Short-lived green band and time evolution of the photoluminescence spectrum of porous silicon

A. V. Andrianov, D. I. Kovalev, V. B. Shuman, and I. D. Yaroshetskiĭ
A. F. Ioffe Physicotechnical Institute, Russian Academy of Sciences, 194021, St. Petersburg, Russia

(Submitted 9 June 1992; resubmitted 30 July 1992)
Pis'ma Zh. Eksp. Teor. Fiz. **56**, No. 5, 242–245 (10 September 1992)

A short-lived emission has been observed in a study of the time evolution of the emission spectrum of porous silicon. The transformation of the spectrum over a broad time interval (10^{-8}–10^{-5} s) was studied.

The observation of an efficient emission in an indirect-gap semiconductor[1] has attracted interest to the study of porous silicon. This interest is increasing in an avalanche fashion.[2] It has previously been believed that the emission of porous silicon occurs in a broad, structureless band in the region 1.7–1.9 eV. In the present study we have observed a transformation of the emission spectrum from porous silicon over time. We have demonstrated that there are two emission bands under certain conditions.

The layers of porous silicon were grown in a 20% aqueous solution of HF during the flow of an anodic current of density $j = 50$–60 mA/cm^2 for 3–5 min. The substrates were polished p-Si wafers with a resistivity of 1 Ω/cm and a [100] orientation.

The Raman-scattering spectrum measured at $T = 300$ K contains a single narrow line, which is shifted 2 cm^{-1} in the lower-frequency direction from the line of the *LO* phonon of bulk silicon. This shift is evidence that there is no significant amount of amorphous structure in the test samples.

The samples were excited by the beam from a pulsed nitrogen laser ($\lambda = 3370$ Å, $t_p = 10$ ns) and also by the beam from a cw argon laser ($\lambda = 4880$ Å). The excitation level was 10–100 W/cm^2 in the case of steady-state excitation and 10^4–10^5 W/cm^2 in the case of pulsed excitation. To detect the signals in the steady-state case, we used a photon counting arrangement. The pulsed measurements were carried out with a stroboscopic detection system (the strobe pulse was 4 ns wide) with a time resolution ~20 ns.

The inset in Fig. 1 shows the photoluminescence spectrum at $T = 300$ K found during excitation by the cw argon laser. We see a broad, structureless band peaking at 1.75 eV. The time-resolved spectra (Fig. 1) are radically different from the spectrum in the inset in Fig. 1. For a detection time coinciding with the peak of the laser pulse ($\Delta t = 10$ ns), the photoluminescence peak falls in the green region. The energy of this peak of the photoluminescence band is 2.36 eV. When the detection time is shifted 15 ns with respect to the peak of the laser pulse ($\Delta t = 25$ ns) we clearly observe two photoluminescence bands: a short-wave one (A1) peaking at 2.5 eV and a long-wave one (A2) peaking at 2.08 eV. A further increase in the delay of the detection time with respect to the laser pulse leaves A1 in essentially the same place, while A2 undergoes a

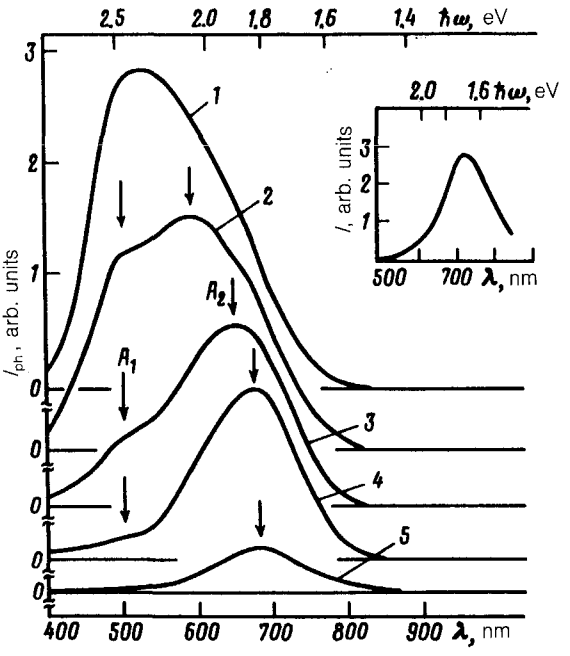

FIG. 1. Time-resolved photoluminescence spectra of porous silicon for various values of the delay (Δt) between the beginning of the laser pulse and the time the spectrum was recorded ($T = 300$ K). 1—$\Delta t = 10$ ns; 2—25 ns; 3—50 ns; 4—75 ns; 5—1 μs. The inset shows the photoluminescence spectrum of porous silicon during steady-state excitation by an argon laser ($\lambda = 488$ Å).

progressive shift in the long-wavelength direction. As can be seen from Fig. 1, A2 becomes predominant; at delays $\Delta t > 100$ ns, A1 is essentially impossible to see in the spectra. The bands A1 and A2 have a half-width (~ 0.4 eV) and therefore overlap. Figure 2a shows time sweeps of the shape of the photoluminescence pulse at different wavelengths. In all cases the shape of the photoluminescence pulse reflects a combination of two signals: a fast one, which reproduces the laser pulse essentially perfectly, from band A1; and a slow one, with a decay time in the microsecond range, from A2. The ratio of the intensities of the fast and slow components varies with the wavelength selected, as can be seen from Fig. 2a.

The situation at $T = 42$ K is quite different. The amplitude of the slow component of the photoluminescence signal is substantially lower. The slow ($\Delta 100$ ns), weak component appears at wavelengths ~ 6000 Å. Only a single, structureless band is observed in the time-resolved spectra. The peak of this band shifts slightly in the long-wave direction with increasing delay. Figure 3 shows a photoluminescence spectrum recorded during steady-state excitation. On the whole, this spectrum differs only negligibly from that found at $T = 300$ K (see the inset in Fig. 1).

The photoluminescence spectra recorded with time resolution at $T = 300$ K thus provide evidence for the existence of two characteristic emission bands, A1 and A2, which differ in emission energy and in luminescence decay time. The long-wave band,

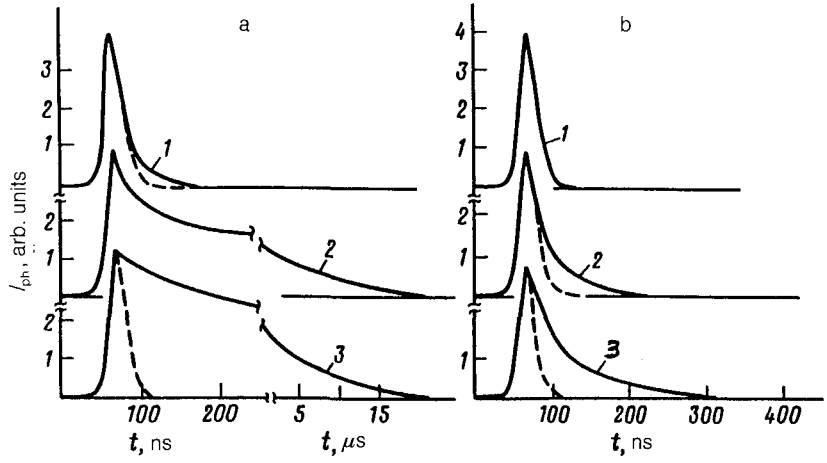

FIG. 2. Kinetics of the photoluminescence of porous silicon at various wavelengths. a: $T = 300$ K. b: $T = 4.2$ K. 1—$\lambda = 5000$ Å; 2—$\lambda = 6000$ Å; 3—$\lambda = 6500$ Å. The dashed lines show the shape of the laser excitation pulse.

with a decay time in the microsecond range, basically determines the photoluminescence spectrum which is observed during steady-state photoexcitation (Fig. 1).

We believe that the spectral-temporal transformation of the photoluminescence observed here can be explained in accordance with the existing picture of porous

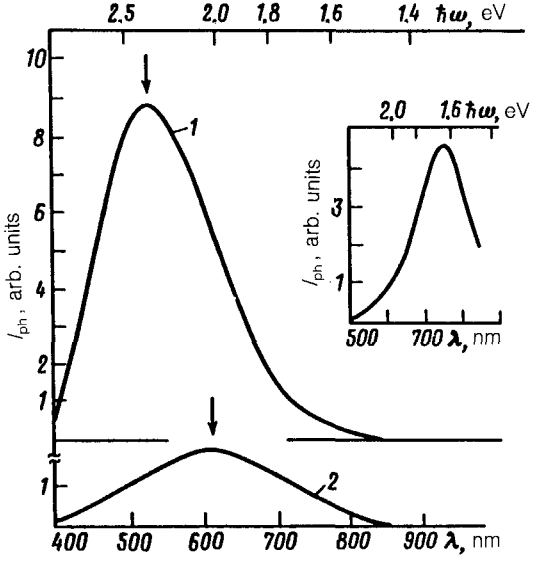

FIG. 3. Time-resolved photoluminescence spectra of porous silicon for various delays (Δt) between the beginning of the laser pulse and the time at which the spectrum was recorded ($T = 4.2$ K). 1—$\Delta t = 10$ ns; 2—50 ns. The inset shows the photoluminescence spectrum of porous silicon during steady-state excitation by an argon laser ($\lambda = 4880$ Å).

silicon as a system of quantum wires. According to these ideas, the photoluminescence spectrum is formed by a radiative recombination of carriers which are localized in potential wells differing in width. The shift of the photoluminescence spectra in the red direction with increasing delay time at $T = 4.2$ K (Fig. 3) is evidence that the mechanism of radiationless recombination, which is responsible for the fast kinetics (Fig. 2b), is more effective for narrow quantum wires and thus for the large energy gaps which are responsible for the luminescence in the green part of the spectrum. The recombination might be caused by (for example) surface states which are responsible for the faster kinetics of the photoluminescence from narrow wells (in the short-wave part of the spectrum), because of the large ratio of the surface area of a quantum wire to its volume. In this case we would expect a shift of the time-resolved spectra in the red direction with increasing delay time (Fig. 3). In addition, a migration of excitation may be manifested in the photoluminescence spectra. At $T = 300$ K, for example, the carrier diffusion length, which is controlled by the short ($\sim$10-ns) radiationless lifetime, is ~ 1 μm. This circumstance may be the reason for an escape of carriers from a region with an effective channel for radiationless recombination. This effect should in turn lead to the appearance of a slow component in the photoluminescence kinetics. This slow component will be seen more clearly in the red part of the spectrum (for potential wells of greater width). As a result, we would expect to find two bands in the luminescence spectra: a first one shifted in the short-wave direction, due to the fast component of the kinetics; and a second one in the long-wave part of the spectrum, with a slow kinetics. We should point out that the slow component of the photoluminescence kinetics appears at $T \sim 120$ K during pulsed excitation.

In this situation, at both $T = 4.2$ K and $T = 300$ K, the luminescence spectra found during steady-state excitation are shaped primarily by the emission from the broad potential wells, in which the radiationless-recombination mechanism is less effective. This circumstance appears to also be the reason why there is substantial difference between the results at these two temperatures (Figs. 1 and 3).

We wish to thank M. A. Bresler, E. L. Ivchenko, and I. N. Yassievich for a discussion of these results.

[1]L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
[2]Abstracts of AA Symposium of MKS Fall Meeting, 1991, Boston.

Translated by D. Parsons