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 is a direct evidence that the visible radiation originates in Si quantum wires wherein 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.

Recently high intensity visible photoluminescence (PL) from porous silicon (PS) layers has been observed [1-3]. That phenomenon was suggested to be due to the two-dimensional quantum size effect in high porosity silicon layers representing a network of quantum Si wires [1-3]. This letter contains report on a well-defined fine structure of the PL band of PS.

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

Fig.1 shows typical PL spectra of different PS samples recorded at liquid helium and room temperatures. The 4.2 K PL band is seen to consist of a set of lines spaced nearly evenly with 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 gets undistinguished after cycling between room and helium temperature.

We suppose that the fine structure is due to quantization of the wire width in PS layers. Si wires are well known to be aligned along the $\langle 100 \rangle$ 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]

$$E^e_{1,1} = \frac{\pi^2\hbar^2}{2d^2}\left(\frac{1}{m^e_t} + \frac{1}{m^e_l}\right), \quad E^h_{1,1} = \frac{\pi^2\hbar^2}{d^2 m^{hh}} \tag{1}$$

Here Si is assumed to remain indirect semiconductor, m^e_t and m^e_l are transverse and longitudinal masses along the $\langle 100 \rangle$ direction, respectively, 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

$$h\nu(d) = E_g - \hbar\Omega + E^e_{1,1}(d) + E^h_{1,1}(d) - E_{ex}(d) \tag{2}$$

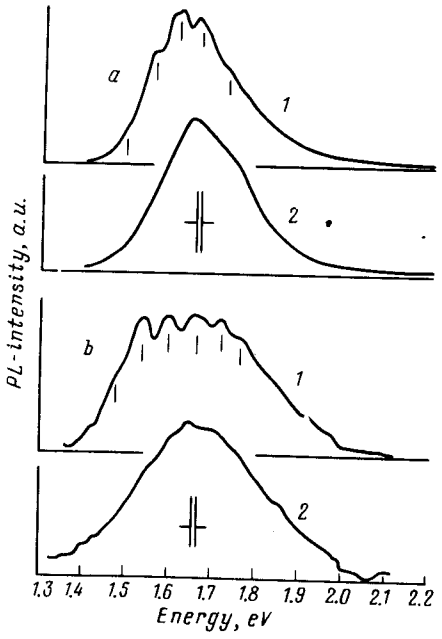

Fig.1.

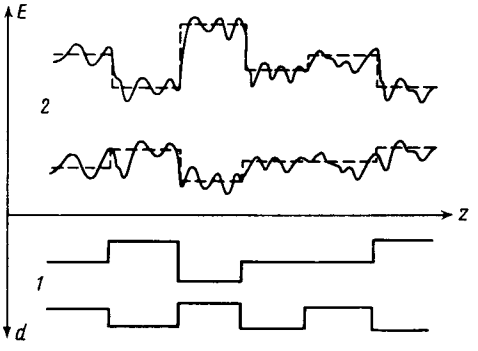

Fig.2.

Fig.1. The PL spectra of different PS layers (*a* and *b*) recorded at temperatures, K: *1*–4.2, *2*–300. The vertical bars show the peak positions.
Fig.2. The sketch of geometry (1) and energy band structure (2) along the wire axis. The influence of geometrical (dashed line) and surface charge fluctuations (full line) on the band energy structure is seen.

where E_g and $\hbar\Omega$ are the bulk band gap and the energy of the short wavelength phonon taking part in optical transition in Si, respectively; E_{ex} is the $1D$-exciton binding energy. The PL spectrum has to be determined with the distribution of transversal size of the wires and/or of their different parts. Such a distribution is rather discrete than continuous because there is a minimum value of the size change which is equal to an interatomic distance in the crystal. The length quantum for $\langle 100 \rangle$ orientation of wires is $a/4$, where a is the lattice constant of Si. The variation of the potential well width 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 $E_{ex} \ll (E^e_{1,1} + E^h_{1,1})$ the quantum fluctuations of the width result in the discrete luminescence spectrum with the interline energy spacing equal to

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

as it follows from (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 one can obtain $\bar{d} = 30$ Å and $\delta(h\nu) \approx 50$ meV in good agreement with experimental results. The appropriate wire geometry and its energy band structure are shown schematically on Fig.2.

As it follows from Fig.1*a*, full width at half maximum of every line is about 50 meV. Such spreading of the fine structure may be induced with both the

potential well shape variations and fluctuations of charge localized on the wire surface (see Fig.2).

The proposed model agrees with 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 PL band to $\approx 40\,\mu$s on the low energy edge. Similar data were obtained by the other authors [7-9]. The life time is expected to decrease with diminishing quantum wire width. It may explain shortening of PL time decay with increase of emitted light energy. The long 'tail' in the decay kinetics observed for all energies within the PL band may be attributed to the indirect recombination of electrons and holes captured in spatially separated deep fluctuations of potential (see Fig.2). That agrees with results on time resolved PL spectra shown on Fig.3. A detailed time decay analysis of PL will be published later.

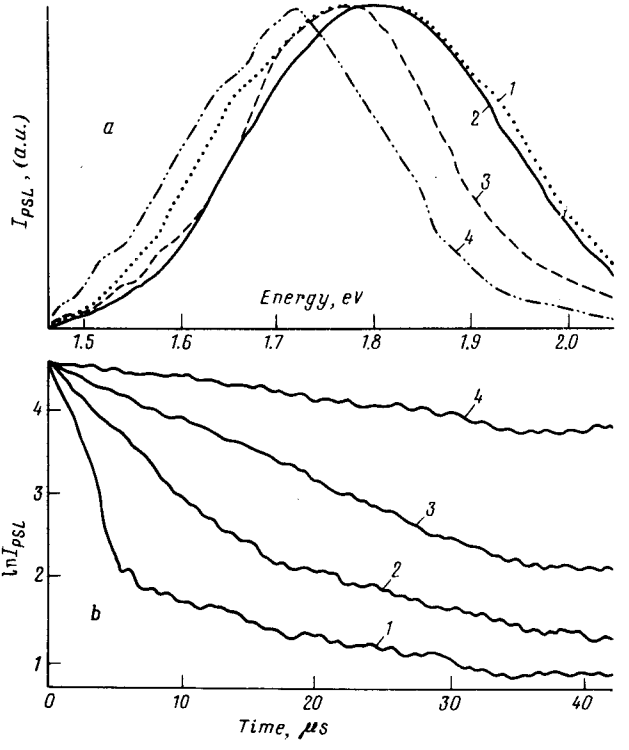

Fig.3. *a*–The time resolved PL spectra recorded under pulse excitation for different time delays, μs: *1*–3, it 2–10, it 3–30, it 4–80. $T = 300$ K. *b*–The decay kinetics for the different energies within the PL band, $h\nu$ (eV): *1*–2.06, *2*–1.95, *3*–1.72, *4*–1.49.

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

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