample was initially exhibiting saturable absorption. After this time period, the samples were recovering, exhibiting their initial absorptive response. Therefore, the observed behavior should be attributed to a nonpermanent modification of the Si–glycerol suspensions.

In order to verify the mechanism responsible for the observed behavior of the Si nanocrystals–glycerol suspensions, the films morphology was examined just after irradiation with an optical microscope. As was observed, for high enough intensity, bubbles of several micrometers' diameter were created within the films. These bubbles are clearly shown in Fig. 3 which presents a part of a film before and after the irradiation with intensity higher than I_{th}. These bubbles seem to be responsible for the change of the optical properties of the films since they can reduce its transmission and result in an illusory saturable absorption response. After a short time period, the bubbles were deformed, the film recovering its original morphology.