Quantum size effect and pronounced optical nonlinearities in porous silicon

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Bleaching bands have been observed in the time-resolved nonlinear transmission spectra of porous silicon. They are attributed to a saturation of optical transitions between quantum-size levels in a system of spatially localized carriers.

The photoluminescence of porous silicon in the visible part of the spectrum can be explained on the basis of a spatial quantization of carriers in thin filaments of silicon which are formed by electrochemical etching of the original bulk material.[1,2] However, discrete structure of the optical transitions associated with the size quantization of carriers has yet to be observed in either linear absorption spectra or luminescence spectra of porous silicon.

In the present study we detected bleaching bands by time-resolved nonlinear transmission spectroscopy. We attribute these bands to a saturation of optical transitions in a system of spatially localized carriers. The nonlinearities which are observed are characterized by high values of the cubic nonlinear susceptibility (up to 10^{-8} cgs units) and short relaxation times (about 40 ps).

The porous silicon samples were grown by anodic etching on a substrate of heavily doped *n*-type silicon in the (111) orientation. The electrolyte was a 50% solution of HF in ethanol; the current density was 30 mA/cm^2. The porous layer was detached from the substrate by briefly raising the current density to 100 mA/cm^2. The resulting samples of porous silicon were plane-parallel platelets 20–30 μm thick. Their Raman spectra revealed a narrow peak at about 520 cm^{-1}, which is characteristic of crystalline silicon. There were no bands which would indicate the presence of an amorphous phase.

The samples (at 300 K) were excited by ultrashort pulses of the second harmonic of a Nd:YAG laser (the pulse length was about 20 ps, and the photon energy 2.33 eV) and probed by ultrashort pulses of "white" light at various times after the pump pulse. From the measured nonlinear transmission we calculated the differential transmission spectra $DT(\lambda) = [T(\lambda) - T_0(\lambda)]/T_0(\lambda)$, where $T(\lambda)$ and $T_0(\lambda)$ are the transmission spectra of the excited and unexcited sample.

The linear absorption spectra (Fig. 1) of these platelets of porous silicon contain no features which would indicate a discrete nature of the optical transitions in this material. The linear absorption coefficient α_0 increases rapidly at photon energies above 1.3 eV (from 60 cm^{-1} at $\hbar\omega = 1.32$ eV to 2.2×10^3 cm^{-1} at $\hbar\omega = 2.36$ eV), in accordance with $\alpha_0 \propto \exp(-\hbar\omega/\Gamma_\gamma)$ with a parameter $\Gamma_\gamma = 0.32 \pm 0.06$ eV. From the

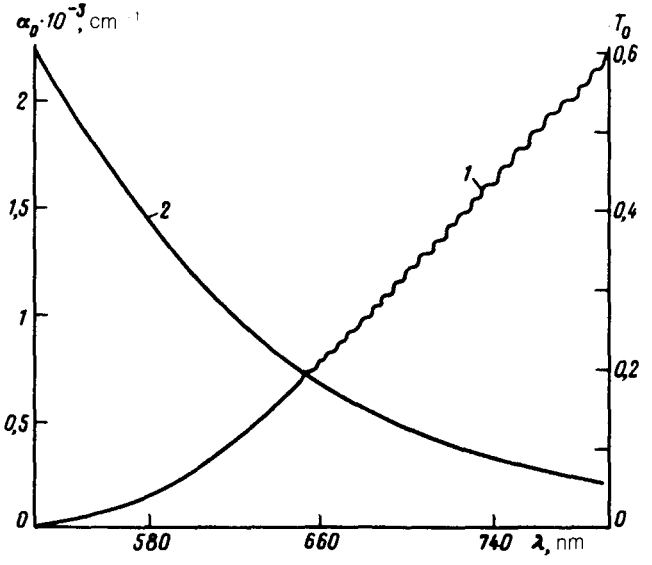

FIG. 1. Transmission (1) and absorption (2) spectra of an unexcited porous silicon sample (of thickness $d=23$ μm, at $T=300$ K).

distance between the peaks of the interference structure in the $T_0(\lambda)$ spectrum (Fig. 1) we found the linear refractive index to be $n_0 = 1.9$. This is smaller than that of bulk silicon by a factor of nearly 2.

Figure 2 shows differential transmission spectra of a porous silicon sample for various values of the delay Δt between the ultrashort exciting and probing pulses. These spectra correspond to positive values of the differential transmission, indicating an effect of induced bleaching. At $\Delta t = 0$, two comparatively narrow bleaching bands, at spectral positions $\lambda_1 = 735.6$ and $\lambda_2 = 620.4$ nm, are well resolved in the $DT(\lambda)$ spectrum. (The widths of the bands at half-maximum are 75 and 56 meV, respectively.) The induced change in the absorption coefficient, $|\Delta\alpha|$, reaches 240 cm^{-1} near λ_1 ($|\Delta\alpha|/\alpha_0 \simeq 0.6$). As the delay Δt is increased to 20 ps, the λ_2 band disappears from the $DT(\lambda)$ spectra. The exponential relaxation time of λ_1 is about 40 ps (see the inset in Fig. 1).

The discrete structure in the $DT(\lambda)$ spectra, in particular, the spectral positions of bleaching bands λ_1 and λ_2, can be attributed to a saturation of optical transitions in a system of carriers localized in quasi-1D wires. The absence of a corresponding structure from the linear transmission spectra is apparently caused by a pronounced nonuniform broadening of the quantum-size levels (due to variations in the transverse dimensions of the wires). This broadening is substantially suppressed in the nonlinear transmission spectra because of a selective effect of the narrow-band laser pump light (we observed this effect earlier in a study of quasi-OD nanocrystals,[3] and it was analyzed in detail in Ref. 4).

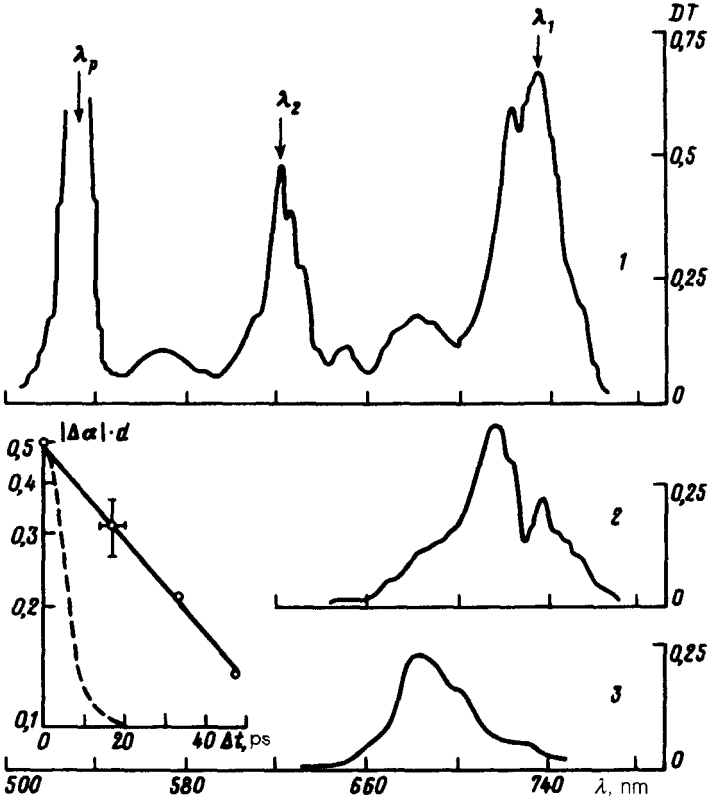

FIG. 2. Differential transmission spectra of a porous silicon sample ($d=23$ μm, $T=300$ K) for various values of the time delay Δt between the ultrashort exciting and probing pulses. *1*—0; *2*—17; *3*—33 ps. The inset shows the relaxation of the induced changes in the absorption coefficient at the peak of bleaching band λ_1. The dashed line shows the changes in the area of the overlap of the ultrashort exciting and probing pulses as the delay Δt is varied.

In evaluating the energies of the optical transitions we considered wires which were long parallelepipeds oriented along the [001] axis (this is the predominant direction during the growth of voids[5] with facets perpendicular to the [110] and [1$\bar{1}$0] directions. To get an idea of the nature of the optical transitions in such structures, we can examine a projection of the band structure of the bulk material onto the 1D Brillouin zone of a quantum wire. Two electron valleys lying in the [001] direction form an indirect minimum (with $k \sim \pm 0.4\pi/a$). The four electron valleys lying in perpendicular directions are projected onto the center of the Brillouin zone and form an absolute direct minimum. As a result, quasi-1D silicon is apparently a direct-gap material,[6] in contrast with the bulk material. The quantum-size shift of the levels corresponding to the center of the Brillouin zone is determined by the electron mass for the [110] direction, m^e_{110}. The energies of the optical transitions in this quasi-1D

structure can be found from the following expression (we are ignoring Coulomb effects and spin–orbit splitting):

$$E_{n_1 n_2}^{l(h)} = E_g^x + \frac{\hbar^2 \pi^2 (n_1^2 + n_2^2)}{2\mu_{l(h)} L^2}, \tag{1}$$

where E_g^x is the size of the indirect energy gap in bulk silicon, $\mu_{l(h)} = m_{110}^e m_{l(h)}^h / (m_{110}^e m_{l(h)}^h)$ is the reduced carrier mass for light (l) and heavy (h) holes, n_1 and n_2 are quantum numbers (which take on the values 1, 2, 3, . . .), and L is the transverse dimension of the wires. The λ_1 and λ_2 bands in the $DT(\lambda)$ spectra can be attributed to a saturation of the two low optical transitions E_{11}^h and E_{11}^l. The short-wave shifts of these bands with respect to E_g^x are 0.57 (λ_1) and 0.89 eV (λ_2). Using expression (1), we see that these figures correspond to transverse dimensions of 2.6–2.8 nm for the wires. The apparent reason why this particular dimension is predominant in the nonlinear transmission spectra is that the energy of the third optical transition, $E_{12}^h(E_{21}^h)$, is close to the energy of the laser photon, so the interaction of this transition with the incident light is highly efficient.

These results can be used to estimate the imaginary part of the resonant nonlinear Kerr cubic susceptibility, $\mathrm{Im}\chi^{(3)}$. In the case of relatively low carrier densities n_e (in which case $\chi^{(3)}$ plays a dominant role in forming the nonlinear-optics response), this imaginary part can be found from

$$\mathrm{Im}\,\chi^{(3)}(\omega) = \frac{c^2 n_0^2}{8\pi^2 \omega} \frac{t_e \alpha_0(\omega) \Delta\alpha(\omega)}{\hbar \omega n_e}, \tag{2}$$

where τ_e is the typical carrier lifetime. Using the results of our measurements in (2), we find $|\mathrm{Im}\,\chi^{(3)}| \simeq 10^{-8}$ cgs units. This result is several orders of magnitude larger than the values characteristic of nonresonant nonlinearities in transparent nonlinear-optics materials.

In summary, these measurements have revealed discrete structure in the time-resolve nonlinear transmission spectra of porous silicon. This structure can be attributed to quantum-size effects. The strong, rapidly relaxing nonlinearities seen in these experiments suggest that porous silicon can be used to develop not only efficient emitters but also fast nonlinear-optics switches, with a speed compatible with the emitters.

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