Fine structure of the red photoluminescence band of porous silicon

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A fine structure of the red photoluminescence band of porous silicon is reported. This observation is direct evidence that the visible radiation originates in Si quantum wires, where two-dimensional quantum confinement of carriers results in a widening of the Si band gap. To explain the fine structure, a model of electronic energy states in the Si wires is proposed.

High-intensity visible photoluminescence (PL) from porous silicon (PS) layers has recently been observed.[1–3] This phenomenon was suggested to be due to the two-dimensional quantum size effect in high-porosity silicon layers which represent a network of quantum Si wires.[1–3] In this letter we report the results of an experimental study of a well-defined fine structure of the PL band of PS.

The experiments were carried out with samples prepared from p-type ($N_B \approx 10^{15}$ cm^{-3}) $\langle 111 \rangle$ Si wafers. The PS layers were formed by anodization of the wafers in HF (48 wt%)—2'-isopropanol solution (1:1 by volume) for 30 min in a custom-built two-chamber electrochemical cell with Pt electrodes at a current density of 10 mA/cm^2. The layer porosity was above 50%, and the layer thickness was (20–30) μm. CW Ar$^+$ and pulsed nitrogen lasers (with 0.1-μs pulse duration) were used for the photoexcitation. Photoluminescence was detected by a photomultiplier or a cooled Ge:Au photoresistor. The kinetic measurements were made with the help of a Ge photodiode with the time response of 0.1 μs.

Figure 1 shows typcial PL spectra of different PS samples recorded at liquid-helium and room temperatures. The 4.2-K PL band consists of a set of lines spaced nearly evenly, with the energy interval equal to about 50 meV. The fine structure is still visible at 77 K and disappears at room temperature. Storing the samples in ambient atmosphere for several months does not affect the structure of the PL band of PS; however, it becomes indistinguishable after cycling between room temperature and liquid-helium temperature.

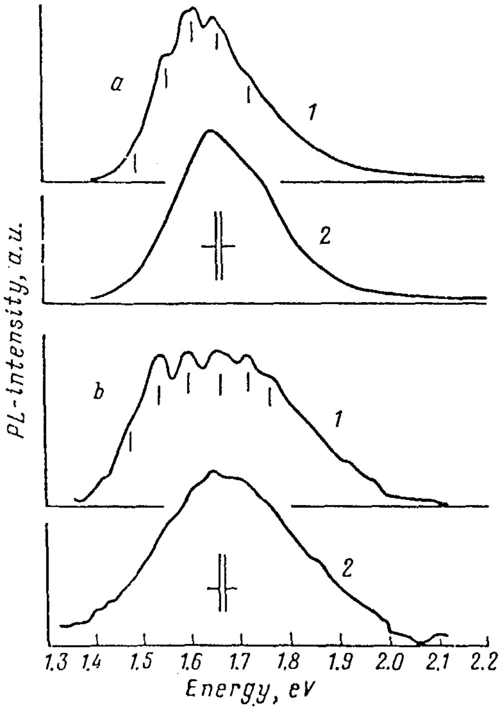

FIG. 1.

We assume that the fine structure is due to quantization of the wire width in the PS layers. Silicon wires are known to be aligned along the ⟨100⟩ crystal axes.[4] In the framework of a simple model of two-dimensional quantum confinement of carriers inside an infinite, square, potential well, the ground state energies of electrons and holes are given by[5]

$$E_{1,1}^{e}=\frac{\pi^2\hbar^2}{2d^2}\left(\frac{1}{m_t^e}+\frac{1}{m_l^e}\right),\quad E_{1,1}^{h}=\frac{\pi^2\hbar^2}{d^2m^{hh}}\,. \tag{1}$$

Here Si is assumed to remain indirect semiconductor, m_t^e and m_l^e are transverse and longitudinal masses along the ⟨100⟩ direction, respectively, and d is the width of the potential well. According to the quantum wire model,[6] the observed PL is induced by the 1D exciton recombination, and the photon energy is given by

$$h\nu(d)=E_g-\hbar\Omega+E_{1,1}^{e}(d)+E_{1,1}^{h}(d)-E_{cx}(d)\,, \tag{2}$$

where E_g and $\hbar\Omega$ are the bulk band gap and the energy of the short wavelength phonon which is involved in optical transition in Si, respectively, and E_{cx} is the 1D exciton binding energy. The PL spectrum is determined by the distribution of transverse size of the wires and/or of their different parts. Such a distribution is discrete rather than continuous, because there is a minimum value of the size change which is

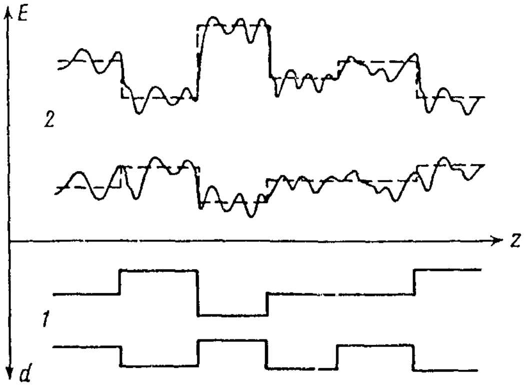

FIG. 2.

equal to an interatomic distance in the crystal. The length quantum for ⟨100⟩ orientation of wires is $a/4$, where a is the lattice constant of Si. The variation of the width of the potential well is therefore $\delta d = ka/4$, where $k=0,\ \pm 1,\ \pm 2\ldots$. If the average wire size, $\bar{d}$, is much larger than δd, and if $E_{ex} \ll (E^{e}_{1,1} + E^{h}_{1,1})$, the quantum fluctuations of the width produce a discrete luminescence spectrum, with the interline energy spacing given by

$$\frac{\delta(h\nu)}{h\nu_{max}} \approx 2\frac{\delta d}{\bar{d}} = \frac{a}{2\bar{d}}, \qquad (3)$$

as follows from Eqs. (1) and (2).

Using standard parameters for Si $m^{e}_{t} = 0.19m_0$, $m^{e}_{l} = 0.92m_0$, $m^{h}_{h}(100) = 0.274m_0$, $a = 5.42$ Å, and $h\nu_{max}$ from Fig. 1, we obtain $d = 30$ Å and $\delta(h\nu) \approx 50$ meV, in good agreement with the experimental results. The appropriate wire geometry and its energy band structure are shown schematically in Fig. 2.

As follows from Fig. 1a, full width at half-maximum of every line is about 50 meV. Such spreading of the fine structure might be induced by the potential well shape variations and by fluctuations of the charge which is localized on the wire surface (see Fig. 2).

The proposed model agrees with the preliminary results of the PL decay kinetics measurements (see Fig. 3). At the early stages of relaxation, a time decay was found to be exponential and to depend on the wavelength, increasing from 2–3 μs on the high-energy edge of the PL band and to $\approx 40\ \mu$s on the low-energy edge. Similar data were obtained by the other authors.[7–9] The lifetime is expected to decrease with decreasing width of the quantum wire, which may explain the shortening of the PL time decay with an increase in the emitted light energy. The long tail in the decay kinetics observed for all energies within the PL band can be attributed to the indirect recombination of electrons and holes captured in spatially separated deep fluctuations of the potential (see Fig. 2), consistent with the results on time-resolved PL spectra shown in Fig. 3. A detailed time decay analysis of PL will be published later.

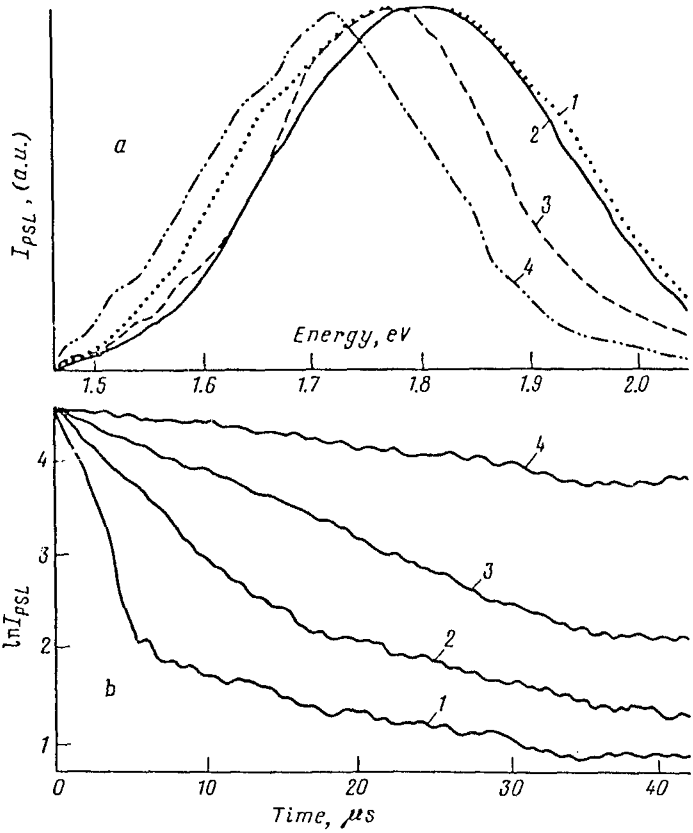

FIG. 3.

In conclusion, the fine structure of the visible PL of PS has been observed. This structure is explained on the basis of the model of a quantum wire array of PS layers.

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