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Nonlinear absorption in silicon nanocrystals

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***Abstract*. The nonlinear absorption of light in silicon nanocrystals suspended in glycerol is studied by the Z-scan method. The experimental data are used for calculating the nonlinear absorption coefficient β_{Si-gl} for silicon nanocrystals in glycerol (with a volume filling factor $f = 2 \times 10^{-4}$), and the coefficient β_{Si} for pure silicon with a hypothetical volume filling factor $f \approx 1$. For the laser radiation wavelength $\lambda =$ 497 nm and the pulse duration $\tau = 0.5$ ns, these coefficients are $\beta_{Si-gl} = 1.2 \times 10^{-8}$ cm W^{-1} and $\beta_{Si} = 7.36 \times 10^{-5}$ cm W^{-1}, while the corresponding values for $\lambda = 532$ nm and $\tau = 10$ ns are $\beta_{Si-gl} = 5.36 \times 10^{-5}$ cm W^{-1} and $\beta_{Si} = 0.25$ cm W^{-1}. Experiments with 540-nm, 20-ps laser pulses performed for two different filling factors equal to 2×10^{-4} and 3×10^{-3} gave nonlinear absorption coefficients $\beta_{Si-gl} = 2 \times 10^{-7}$ and 3.6×10^{-6} cm W^{-1}, respectively. Optical absorption and Raman scattering spectra of silicon nanocrystals are also studied. A theoretical analysis of the experimental results shows that optical absorption can be related to the localisation of photoexcited carriers in the conduction band. The localisation is caused by the action of strong static electric fields on an electron in a nanoparticle.**

Keywords: *nonlinear absorption, Z-scan, silicon nanocrystals, strong static electric fields, Raman scattering, LO- and TO-phonons in silicon.*

1. Introduction

Nonlinear optical properties of semiconductor nanoparticles attract persistent attention of the researchers in the last years [1 – 6]. A decrease in the size of semiconductor particles to a few nanometers changes the energy band structure and often increases the matrix element of the transition dipole moment. This results in turn in a high nonlinear susceptibility of the nanosize semiconductor. In this connection, various types of silicon nanocomposites are being studied extensively.

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Nanosilicon obtained by laser ablation of the crystalline target and by ion implantation of silicon in fused quartz was studied in Ref. [2]. It was found that the maximum nonlinear susceptibility $\chi^{(3)}$ is observed for nanoparticles having a diameter of the order of 12 nm. The nanocrystals obtained by ablation exhibited only induced bleaching, while the ion-implanted silicon revealed nonlinear absorption only. A high nonlinear susceptibility, as well as induced bleaching and nonlinear absorption were observed in nanodisperse silicon obtained by laser-induced deposition from the gas phase [4 – 7]. The distinct dependence of the nonlinear properties of nanosilicon on the material covering the nanoparticles was demonstrated in Ref. [5]. An analysis of the previously published works shows that the optical properties of semiconductor nanoparticles depend on their size [2], the material covering the nanocrystal [2, 5], the charge state of the phase interface, and the separation between the particles.

In this work, we study the optical nonlinearity of silicon nanocrystals suspended in glycerol with a very low volume filling factor in such a way that the separation between individual nanoparticles considerably exceeds the wavelength of the laser radiation used in the experiments

2. Experimental

The nanoparticles were prepared in the laboratory of G P Kuz'min at the General Physics Institute, Russian Academy of Sciences, by decomposing monosilane (SiH_4) by focused radiation from a cw CO_2 laser. According to the diffractometry and scanning electron microscopy data, the particles are spherical and have a size 10 – 40 nm, possess a crystalline structure, and are covered by a thin layer of natural oxide [7]. Glycerol, which is capable of producing a homogeneous suspension of silicon nanocrystals in the bulk, was chosen as the viscous liquid. The refractive index of glycerol is close to that of glass, which excludes any stray reflection at the interface between the two media. The volume filling factor (the ratio of the silicon and glycerol volumes) was $f = 2 \times 10^{-4}$. The medium was placed between two plane-parallel glass plates, and the thickness D of the layer was 120 μm.

Nonlinear optical absorption was investigated by the standard Z-scan method [8] in which the transmission of laser radiation through the sample is measured as a function of the sample position relative to the 'focal point' $z = 0$ of the radiation (i.e., of the radiation intensity in the sample). The diameter of the laser beam in front of a lens of focal length 40 cm was 3 mm. Measurements were made at laser

radiation wavelengths 497 nm (pulse duration $\tau = 0.5$ ps), 540 nm ($\tau = 20$ ps) and 532 nm ($\tau = 10$ ns). The optical transmission spectra of silicon nanocrystals in glycerol were studied using a double DFS-24 monochromator. A 15-mW, 632.8-nm He – Ne laser and the same monochromator were used for analysing the Raman spectra.

3. Experimental results

Fig. 1 shows the experimental nonlinear transmission curves for glycerol with silicon nanocrystals for two maximum intensities of laser radiation at 497 nm and laser pulse duration of 0.5 ps. Note that the qualitative behaviour of nonlinear absorption is identical for all three wavelengths and pulse durations mentioned above. The nonlinear absorption Z-scan curve differs considerably from the symmetric curve for which the computational models of this method are applicable. A self-induced bleaching is observed at the radiation intensity of 29 GW cm^{-2}. One can see that the bleaching is replaced by nonlinear absorption at an intensity of 43 GW cm^{-2} and therefore the standard method for measuring the nonlinear absorption coefficient is not applicable for this sample. For this reason, the nonlinear transmission of laser radiation of samples was measured over a wide range of intensities. For low intensities of laser radiation, bleaching alone is observed. As the laser intensity increases, a linear dependence of the transmitted energy on the incident energy is observed within two intervals (with different slopes), which apparently correspond to different nonlinear absorption regimes in the sample. The nonlinear absorption coefficient was calculated using expressions obtained in Ref. [8].

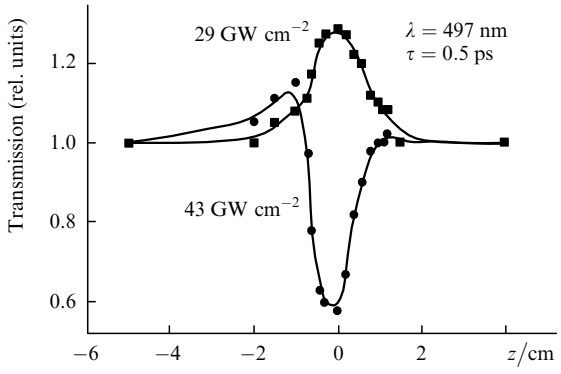

Figure 1. Experimental Z-scan curves (open aperture) for two radiation intensities in air for $z = 0$.

We calculated nonlinear absorption coefficients $\beta_{\mathrm{Si-gl}}$ for silicon in glycerol with a volume filling factor $f = 2 \times 10^{-4}$, and β_{Si} for a hypothetical system with $f \approx 1$. For $\lambda = 497$ nm and $\tau = 0.5$ ps, we obtained $\beta_{\mathrm{Si-gl}} = 1.2 \times 10^{-8}$ cm W^{-1} and $\beta_{\mathrm{Si}} = 7.36 \times 10^{-5}$ cm W^{-1}. For $\lambda = 532$ nm and $\tau =$ 10 ns, the corresponding values were $\beta_{\mathrm{Si-gl}} = 5.36 \times 10^{-5}$ cm W^{-1} and $\beta_{\mathrm{Si}} = 0.25$ cm W^{-1}. The values of the nonlinear absorption coefficient $\beta_{\mathrm{Si-gl}}$ obtained in the experiment using 540-nm, 20-ps laser pulses for filling factors $f = 2 \times 10^{-4}$ and 3×10^{-3} were 2×10^{-7} and 3.6×10^{-6} cm W^{-1}, respectively. Thus, a 15-fold increase in the filling factor of silicon nanoparticles in glycerol increases the value of $\beta_{\mathrm{Si-gl}}$ by a factor of 18. The nonlinear absorption coefficient $\beta_{\mathrm{Si-gl}} = 3.6 \times 10^{-6}$ cm W^{-1} obtained by us for quite low filling factor equal to 3×10^{-3} is comparable with the nonlinear absorption coefficient for well-known CdS and porous silicon [3], which makes silicon nanocrystals promising objects for the fabrication of devices for limiting the intensity of transmitted laser radiation.

Our measurements show that the imaginary part of the permittivity of silicon nanocrystals is ~ 10 ($\lambda \approx 500$ nm). Therefore, by estimating the nonlinear absorption coefficient from expressions in Ref. [8], we should use the intensity that is lower than the intensity of the light wave incident on the sample. As a result, the real value of β is higher than the measured one. Note that a considerable increase in the third-order optical nonlinearity for dielectrics with microscopic semiconductor inclusions was reported earlier in Ref. [9].

4. Additional investigations and analysis of experimental results

To understand the mechanisms responsible for bleaching of the medium and high optical nonlinearity, we studied additionally the interaction of laser radiation with the electron and phonon subsystems of silicon nanocrystals by analysing their absorption and Raman spectra.

4.1 Optical absorption

The absorption spectrum of silicon nanocrystals in the wavelength range 300 – 700 nm differs significantly from the absorption spectrum of crystalline silicon. The absorption spectra of nanopowder and nanosilicon in glycerol were obtained earlier in Refs [5, 7]. The coefficient of linear absorption $\alpha = 1.85 \times 10^5$ cm^{-1} for these materials at 497 nm was found to be 20 times that for crystalline silicon. The spectral absorption curve (Fig. 2) displayed a distinct peak at 3.18 eV. This peak may be related to the singularities in the electron density function (Van Hove singularities) at 3.31 and 3.41 eV [10], but it is shifted to the red as compared to bulk silicon. We analysed the models [10, 11] describing the transitions from the valence band to the conduction band (taking into account the electron-hole interaction and neglecting it), from the localised defect states in the band gap to the conduction band, and from the valence band to the localised states in the conduction band. None of these models could provide an appropriate description of the experimental curve.

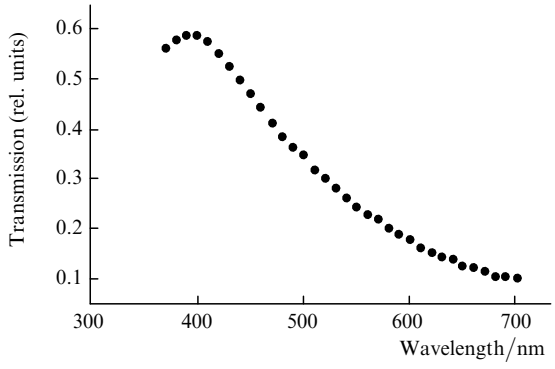

Figure 2. Experimental dependence of optical absorption by nanocrystalline silicon particles in glycerol on the wavelength.

To explain the behaviour of the absorption spectra of silicon nanocrystals in glycerol, we used the model of internal emission in an electric field (Zener effect), which describes the absorption of radiation by electrons excited to the deep levels of the conduction band of a semiconductor. The absorption of light in this case is determined by the interband tunnelling of electrons in the semiconductor placed in a homogeneous electric field. The Bouguer absorption coefficient α is proportional to $\exp[-\gamma(\omega_0-\omega)^{3/2}/E]$ [11], where $\gamma = 4(2\mu\hbar)^{1/2}/3e$; μ is the reduced electron mass; $\hbar$ is Planck's constant; E is the static electric field strength; ω_0 is the transition frequency at the singularity corresponding formally to the bottom of the 'conduction band' of nanocrystalline silicon; e is the electron charge; ω is the radiation frequency. Fig. 3 shows the experimental dependence of $\ln(10^2\alpha L)$ on $(1/\lambda_0 - 1/\lambda)^{3/2}\times 10^{4.5}$ nm$^{-3/2}$, where λ_0 is the transition wavelength at the singularity. The slope of the straight line obtained corresponds to a strong static field $E \simeq 2.8\times 10^7$ V cm^{-1} inside nanoparticles.

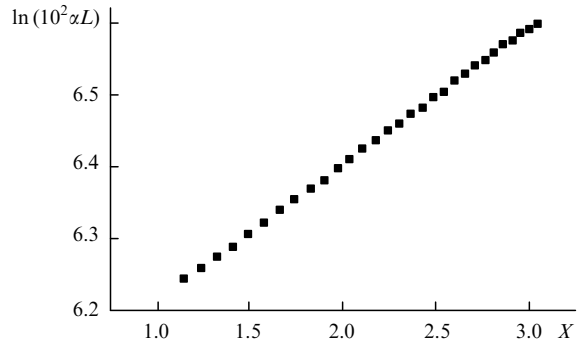

Figure 3. Experimental dependence of $\ln(10^2\alpha L)$ on $X = (1/\lambda_0 - 1/\lambda)^{3/2}\times 10^{4.5}$ nm$^{-3/2}$.

4.2 Raman scattering of light

The symmetry $\mathbf{O}_h$ of the silicon crystal lattice determines the selection rules for Raman scattering of light by phonons. Two phonons (TO and LO) having a dynamic symmetry $\mathbf{\Gamma}^{(25+)}$ at the point $\mathbf{\Gamma}$ of the Brillouin zone are allowed in Raman scattering [12]. These phonons are triply degenerate in energy and cannot be resolved in the experiment for any scattering geometry. The geometry of backward scattering was determined by the direction of propagation and polarisation of the incident and scattered beams [12]. In our experiment, the polarisation of the beam incident on the sample remained unchanged and the analyser was installed in the scattered radiation parallel $[-xzzx]$ or perpendicular $[-xzyx]$ to the incident beam polarisation.

Fig. 4 shows the spectra of Raman scattering of light from the TO-LO phonon mode. The upper spectrum corresponds to the scattering geometry $[-xzzx]$ and the lower one to $[-xzyx]$. For two mutually perpendicular orientations of the analyser, the Raman peak positions differed by 3 cm^{-1}. In our opinion, this peak corresponds to scattering by optical phonons in a particle with a modified symmetry of the crystal lattice.

It is known that the symmetry of the silicon crystal lattice may change under static mechanical stresses and in an electric field [12, 13]. In our case, there are no static

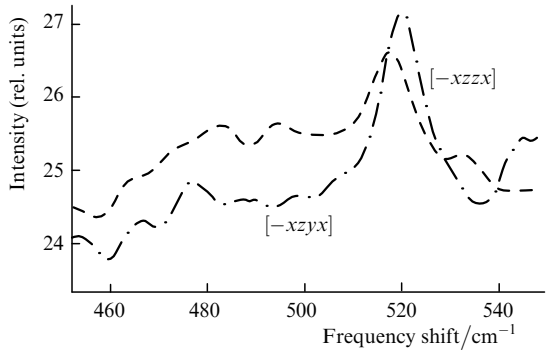

Figure 4. Raman spectra of silicon nanocrystals for two different geometries.

mechanical stresses. Therefore, we can naturally assume that a strong electric field, which should noticeably change the crystal lattice symmetry, exists inside a nanoparticle or in its near-surface region. This not only removes the energy degeneracy for the TO – LO phonon mode, but also leads to the blue shift of the phonon frequency due to an increase in the lattice rigidity in the direction of the constant electric field. In our opinion, the blue shift and the splitting of the Raman peak indicate the presence of a strong static electric field inside the silicon nanocrystal.

We observed the evolution of the Raman spectra of silicon nanocrystals exposed to the radiation from a He – Ne laser. After prolonged exposure (for several hours), the Raman peak shifted to 522 cm^{-1}. Note that the intensity of laser radiation (not exceeding 15 mW) was insufficient to heat the sample strongly and cause structural changes in the crystal lattice of the nanocrystal or to initiate any photochemical reactions. The absence of any irreversible chemical reaction is also proved by the fact that the sample always reverted to its initial state after being held in dark for several hours. A possible reason behind such a behaviour of silicon nanocrystals is the charge exchange between defects at the semiconductor boundary under the action of laser radiation. Further investigations are required to determine the origin of these defects.

4.3 Localisation of electrons

An analysis of the absorption and Raman spectra of silicon nanocrystals suspended in glycerol revealed that the peculiarities in the behaviour of the medium in the optical frequency range, as well as phonon anomalies, can be attributed to the presence of a strong static electric field inside silicon particles. The strength of this field achieves $(2-3)\times 10^7$ V cm^{-1}.

We considered the possible mechanism of the emergence of an electric field in silicon nanocrystals in Ref. [4], where we calculated the strength of the internal electric field produced by dipoles arranged equidistantly on the surface of a spherical particle. The dipoles are formed as an electron is transferred from silicon to oxygen. Note that a high static electric field strength ($E \sim 10^8$ V cm^{-1}) near a weakly oxidised silicon surface was observed earlier in the study of the Stark shift of the absorption line of the dye molecules adsorbed at the surface [14].

It is known [10] that the application of strong electric fields to a semiconductor leads to a dynamic spatial localisation of electrons excited to the conduction band of the

semiconductor (to Bloch oscillations). An electron in the conduction band is accelerated in an electric field. Consequently, an electron in strong fields moves within a few bands in the momentum space of reciprocal vectors and, hence, is localised in space. We estimated the size of the spatial localisation region for electrons in the parabolic conduction band approximation. It was found that an electric field of strength $E = 2.5 \times 10^7$ V cm^{-1} localises an electron within a silicon lattice period, i.e., in a region of size about 0.5 nm. This estimate shows that the calculated static electric field inside a nanoparticle ($E = 2.8 \times 10^7$ V cm^{-1}) is capable of confining an electron in the vicinity of a hole created in the valence band.

If the correlation of the relative motion of an electron and a hole is taken into account, the linear absorption coefficient α increases to the same extent as the probability density of finding the electron at the position of the hole as compared to the state described by a plane wave (other conditions remaining the same). To take into account the Coulomb interaction between the electron and the hole, it seems natural (following Elliot [15]) to introduce in the expression for α a weight factor equal to the ratio of the probability density of finding a localised electron at a certain point in the coordinate space to the probability density of finding an electron described by a Bloch wave at the same point. This ratio depends on the size of the localisation region and may be quite large. Hence, it is not surprising that the absorption coefficient in nanocrystals is 20 times larger than that for bulk silicon crystals.

Apparently, an increase in the optical absorption coefficient is not the only effect caused by the localisation of electrons. We are not aware of any investigations of electron localisation in an electric field in 3D objects like nanocrystallites. At the same time, localisation of charge carriers in semiconductor superlattices leads to induced transparency [16] and to a high nonlinear absorption coefficient [17].

5. Conclusions

The high values of the nonlinear absorption coefficients β for silicon nanocrystals introduced in a glycerol matrix indicate that this medium is promising for creating nonlinear optical devices with short switching times. The optical processes occurring in such media are studied. The mechanism responsible for optical absorption, a high nonlinear susceptibility, and an induced bleaching of the medium is analysed. The suitability of the mathematical model used for a continuous medium remains questionable at this stage.

In our opinion, the most probable explanation is the presence of a strong static electric field inside silicon nanocrystals [4]. The origin of such strong fields, however, is not clear. These fields could be produced by a double electric layer formed due to the escape of electrons from the centre of a silicon nanocrystal to the defects in the oxide layer at the surface of this nanocrystal, by protonation of the silicon nanocrystal due to incomplete decomposition of monosilane (the starting material for obtaining nanocrystals), or by the existence of an intermediate region between silicon and the oxide. Further studies are required to find an answer to this question.

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