# New mechanism of charge carriers localization in silicon nanowires*

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**Abstract**

The results of spectral investigations of thermostimulated luminescence and temperature dependence of tunneling luminescence in the range of 4.2–300 K of highly oxidized porous silicon samples have been reported. Large dispersion of activation energies of trapping states connected with the main red-orange emission band, $\Delta E_{\rm a} \approx 0.3$ eV, and the nonmonotonic temperature dependence of the Beckerel index of tunneling luminescence component decay have been experimentally established. To explain the obtained results a model has been proposed of charge carriers localization by "topological" traps related to undulating structure of silicon nanowires.

## 1 Introduction

Highly oxidized porous silicon (por-Si) samples are known to be a complex mixture of irregular in size, form, and structure silicon nanocrystallites (see e.g. [1]). In this diverse ensemble, quantum dots (QD) and quantum wires (QW) can be distinguished according to their size and form. Besides the large dispersion of size distribution there are other kinds of structural inhomogeneity such as inhomogeneity of $SiO_x$ ($x \leq 2$) layers enveloping silicon nanocrystallites and thickness variation (undulation) of quantum wires. Obviously the noted structural features appear in properties of electronic excitations of por-Si samples, making them very sensitive to particular technology of samples preparation. The energy spectrum of electronic excitations acquires strongly pronounced inhomogeneous broadening due to the large dispersion of nanocrystallites size distribution. Another influence of the structural factor is a localization of electronic excitations determined by size effect and structural inhomogeneity. This was demonstrated in the papers [2, 3, 4] for the case of quantum dots which have shell structure consisting of silicon nanocrystalline core, enveloping nonstoichiometric $SiO_x$ layer, and surrounding amorphous $SiO_2$. The distinctive feature of the charge carriers localization in such systems is its activation character, that is "selfejecting" of charge carriers from photoexcited silicon core to traps in peripheral $SiO_x$ layer. It is realized by the electronic Auger process which provides overcoming of potential barriers between states in silicon nanocrystalline core and $SiO_x$ traps. It should be emphasized that the Auger process is the dominating dynamical process in nano-Si since its intensity is proportional to $R^{-6}$, where $R$ is the distance between particles [5]. Estimating $R$ to be of the order of nanocrystallite's size, e.g. 10 nm, the cross-section of the Auger process is about $10^{15}$ cm$^{-2}$, which is close to the cross-section of elementary cell [5]. In the paper [4]

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the so called "two-stroke charge pump" model was proposed, which is based on the Auger process ejecting electrons and holes by turns from a photoexcited nanocrystalline core to localized states in $SiO_x$ layer. This model explains in a unified way some specific features of the main red-orange emission band of por-Si: nonlinear lux-intensity characteristics, nonmonotonic temperature dependence of its integral intensity, "fatigue" effect with its spectral and temperature dependencies, spectral structure of thermostimulated luminescence (TSL) etc. [3, 4] Nevertheless some questions remained unanswered. One of them is the explanation of surprisingly large dispersion of activation energies of trapping states genetically connected with the red-orange photoluminescence (PL) band, $\Delta E_{\rm a} \approx 0.3$ eV.

In the present paper the results of spectral investigations of thermostimulated luminescence (TSL) and temperature investigations of tunneling luminescence (TL) of highly oxidized porous silicon samples are reported. The large dispersion of the activation energies distribution and established nonmonotonic temperature dependence of the Beckerel index $\beta(T)$ of TL decay are explained by specific character of charge carriers localization and their tunneling transport in undulating quantum wires (fluctuation of the wire's diameter along its length).

## 2 Experimental technique

We have investigated highly oxidized por-Si samples with thickness up to 10 $\mu$m obtained by traditional methods described in [6]. Final removal of etching products from por-Si developed surface and after-oxidation was carried out by irradiation of the samples by powerful impulses of excimer XeCl laser ($\lambda = 308$ nm) that is described in the same paper [6]. Two emission bands were observed in PL spectra of these samples: main red-orange band peaked at 680 nm, which is ascribed to electronic excitations in silicon nanocrystallites, and less intensive blue band peaked at 440 nm, which is usually ascribed to localized electrons and holes recombination in $SiO_2$ layer (see e.g. [1]).

Spectral TSL measurements were performed in two different regimes: under the constant heating rate of 0.15 K/s and by the fractional glow technique in the temperature range of 4.2–300 K. The kinetics of TL was measured in the same temperature range. After terminating the excitation, with delay times of 1–1000 s, the luminescence signal was detected with the accumulation time equal to 1 s. Spectral dependence of TL was not measured because of its very low intensity. Other details of experiments are described in [4].

## 3 Experimental results and their discussion

### 3.1 Spectral dependence of TSL

Fig. 1 demonstrates the components of TSL corresponding to different spectral ranges of PL of highly oxidized por-Si. The main feature of obtained results is unambiguous correspondence of the main 680 nm PL band to the wide component of TSL (about 90 K) and the correspondence of the blue 440 nm PL band to the narrow doublet at 25 K in TSL. These relations together with other arguments were considered in [3, 4] as a confirmation of the effect of "selfejecting" of charge carriers from photoexcited nanocrystalline core to peripheral $SiO_x$ layers with their subsequent localization in traps.

The present paper concentrates on the another feature of TSL — large width of its higher temperature component related to the main red-orange PL band. The value $\Delta E_{\rm a}$ was derived from TSL by using the formula [7]:

$$E_{\rm a} = -\frac{d \ln I_{\rm TSL}(T)}{d(1/kT)}, \qquad (1)$$

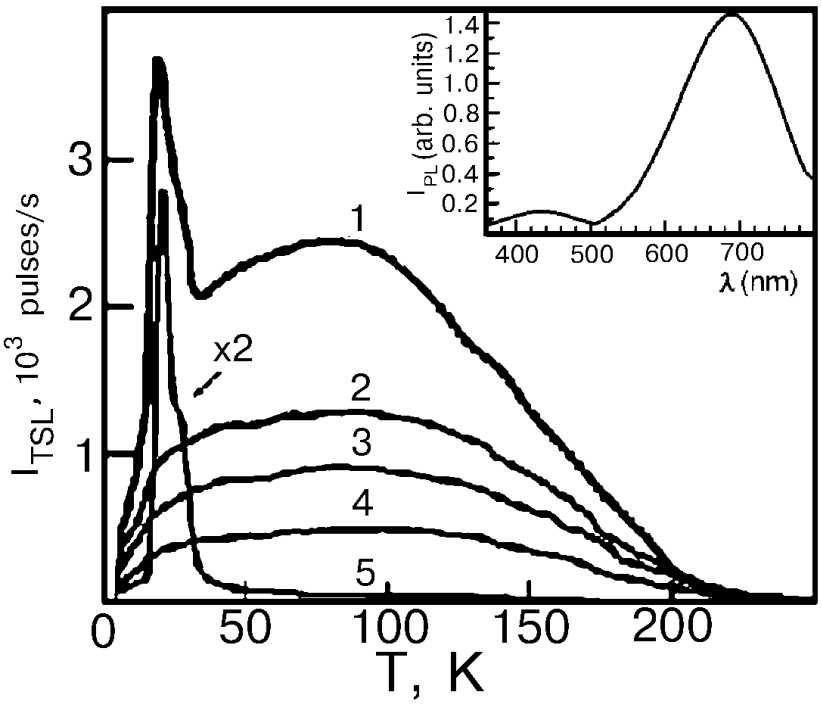


Figure 1: The spectral dependence of TSL for por-Si: 1) total signal ($\lambda \leq 800$ nm); 2) $\lambda > 640$ nm; 3) $\lambda > 690$ nm; 4) $\lambda > 730$ nm; 5) $\lambda < 580$ nm.

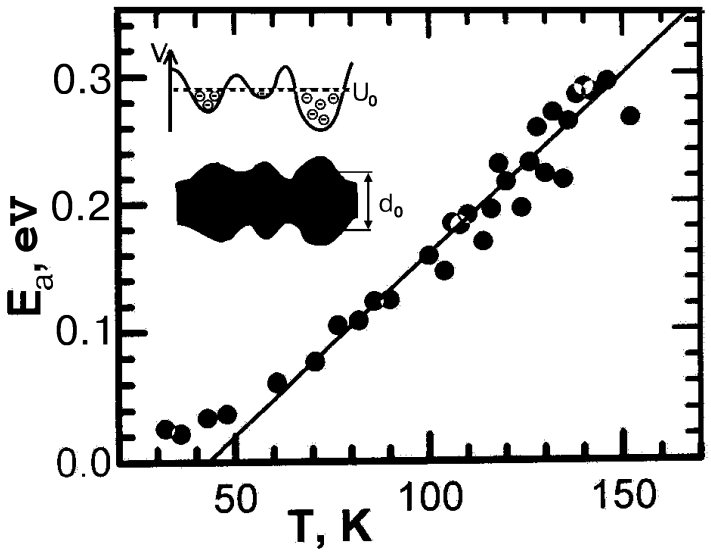


Figure 2: Temperature dependence of the mean activation energy $\langle E_{\rm a} \rangle$. The TSL data was fitted by using the equation (1).

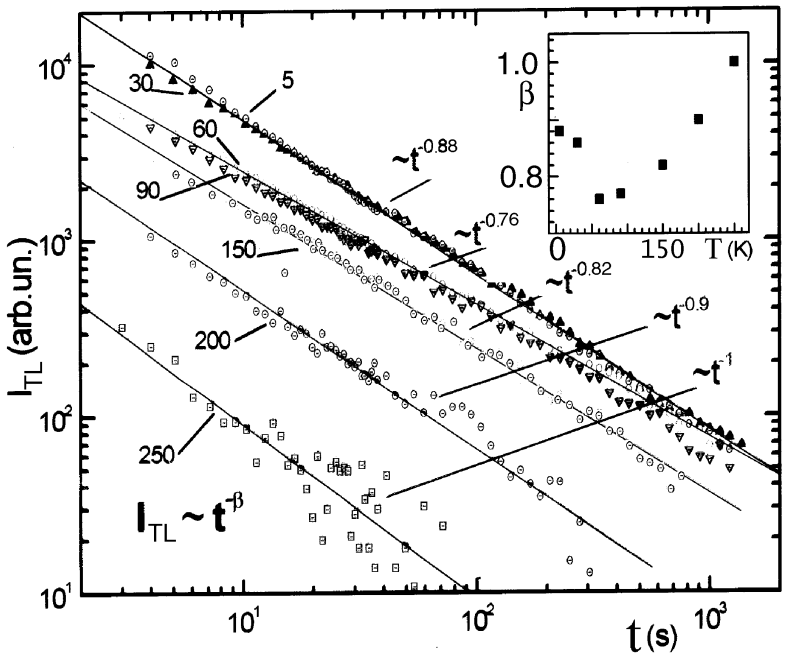


Figure 3: Por-Si TL decay at different temperatures (indicated in Kelvins), $\lambda_{\rm exc}$=405 nm. For each temperature the Beckerel decay index is calculated as shown in the inset.

where $I_{\rm TSL}(T)$ is the TSL intensity, $T$ is the temperature, and $k$ is the Boltzmann constant (see Fig. 2). The calculated value of $\Delta E_{\rm a}$ turned out to be very large, about 0.3 eV, that is about the halfwidth of the main PL band. To determine the origin of such a wide spectrum of activation energies of trapping states related to silicon nanocrystalline core, various models were considered. In the present paper we consider the model which takes into account undulating structure of quantum wires.

Numerous structure investigations of por-Si indicate that quantum wires have a complicated topological structure. This results in the existence of a large number of "topological" traps. In the simplest approach quantum wire can be considered as a potential cylinder with irregular varying diameter along its axis. This undulation generates fluctuation of intracrystalline potential and under some conditions wells of this potential can produce "topological" traps (see inset in Fig. 2). In other words traps arise in bulge segments of a quantum wire. An example of such "topological" traps, connected with the regions of the maximum surface curvature, is calculated in the paper [8]. It should be noted that experiments testify that the diameter varies in a wide range up to insulating some segments. This can yield in principle extremely large dispersion of activation energies. To verify this model we have measured and analyzed temperature dependence of TL.

### 3.2 Temperature dependence of TL

Radiative recombination of charge carriers resulted from tunneling (underbarrier) transitions is called tunneling luminescence. This is a low intensity radiation. Its distinctive feature is the powerlaw time dependence, so called Beckerel decay, $I_{\rm TL} \sim t^{-\beta}$, where $\beta$ is the Beckerel index and $t$ is the time. Some results of TL measurements are considered in the papers [3, 4]. In the present paper we will discuss only new features. The temperature dependence of the Beckerel index $\beta(T)$ is shown in the inset of Fig. 3 (Fig. 3 contains the original TL data used for calculating $\beta(T)$ dependence). Its main feature is its nonmonotonic character. To explain this nonmonotonic dependence various models were proposed which take into account tunneling

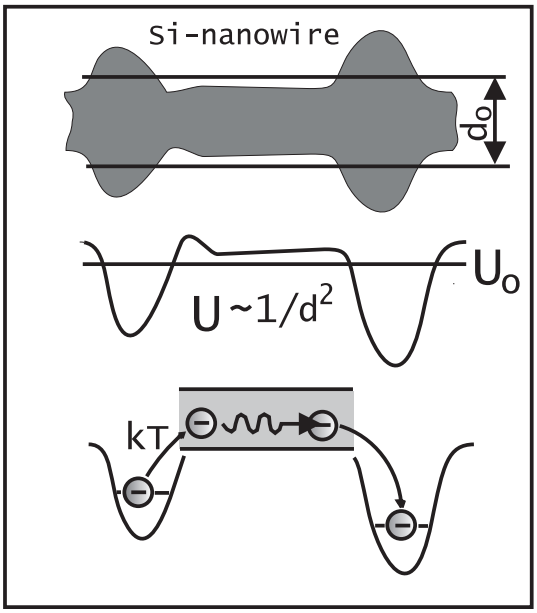


Figure 4: The sketch of processes of carriers retrapping by various localization centers.

transport between localized states.

Some fruitful approaches are developed in the papers [9, 10]. Their details are as follows. In [9] it is suggested that all localization states can be divided into two groups: in the first group the states are well separated in the space so that there is no tunneling between them, and in the second group, so called "diffusion clusters", tunneling is possible. Concerning tunneling transport, it is well known that charge carriers transport in disordered systems can be realized by two basic mechanisms: hopping between localized states and trapping-excitation to the conduction band (see e.g. [11]). The second kind of transport is sometimes called dispersive or nongaussian diffusion. The processes of multiple retrapping of charge carriers within the "diffusion clusters" considered in [10] can qualitatively explain the nature of the nonmonotonic temperature dependence of the Beckerel index $\beta(T)$ as was shown in [9]. These ideas can be applied to por-Si. In this case the localized states are "topological" traps in bulge segments of a quantum wire and band states correspond to extended segments of constant diameter of the wire (the illustration is in Fig. 4). A large range of diameter fluctuations is the origin of the large dispersion of activation energies distribution derived from TSL data.

To uncover the origin of the nonmonotonic temperature dependence of the Beckerel index in view of the fact that this phenomenon occurs not only in por-Si but also in disordered conducting organic polymers [13] we considered a very simplified model which in our opinion represents the essence of the phenomenon. We treat the hopping transport between localized states in the framework of the well known Miller–Abrahams model [12] of thermally activated tunneling transitions. The rates of the transitions are given by

$$w_{if} = \Gamma_{if} e^{-\frac{E}{kT}}, \text{ where } E = \begin{cases} 0, & \varepsilon_i \geq \varepsilon_f \\ \varepsilon_f - \varepsilon_i, & \varepsilon_i < \varepsilon_f \end{cases}, \tag{2}$$

where $\varepsilon_i$ and $\varepsilon_f$ are the carrier energy at initial and final states (we neglect the Coulomb interaction energy), $E$ is the activation energy of the transition, $T$ is the temperature, $\Gamma_{if} \equiv \Gamma_{fi}$ is the activationless part of the transition rate, determined mainly by $\psi_i$ and $\psi_f$ wave functions overlap (in the simplest variant $\Gamma_{if} = \nu \exp(-2\gamma R_{if})$, where $\gamma$ is the inverse localization radius and $R_{if}$ is the distance between the localization centers).

It should be noted that our present knowledge of the electronic structure of por-Si is rather

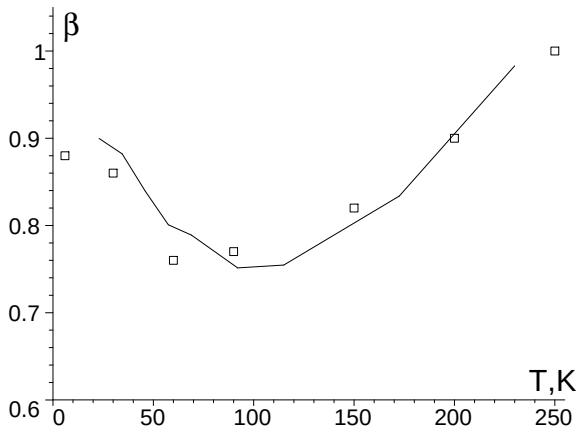


Figure 5: Temperature dependence of the Beckerel index: the boxes is the experimental data and the line is the results of Monte-Carlo simulations.

poor [1]. This together with the goal of obtaining some general results are the reasons to consider a very simplified model. Having this in mind we set $\Gamma$ to be constant (site independent) because it does not depend explicitly on temperature and its actual distribution depends strongly on the specificity of sample's structure. We also assume the carriers onsite recombination to be instant and consider one-dimensional case to take effectively into account the actual dispersion of $\Gamma$ (which is neglected in our model) using the same arguments as in the paper [9]). Now we perform Monte-Carlo modelling of this system with various sets of the following parameters: system size, initial conditions (e.g. the initial separation of carriers), energy distributions. The typical temperature dependence of the Beckerel index fitted to the experimental data is shown in Fig. 5. The parameters of the model corresponding to the best fit are as follows (it should be emphasized that we do not intend to obtain good quantitative correspondence within this simplified model). The initial separation of carriers is 4, this means that carriers make 4 jumps on average before to recombine. The dispersion of energies is roughly 0.03 eV. This too small value is explained by the shrinkage of the effective dispersion of energies at low temperatures when the variable range hopping becomes to dominate other transport mechanisms. Other explanations include the difference between the distribution of site energies and the distribution of the occupied site energies, the correlations between energies of localized states and other effects connected with rough simplifications made and sample-dependent nature of por-Si. The derived value of $1/\Gamma$ is of the order of 1 s which is in a rough agreement with the value obtained in our previous paper [3] by another method. In any case the results of simulations clearly reproduce the nonmonotonic nature of the temperature dependence of the Beckerel index.

Thus the origin of the nonmonotonic temperature dependence of the Beckerel index is carriers separation together with multiple retrapping of carriers. This is confirmed by the results of simulations which show that the depth of the $\beta(T)$ minimum increases with increasing the initial carriers separation. If the separation decreases to the value of one tunneling transition before onsite recombination then the minimum of $\beta(T)$ disappears. This case is observed in a class of materials like KCl-Yb [14].

## 4 Conclusions

The results of the present study demonstrate the high efficiency of charge carriers localization in silicon nanowires of the varying diameter caused by existence of "topological" traps, e.g. in the bulge segments of the wire. It was shown in [8] that the presence of such "topological" traps also leads to the autoionization of shallow hydrogen-like doping centers by these traps. At

sufficiently low temperatures this process produces substantial static charge along the quantum wire concentrated in the bulge regions. This can be important for understanding the physics of por-Si gas sensors.

## 5 Acknowledgements

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