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Stochastic approach to the smart quantum confinement model in porous silicon

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Abstract

A model that encompasses two approaches to explain the photoluminescence in p-type porous silicon is proposed. The model considers a stochastic distribution of nanocrystallite sizes within the porous matrix and explain the luminescence emission of air-exposed specimens in terms of the presence of Si=O and Si=H bonds. Fitting of experimental data is performed to extract size-related statistical parameters. The results are in good agreement with the band-to-band and localized state-to-band transition theoretical framework.

Keywords: Semi-empirical models and model calculations; Electrochemical methods; Photoluminescence; Silicon; Silicon oxides; Quantum wells; Semiconducting films

The mechanism of photoluminescence (PL) in porous silicon (PS) has been a source of controversy since its discovery by Canham [1]. Many models have been proposed to explain the spectrum shape [2], but it is generally accepted that the PL emission follows a widening in the band gap due to the presence of nanocrystalline structures formed by the electrochemical etching process [3]. Raman studies [4–6] and XTEM [7] report the presence of spherical crystallites in the nanometer range (“quantum dots”, QD), although some SAXS measurements [8,9] are consistent with a network of extended silicon quantum wires (QW). Recently, Wolkin and coworkers [10] proposed a comprehensive model which states that the PL spectra belonging to specimens held at ambient air are characteristic of transitions from localized-to-band states that lie deep in the band gap. They claim that the origin of these states come from the trapping of an electron (or an exciton) by silicon–oxygen bonds in nanocrystals smaller than 3 nm, but they do not provide further information on distribution sizes. In contrast, a study from John and Singh [11] describes a method to determine their structural parameters (diameter and variance). The purpose of this letter is to combine both approaches to deduce the size distribution of crystallites and their luminescent properties in PS samples.

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The theoretical model employed by Wolkin et al. to calculate the electronic structure of silicon clusters as a function of nanocrystalline QD sizes for oxygen and hydrogen surface passivation uses a self-consistent tight-binding method [12]. The details are listed in Ref. [10]. The results from these calculations are presented in Fig. 1. Three important zones have been identified in the process of recombination. Firstly, a zone for diameters larger than ~3 nm where the recombination takes place through free excitons, and therefore the PL spectra is directly related with the band gap. Notice that in this case, a reduction in the QD size results in an enlargement of the gap and in the spectra blue shift. Secondly, a zone for diameters between 2 and 3 nm where a trapped electron state arises. This state seems to be a p-state in the silicon atom of the Si=O bond. In this regime, recombinations are performed between this trapped state and a free hole from the valence band. As the QD size decreases, the shift in PL spectra is towards the blue but not as fast as in zone I. Lastly, a zone for diameters lower than ~2 nm is characterized by the presence of this silicon trapped state in addition to a new oxygen trapped state. The recombination process is consequently through trapped excitons where no shift in the PL is observed. This effect was also observed by Kanemitsu and coworkers [13]. It is worth to point out that theoretical calculations rule out possible recombinations through dangling bonds, at least for the usual red PL [14].

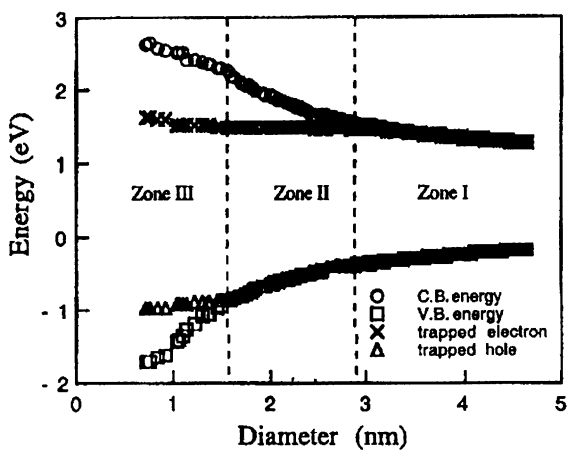

Fig. 1. Electronic states energy as function of crystallite size in PS exposed to ambient air. In zone I there is only influence of quantum confinement; in zone II an electron p-state on the silicon atom shows up; in zone III a hole p-state on the oxygen atom also arises (figure taken from Ref. [9]).

One of the drawbacks of the Wolkin's model is that it does not account for a statistical distribution of crystallites sizes. Some studies propose a Gaussian function [11,15,16] while others claim that a log–normal distribution is more accurate [17,18]. We assumed in this study a Gaussian-like distribution function for the reasons that follow.

The stochastic model was originally proposed by John and Singh [11], but later refined by Elhouichet et al. [15]. Consider a Gaussian distribution of QD and QW nanostructures with respective diameters d_d and d_w centered about means d_{0d} and d_{0w} and with standard deviations σ_d and σ_w. The distributions are:

$$P_d = \frac{1}{\sqrt{2\pi}\sigma_d} \exp\left[-\frac{1}{2}\left(\frac{d_d - d_{0d}}{\sigma_d}\right)^2\right] \quad (1)$$

$$P_w = \frac{1}{\sqrt{2\pi}\sigma_w} \exp\left[-\frac{1}{2}\left(\frac{d_w - d_{0w}}{\sigma_w}\right)^2\right] \quad (2)$$

The probability distribution of the PL process for both QD and QW are:

$$P_d(\Delta E) = K_d(\Delta E)^{-3.88} \exp\left[-\frac{1}{2}\left(\frac{d_{0d}}{\sigma_d}\right)^2 \times \left(\frac{c_d^{0.72}}{d_{0d}}(\Delta E)^{-0.72} - 1\right)^2\right] \quad (3)$$

$$P_w(\Delta E) = K_w(\Delta E)^{-3.16} \exp\left[-\frac{1}{2}\left(\frac{d_{0w}}{\sigma_w}\right)^2 \times \left(\frac{c_w^{0.72}}{d_{0w}}(\Delta E)^{-0.72} - 1\right)^2\right] \quad (4)$$

where $K_{d,w}$ are normalization constants, and $\Delta E = c_{d,w}/d^{1.39}$ is the quantum confinement energy ($c_{d,w}$ are their associated constants) [14]. ΔE is related with the PL energy ($h\nu$), the bulk silicon gap ($E_g \sim 1.15$ eV) and the exciton binding energy ($E_b \sim 0.15$ eV) by: $\Delta E = h\nu - (E_g - E_b) \approx h\nu - 1$ (eV). The PL spectrum shape is therefore a weighted addition of these two expressions plus a

contribution from the localized-to-band state proposed by Wolkin et al. and applicable for zones II and III. It will also be assumed a Gaussian like contribution in the form:

$$P_{\mathrm{loc}}(\Delta E) = K_{\mathrm{loc}} \exp\left[-\frac{1}{2}\left(\frac{(\Delta E)-(\Delta E)_0}{\sigma_{\mathrm{loc}}}\right)^2\right] \quad (5)$$

where K_{loc} is a normalization constant, $(\Delta E)_0$ the mean of the distribution and σ_{loc} its standard deviation.

Our PS samples were prepared by usual electrochemical etching in HF:EtOH aqueous solution in the proportion 1:1 on boron-doped, (1 0 0) crystallographic plane and 30–50 Ω cm resistivity wafers. The current density was kept at 100 mA/cm^2 in all cases, and the time of the etching process were from 2 to 30 min. The PL was determined in air at room temperature after rinsing and drying by the use of a fiber optics, CCD-based spectrophotometer with a He–Cd 442 nm, 1 mW laser as a light source. An optical band-pass filter was employed to filter out the laser plasma lines. Fig. 2 shows typical spectra from these samples. Once the spectra were recorded and stored in a computer system, a Gaussian fitting procedure software was employed to first determine the statistical parameters of Eqs. (3) and (4), assuming initially that only QD and QW were responsible for the obtained PL. With the mean diameters extracted from the fitting method, it was decided whether the actual PL spectrum belonged to zone I, II or III (see Fig. 1). If zone I was selected, then no localized-to-band transition was considered and the process stopped. If zone II was selected, a new fitting process was performed with the additional presence of localized states. None of our samples were attributed to zone III due to the obtained values of d. Statistical parameters of Eqs. (3)–(5) were therefore extracted. Typical fits from PL spectra of zones I and II are shown in Fig. 3.

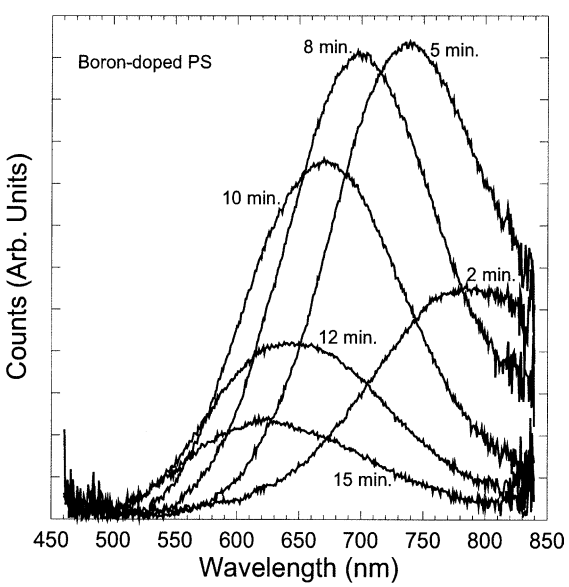

Fig. 2. PL spectra for various electrochemical etching times, as marked in the figure. Notice a blue shift in the maximum peak of the spectra for increasing times.

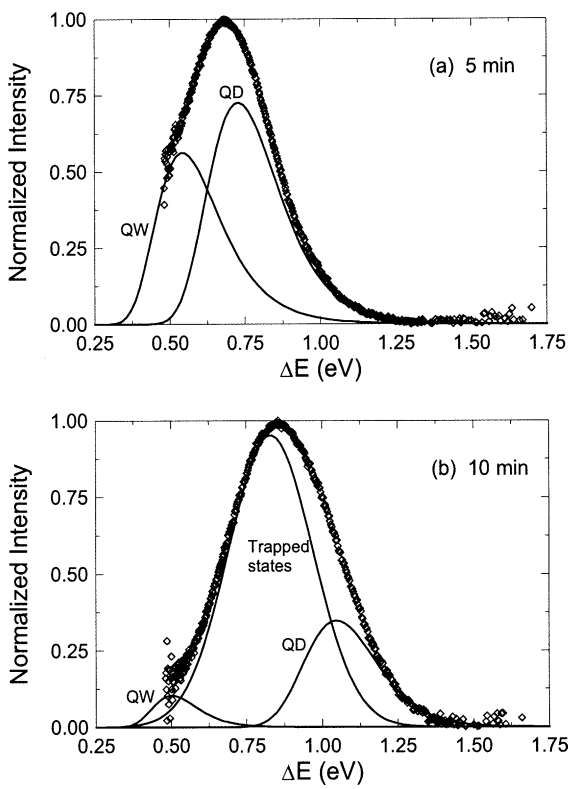

Fig. 3. Typical PL spectra as a function of ΔE for 5 min (a) and 10 min (b) etching time. In (a), only the contributions of QD and QW are sufficient to fit the experimental data, which is characteristic of zone I. In (b), a taller Gaussian peak (attributed to trapped states and characteristic of zone II) is necessary to fit the data. QD and QW contribution are notably smaller but still present. The statistical parameters of both cases are listed in Table 1.

Table 1
Statistical parameters extracted from the fitting procedure

Sample label	Etching time (min)	Zone	d_{0d} (nm)	σ_d (nm)	d_{0w} (nm)	σ_w (nm)	$E_{0,loc}$ (eV)	$\sigma_{0,loc}$ (eV)
S1-02	2	I	3.16	0.64	4.59	0.16	–	–
S1-05	5	I	3.04	0.40	4.09	0.66	–	–
S1-08	8	II	2.77	0.42	3.66	0.87	1.77	0.16
S1-10	10	II	2.55	0.22	4.56	0.52	1.83	0.14
S1-12	12	II	2.25	0.22	4.19	1.81	1.87	0.16
S1-15	15	II	2.23	0.24	3.70	0.14	1.98	0.23
S2-10	10	II	2.77	0.35	4.67	0.01	1.65	0.19
S2-15	15	II	2.55	0.49	3.60	0.69	1.86	0.16
S2-20	20	II	2.27	0.18	3.58	0.61	1.92	0.20
S2-25	25	II	2.21	0.18	3.43	0.34	1.92	0.25
S2-30	30	II	2.12	0.24	3.92	0.40	1.86	0.16

d_{0d}, σ_d, d_{0w} and σ_w are related with the QD and QW crystallites, respectively. $E_{0,loc}$ and $\sigma_{0,loc}$ are the actual mean energy and the standard deviation of the expected localized-to-band transitions, respectively.

The statistical results from these fittings are presented in Table 1 for two sets of samples. It is noticeable the reduction of crystallite size as the etching time increases. This agrees well with the blue shift that predicts the quantum confinement model. From the data of d_{0d} it is possible to calculate the mean quantum confinement energy ΔE and the peak PL energy from $h\nu \approx \Delta E + 1$ (eV). Fig. 4 shows the plot reported by Wolkin's group [10] but with our results added. The figure does not include standard deviation bars (corresponding to the σ values) to avoid confusion. The curves correspond to the theoretical cases deduced for spherical crystallites, and therefore we only show the results for QD (QW mean diameters lie outside the plotted region in any case, and its contribution is a subject of a further study not included here). The agreement between the experimental points and the theoretical curves is notable. Full symbols represent band-to-band transitions where the PL emission is explained by pure quantum confinement. Empty symbols are localized-to-band transitions explained by the presence of Si=O bonds. The fact that for every situation depicted in Table 1 there is a coexistence of both kinds of transitions may be surprising at first glance. We attribute this duality to the following: after being exposed to ambient air, the nanostructures are partially passivated with H bonds and partially with O bonds [19]. As a consequence, depending on the proportion of Si=O to Si–H bonds, there must be two competing channels of radiative recombination. The observed PL spectrum is indeed the result of these two processes.

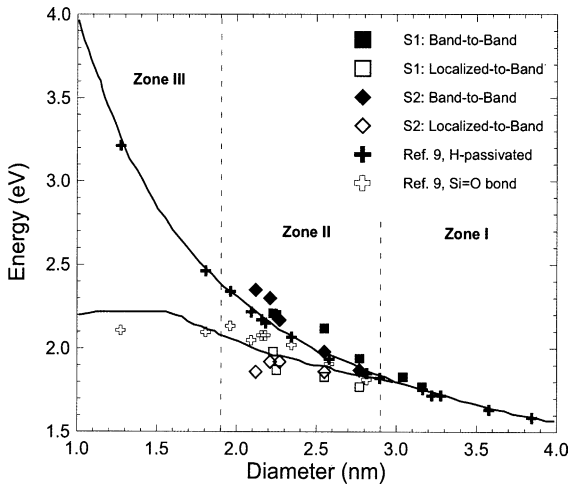

Fig. 4. PL energy as a function of crystallite diameter for theory (solid lines) and experimental results. The full and empty crosses come from Ref. [9], and the squares are our results. The full symbols consider radiative band-to-band recombinations, whereas the empty symbols represent localized-to-band recombinations.

In summary, a unified model accounting for the Si=O trapped state approach and the stochastic distribution of nanocrystal sizes approach has been proposed. The results for QD are in good agreement with previous published theoretical results and indicate that the mayor part of the PL

spectra comes from transitions from localized-to-band states and, in lesser extent, from band-to-band, at least in zone II. These results support therefore the so-called smart quantum confinement model even in the presence of stochastic oscillations of nanostructure sizes.

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