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Strong optical nonlinearities in porous silicon: Femtosecond nonlinear transmission study

V. Klimov* and D. McBranch
Chemical Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

V. Karavanskii
Institute of General Physics, Vavilov Street 38, 117942 Moscow, Russia

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Large photoinduced absorption is observed in free-standing porous-silicon films in the spectral range from 1.1 to 2.5 eV by using a femtosecond pump-and-probe technique. The measured nonlinear transmission spectra have a very fast component with initial decay on the subpicosecond time scale. The spectral structure and temporal behavior of induced absorption show the presence of molecularlike Si complexes with well-defined energy levels and spectrally uniform picosecond relaxation dynamics.

The observation of efficient visible photoluminescence (PL) from porous silicon[1] (PS) has generated considerable interest in this material in view of possible applications in all-silicon-based optoelectronics. Although the microscopic origin of PL is still a matter of controversy, it is widely accepted that the main PL band from PS in the red-orange spectral region originates from quantum-confined states within crystalline silicon nanostructures.[2] The important role of quantum size effects in PS was demonstrated by linear[3–5] and time-resolved nonlinear transmission[6,7] studies. On the other hand, there are a number of experimental observations that cannot be explained by a simple quantum-confinement model. These are, e.g., blue emission from PS,[8–10] anomalous temperature dependence[11,12] and surface sensitivity[13] of the red-orange emission, complex behavior of the photoluminescence-excitation (PLE) spectra,[14] and the presence of fast picosecond components in both PL (Refs. 15 and 16) and nonlinear transmission.[16,17] This shows that photoinduced processes in PS have likely a number of different origins involving not only quantum-confined states of nanocrystallites (NC's), but also the surface (interface) states[13,17–19] and/or states in molecularlike Si complexes (clusters).[14,20]

Experimental studies of PS have mainly concerned PL, yielding information on the energy structure and population dynamics of the low-energy relaxed states in the material. Time-resolved nonlinear transmission measurements can provide complementary information to conventional PL spectroscopy, revealing the structure of higher-lying states and fast carrier dynamics in the initial stages after photoexcitation. These measurements proved to be a powerful tool for study of bulk and low-dimensional semiconductors (see, e.g., Ref. 21).

Both types of effects—photoinduced bleaching[6,7] and increased absorption[16,17,22]—were reported for PS. The nonlinearity relaxation constants observed vary from milliseconds[22] to several picoseconds.[17]

In the present paper, we report femtosecond transient absorption spectra of PS films. The spectral structure and dynamics of the photoinduced absorption are suggestive of the presence of molecularlike complexes (clusters) being most likely intrinsic to PS layers.

PS samples of different porosities were prepared by a two-stage anodization of n^+-type Si substrates [resistivity 0.01 Ω cm, orientation (111)] in an aqueous solution of HF (49%). In the first stage, substrates were treated at small current densities from 7 to 100 mA/cm^2 for 30 min to form layers of required porosities. In the second stage, the current densities were sharply increased up to values ~10 times larger than those in the first stage. This allowed the easy separation of thin porous films (thickness $d=5$–20 μm) after the substrates were rinsed in ethanol and dried in an air stream. The PS films under investigation were fabricated as described above about two years ago and were exposed to air until the present study.

The samples studied exhibit Raman spectra characteristic of crystalline Si NC's and clearly show the high-energy shift of the absorption edge from that in bulk Si.[6] As distinct from light-emitting PS layers prepared on p-doped Si substrates, the films under investigation do not exhibit efficient PL. A weak PL band recorded under UV excitation is located in the red region and has a maximum at 1.7–1.8 eV.

Time-resolved nonlinear transmission spectra were measured using a femtosecond pump-and-probe experiment. The samples were excited at 3.1 eV by frequency-doubled 200-fs pulses from a regeneratively amplified mode-locked Ti-sapphire laser (repeating rate 1 kHz). Pump-induced transmission changes were probed by delayed pulses of a femtosecond continuum. A 0.15-m spectrometer and a cooled charge-coupled device were used to measure the transmission in the absence (T_0) and in the presence (T) of the pump, from which we derived the differential transmission spectra (DTS) $\mathscr{D}=(T-T_0)/T_0=\Delta T/T_0$. For DTS well below 1 the differential transmission is proportional to the absorption changes $\Delta\alpha$: $\mathscr{D}\approx-\Delta\alpha d$.

Figure 1 shows the linear transmission spectra of two samples prepared at current densities 7 (1) and 100 mA cm^{-2} (2). The sample porosities are 55% (1) and 64% (2). The bulk-equivalent absorption[23] derived by taking into account the sample porosities is shown in the inset to Fig. 1. The blueshift of the absorption edge clearly seen for the sample of higher porosity can be explained in terms of size quantization within Si NC's of reduced dimensions.[24]

The results of transient absorption measurements for sample 2 are shown in Fig. 2 (pump fluence $w_p=12$ mJ cm^{-2}). The spike at 1.55 eV corresponds to the laser fundamental frequency. The oscillations observed clearly at

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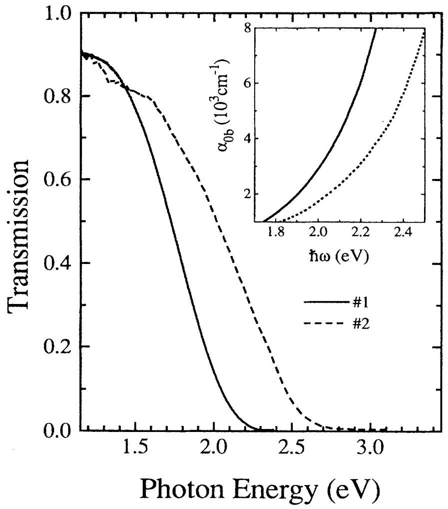

FIG. 1. Linear transmission spectra of two PS samples prepared at current densities 7 (sample 1; solid line) and 100 mA cm^{-2} (2; dashed line). Sample thicknesses are 14 (1) and 8 μm (2). Inset shows the bulk-equivalent absorption (α_{0b}) for these samples.

low energies result from an etalon interference, indicating the high optical quality of the samples. Due to the chirp of the probe pulses (~2.5 ps in the spectral range under investigation) the DTS are distorted at small delay times between pump and probe pulses ($\Delta t <$ 2.5 ps). Therefore, shown in Fig. 2 are only the spectra at longer delays that correspond to the DTS relaxation. The DTS dynamics derived for fixed spectral energies and corrected for chirp are shown in Fig. 3.

The differential transmission observed is negative in the whole spectral range, indicating photoinduced absorption. The DTS consist of a low-energy band at 1.23 eV (ω_1) and a broad high-energy band with a maximum around 2.2–2.3 eV. The low-energy band disappears nearly completely during the first 10 ps after excitation. Starting from this point, the DTS decay is essentially uniform in the whole spectral range measured. At delay time Δt = 200–300 ps the decay slows down dramatically, so that the spectra measured at ~300 ps and 1 ms are nearly identical (see Fig. 2). This shows the presence of a very slow component peaked at ~2.3 eV (ω_3) and having a long low-energy tail. By subtracting the slow-relaxing background from the DTS measured at short delays we find that the fast (picosecond) DTS component in addition to the ω_1 maximum exhibits a maximum at ~1.95 eV (Fig. 4; solid line). This second fast band (ω_2) is manifested in the DTS in Fig. 2 as a bump around 1.95 eV.

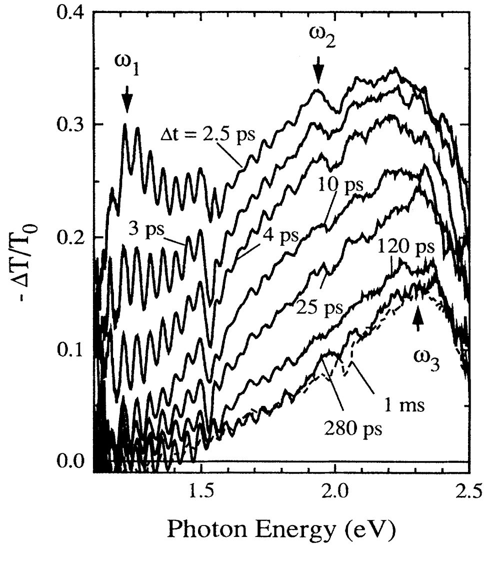

FIG. 2. DTS of PS sample 2 at different delay times between pump and probe pulses (pump fluence w_p = 12 mJ cm^{-2}).

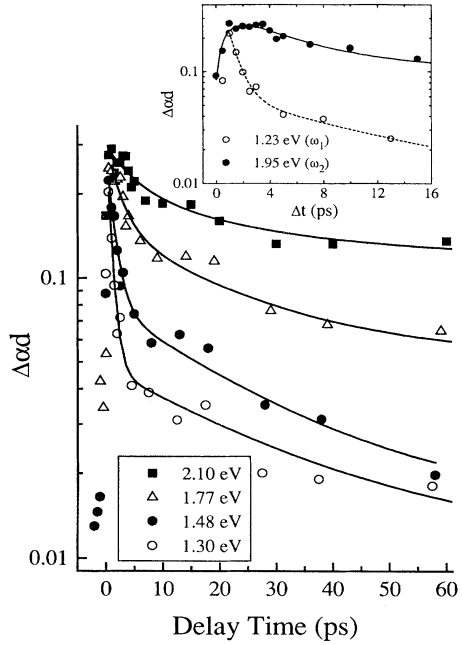

FIG. 3. Time transients derived from the time-resolved DTS (sample 2) at different spectral energies (symbols) and results of the double-exponential fit (lines) at 2.1 eV (τ_1 = 5 ps, τ_2 = 26 ps), 1.77 eV (τ_1 = 2.6 ps, τ_2 = 25 ps), 1.48 eV (τ_1 = 1.4 ps, τ_2 = 25 ps), and 1.3 eV (τ_1 = 0.8 ps, τ_2 = 29 ps). Inset shows short-term dynamics of induced absorption at 1.23 and 1.95 eV (symbols). The fitting curves are calculated for the initial decay times 800 fs (1.23 eV) and 5 ps (1.95 eV), and for the rise time 900 ps (1.95 eV). Experimental data are corrected for chirp.

Interestingly, the spectral positions of the fast-relaxing bands are preserved for the sample of lower porosity [Fig. 5(a)], whereas the slow-relaxing background notably shifts to lower energies [Fig. 5(b)], correlated with a shift of the absorption edge (see Fig. 1).

To analyze the short-term DTS dynamics we fit the time transients derived for different spectral energies to a double-exponential decay: $y=y_0+A_1e^{-(t-t_0)/\tau_1}+A_2e^{-(t-t_0)/\tau_2}$. The results of the fitting procedure for sample 2 are shown in Fig. 3 ($\Delta t<$60 ps). The fast relaxation time τ_1 gradually increases in going to higher spectral energies from 800 fs at 1.3 eV to 5 ps at 2.1 eV, whereas the constant of the slower decay τ_2 is nearly spectrally independent (spectrally uniform decay) and is in the range 25–30 ps. These data are in reasonable agreement with single-wavelength measurements in Ref. 17, where the double-exponential decay with time con-

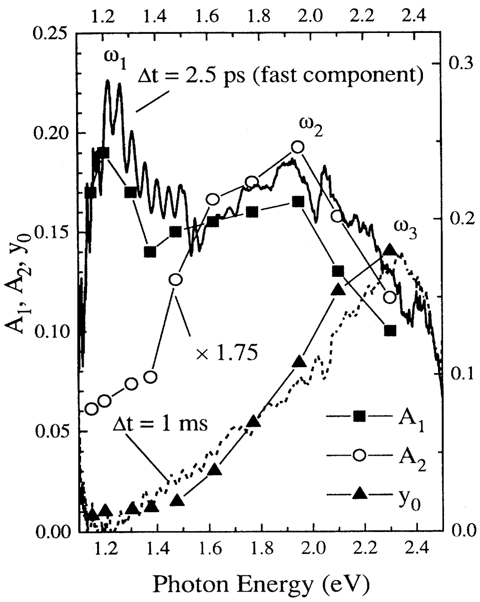

FIG. 4. Spectral distributions of the amplitudes A_1 (fast picosecond component), A_2 (slow picosecond component), and nonrelaxing background y_0 derived from the double-exponential fit to the measured DTS in comparison to the fast DTS component derived for 2.5 ps and DTS recorded at 1 ms (sample 2).

stants 5 and 15 ps was reported. The spectral uniformity of the decay is preserved on the longer time scale. The three-exponential fit performed for delays up to 400 ps shows the presence of the component with relaxation time 120–150 ps. This decay is probably similar to that studied in picosecond experiments in Ref. 16.

The results of the double-exponential fit for the spectral distributions of the amplitudes A_1, A_2, and the nonrelaxing background y_0 are shown in Fig. 4 in comparison to the DTS measured at 1 ms (dashed line) and the fast DTS component at 2.5 ps (solid line). As expected, the magnitude of the offset y_0 increases gradually with increased spectral energy, following closely the shape of the nonrelaxing DTS portion measured at 1 ms. The 20–25-ps component is peaked at the position of the ω_2 band and decreases in the spectral regions of the ω_1 and ω_3 bands. The amplitude of the fast picosecond component (τ_1 = 0.8–5 ps) exhibits two maxima around ω_1 and ω_2. The observed picosecond dynamics can be explained assuming the existence of the two broad overlapping transitions (ω_1 and ω_2) with different relaxation dynamics: single-exponential ($\sim$1 ps) for the ω_1 transition and multiexponential ($\sim$3–5 ps, $\sim$25–30 ps, $\sim$120–150 ps) for the ω_2 transition.

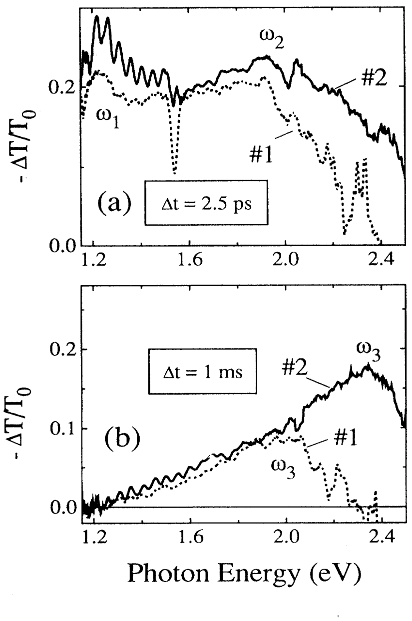

FIG. 5. Fast DTS components derived at 2.5 ps (a) and DTS taken at 1 ms (b) for PS samples 1 (dashed line) and 2 (solid line).

The analysis of the buildup dynamics (see inset to Fig. 3) shows that the rise time of the ω_1 band is shorter than 0.5 ps. The buildup of the ω_2 band is complementary to the decay of the ω_1 band and is characterized by a time of about 900 fs.

A very slow increased absorption similar to that observed by us as the ω_3 band was previously reported in Ref. 22, and was assigned to carriers localized in the surface states of Si NC's. We think, however, that a mechanism for the slow-relaxing portion of the DTS arising from a thermal shift of the absorption edge is more likely. Our estimates show that the heating of the excited part of the sample under our experimental conditions can be around 100–150 K. This can lead to a low-energy shift of the absorption edge by at least 30 meV, resulting in the large increased absorption at the band-edge spectral energies. The observed correlations between the position of the ω_3 band and that of the absorption edge in the samples of different porosities provide additional evidence for the thermal origin of the slow-relaxing portion of the DTS.

The short-lived DTS component certainly has a nonthermal electronic origin, given its fast relaxation dynamics. However, it can hardly be interpreted in terms of carriers occupying spatially confined states within Si NC's. The data available for other quasi-zero-dimensional structures such as CdSe,[25,26] Zn$_{1-x}$Cd$_x$S,[27] CdTe,[28] CuCl,[29] and Cu$_x$S (Ref. 30) NC's show that DTS in these systems are dominated by a positive signal of pump-induced bleaching due to a state-filling effect. The increased absorption resulting from biexciton[31] or trapped-carrier-induced Stark[32] effects are usually located in the narrow spectral regions near main bleaching bands. The broad bands of induced absorption observed by us in PS are rather characteristic of molecular systems such as fullerenes[33] or conjugated polymers[34] but not inorganic semiconductors. The nonlinearities in these molecular systems arise from strong new absorptions from discrete excited states to higher-lying bands. A molecularlike origin of the effects observed by us is also suggested by the insensitivity of the spectral positions and dynamics of the short-lived bands ω_1 and ω_2 to changes in the sample porosity. This shows the presence of energy levels with fixed spectral positions, independent of the dimensions of the NC's (independent of the spatial confinement manifested in the linear transmission; see Fig. 1). The other molecularlike feature of the measured DTS is the spectrally uniform relaxation dynamics at $\Delta t > 10$ ps, which are characteristic of homogeneously broadened transitions and can hardly be expected for the quantum-confined NC states in view of the broad dispersion of the sizes and shapes of the NC's.

The complementary subpicosecond dynamics of the ω_1 and ω_2 bands can be explained in terms of the excited-state absorption involving two energy levels within the same molecularlike complex. Laser pumping results in the fast population (during less than 500 fs) of the higher-lying state associated with the ω_1 transition. The depopulation of this state into a lower-lying one (associated with the ω_2 transition) is seen as a buildup of the ω_2 band accompanied by a complementary decay of the ω_1 band. The slower 3–5-ps decay observed for the ω_2 band can be considered as continuing energy relaxation into the low-lying states within the same molecular complex and/or into the NC surface or confined states. The subsequent decay on the time scale of tens of picoseconds seen in the final stage of fast relaxation may be explained by carrier recombination, which dominates the relaxation process after the thermal quasiequilibrium in the system is already achieved.

In our previous measurements[6] performed with a low-repetition rate (2 Hz) picosecond system (20-ps pulse duration) and a pump at 2.33 eV we saw a positive signal of the photoinduced bleaching that was explained in terms of the state filling inside Si quantum wires and/or dots. However, this signal is not observed under present excitation conditions. We believe that this is mainly due to the difference in the pump-photon energy resulting in the predominant excitation of the spieces that are different from those excited by 2.33-eV photons. The pump-photon energy used in the present experiments (3.1 eV) is close to the maximum of the molecularlike PLE band (3.35–3.4 eV) reported in Ref. 14, which may lead to more efficient excitation of the moleculariike complexes than the Si NC's. Additionally, the "photodarkening" well known for CdS_xSe_{1-x} NC's (Ref. 35) can also play a role in Si NC's. This effect results in the reduction of the state-filling-induced bleaching under intense and prolonged laser illumination, as is the case in the measurements performed.

Although the detailed microscopic nature of the nonlinearities observed in the present paper is not quite clear, this effect is of considerable interest in view of possible applications for optical limiting (slow DTS component) and ultrafast optical switching (fast DTS component). An attractive feature of the nonlinearity observed is its photostability. We did not see any reduction in the nonlinear signal after several hours of illumination at the intensity of 10 mW cm^{-2}.

In conclusion, we have observed large photoinduced absorption (differential transmission up to 60% in some samples) in PS films by using a femtosecond pump-and-probe technique. The measured signal has fast components with relaxation constants from 800 fs to tens of picoseconds superimposed on a slow-relaxing background. The spectral structure and relaxation dynamics of the short-lived DTS component are suggestive of the presence of molecularlike complexes with well-defined energy levels (independent of the sample porosity). The observed large, stable, and fast optical nonlinearities are of considerable interest in view of possible applications in optoelectronics and signal processing.

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*On leave from Institut für Halbleitertechnik II, RWTH Aachen, Sommerfeldstr. 24, D-52074 Aachen, Germany.

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