INTERPRETATION OF EXCITON PHOTOLUMINESCENCE SPECTRA IN FILMS WITH SILICON QUANTUM DOTS

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The photoluminescence (PL) spectra in films with silicon quantum dots (Si QDs) — the Si nanocrystal (Si NC)/SiO_x-matrix ($x \to 2$) system — have been considered in the framework of the excitonic photoluminescence model. The calculations made allowance for the discreteness of emitting Si NCs by size, which was determined by the minima in the oscillatory dependence of the exciton radiative lifetime on the Si NC dimensions, and the quantum-mechanical mesoscopic broadening of PL bands. A satisfactory agreement between measured and calculated PL spectra has been obtained.

1. Introduction

Effective PL in the visible range of the spectrum is inherent to Si QDs of the "Si NC/SiO_x-matrix" ($x \to 2$) system. Si QDs are formed by means of electron-beam lithography, quantum wire oxidation, plasma-enhanced chemical vapor deposition, suboxide decomposition, spark discharge, implantation of Si ions into SiO_2 layers, vacuum methods (magnetron sputtering and laser ablation), and so on. Investigated are the PL spectra of both Si QD ensembles and individual Si QDs. Usually, PL studies are carried out in the spectral range 1.4–3.2 eV, and the times of PL relaxation fall within the interval from nanoseconds to tens of microseconds. PL spectra vary by shape and can contain several peaks. As a rule, the low-energy bands are narrow and characterized by slow recombination, while the high-energy ones are broad, separated from one another by larger energy intervals, and characterized by faster recombination. The PL kinetics curves for Si QDs with small dimensions usually look like "piecewise" exponents.

Today, the role of the quantum-size effect, dielectric amplification, and radiative annihilation of excitons in visible PL of Si QDs is beyond doubt [1]. But the mechanisms of those processes have not been revealed once and for all. Along with the models, where photons are both absorbed and emitted in the Si NC bulk [1, 2], other models are considered, where the emission takes place from the Si NC surface states [3], states located in the potential well of the Si NC/SiO_2 interface [4] or at local centers of the SiO_2 barrier phase [5]. The independence of the position of a PL spectrum maximum on the Si NC dimensions (provided the latter are smaller than 1.5 nm) was explained by the exciton localization at the Si=O bond states [6].

In work [7], a discrete model of Si NC dimensions with an increment of 0.628 nm, the width of two silicon monolayers, has been proposed. Only Si NCs with closed external shells were supposed to contribute to PL, because Si NCs with unclosed shells possess short times of nonradiative recombination. The discreteness of nanocrystal dimensions is a specific feature of this model which distinguishes it from practically all the others, where the PL spectra were analyzed while assuming that Si NCs are distributed over dimensions with that or another dispersion. It has allowed the multimodal character of the spectra to be explained. But the question why the high-energy PL bands (they are connected with small Si NCs, whose dimensions are characterized by a small dispersion) are broad, whereas the low-energy ones (these, on the contrary, are connected with large Si NCs, whose dimensions are characterized by a large dispersion) are narrow, this question remained unanswered in work [7] as well as in others.

The authors of almost all works, when analyzing PL spectra, did not take the oscillatory character into consideration, which has the dependence of the elements of the transition probability matrix on the Si NC size; this phenomenon for por-Si was considered in work [8]. Nevertheless, a success in explaining the issue why only some of a good many Si QDs, which are small but close by dimensions, emit has not been attained. Most of these questions were answered in theoretical works [9, 10] devoted to studying the exciton PL in quantum wells and quantum wires, as well as in Si QDs. The PL models, which were used in those works for calculations, took into account such parameters as the oscillatory dependence of the zero-phonon exciton lifetime on the Si QD dimensions ($\tau_r^0(d)$) and the quantum-mechanical mesoscopic broadening of the bands which is caused by fluctuations of both the Si NC shape and the composition of the Si NC environment.

The purpose of this work is, making use of this approach, to interpret the PL spectra of films with Si QDs fabricated by the pulsed laser deposition method.

2. Experimental and Calculation Methods

1. Films with Si QDs were fabricated in a vacuum chamber, using the pulsed laser deposition of low-energy particles from an erosion plume onto a single-crystalline silicon (c-Si) substrate placed in the target plane, provided high pressures of inert gas (argon, helium). The c-Si target was scanned by the beam of a Nd-laser with a wavelength of 1.06 μm, pulse duration of 10 ns, energy density of 20 J/cm^2, and repetition frequency of 25 Hz. The method of the film formation ensured the selection of Si NCs by dimensions, as well as the doping of films with metals in the course of their growing [11, 12, 13]. It has been shown [11] that Au atoms, being characterized by a high energy of electron affinity, passivate nonsaturated bonds of silicon and promote the oxidation of the barrier phase SiO_x, hence, the formation of a high potential barrier at the Si NC/SiO_2 interface and a decrease of the dielectric constant of the medium which surrounds Si NCs ($\varepsilon_{SiO_2} < \varepsilon_{SiO_x}$ $(x < 2)$).

The objects of researches comprised two types of films: (i) with smaller Si NCs, whose dimensions were characterized by a small dispersion, and (ii) with larger Si NCs with a greater dispersion of dimensions. The average sizes of Si NCs amounted to 2—4 nm. The analysis of the IR-transmission band, connected to the valence vibrations of the bridge oxygen in Si—O—Si bonds, showed that the composition of the barrier phase of the films is determined by six- and four-member Si—O_4 molecular complexes, i.e. it is close to that of the SiO_2 phase [14].

2. PL spectra were studied in the energy range 1.4–3.2 eV and the time interval from 50 ns to tens of microseconds. PL was excited by the emission of a nitrogen laser ($\lambda = 337$ nm, $t_{\rm pulse} = 8$ ns). The PL signal was registered stroboscopically in the mode of photon count, by varying the excitation-pulse-delay time T_d and the strobe-pulse width T_s, the minimal value of the latter being 250 ns. Summing the measured spectra up, we obtained the integrated-in-time PL spectrum which was subjected to the analysis.

3. The experimentally measured integrated-in-time PL spectra were confronted with the spectra calculated in the framework of the approach of excitonic PL in Si NCs [9, 10]. The oscillatory character of the dependence $\tau_r^0(d)$ with an increment of 0.64 nm, which was determined by the position of the K_0 point in the Δ-valley of the Brillouin zone of silicon, was made allowance for. The size distribution of Si NCs was not taken into account at that.

3. Theoretical Calculations

The dependence of the energy of exciton transitions E on the Si NC dimensions d, $E(d) = 1.12 + 3.32d^{-1.32}$, which is characteristic of the Si NC/SiO_2 barrier height (see Fig. 1, curve *1*), was taken from the experimental work [7].

Curve *2* in Fig. 1 corresponds to the calculated dependence $\tau_r^0(d)$ of the exciton radiative lifetime on the Si NC dimensions, provided that the shape of the Si NC is cubic and the barrier phase is composed of SiO_2. One can see that this dependence oscillates, with its six minima corresponding to the following values of the Si NC size d: 1.95, 2.59, 3.23, 3.87, 4.51, and 5.15 nm. These are consistent with the energies of exciton transitions of 2.57, 2.09, 1.85, 1.71, 1.61, and 1.54 eV, respectively. Taking into account the dependence $\tau_r^{\rm ph} = 0.002 \times (d/3)^6$ of the phonon-assisted radiative lifetime of excitons [10] and its restriction in the bulk by the value $\tau_r^{\rm ph} = 2 \times 10^{-4}$ s, the dependence $\tau_r(d)$ of the total radiative lifetime of excitons on the Si NC dimensions looks like curve *3* in Fig. 1. This curve testifies that phonon-assisted transitions make the oscillations of the dependence $\tau_r^0(d)$ smoother at $d > 4$ nm. The values of the total radiative lifetime fall within the interval $10^{-6} - 10^{-4}$ s and decrease as the Si NC dimensions diminish.

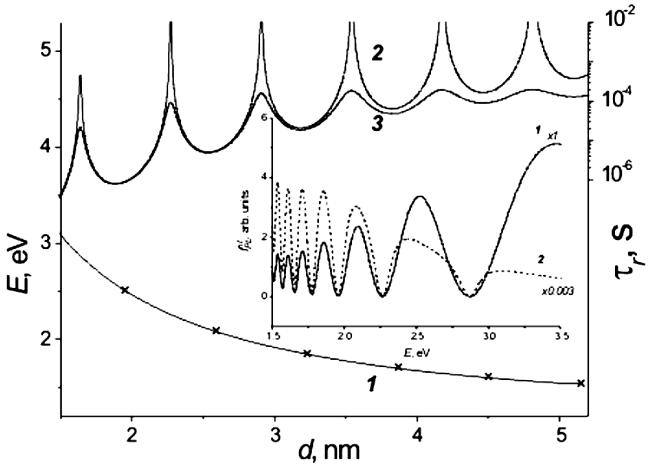

Fig. 1. Dependences of the energy of excitonic transitions (*1*), the radiative zero–phonon lifetime of an exciton (*2*), and the total radiative lifetime of an exciton τ_r^0 (*3*) on the Si NC dimensions. The inset exhibits the integral PL spectra calculated, provided the uniform distribution of the Si NC sizes, for various nonradiative exciton lifetimes $\tau_{\rm nr} = 10^{-7}$ (*1*) and 10^{-5} s (*2*)

The integral PL spectra calculated for the times of nonradiative recombination $\tau_{\rm nr} = 10^{-7}$ and 10^{-5} s under the assumption that all the six Si NC dimensions are distributed uniformly are shown in the inset of Fig. 1 by curves *1* and *2*, respectively. One can see that the PL spectra possess the oscillatory character and reflect the nonmonotonous behavior of the dependence $\tau_r(d)$. Broader widths of the high-energy bands are explained by the effect of quantum-mechanical mesoscopic broadening. The role of the nonradiative recombination channel is stronger for greater Si NCs, because their larger surface contains more defects. Nevertheless, provided that those defects are heavily passivated, the low-energy bands can be more intense than the high-energy ones, notwithstanding the fact that the oscillator strengths of the latter are stronger, i.e. their radiative lifetimes are shorter.

The measured PL spectra were resolved into six band-components. Making use of the corresponding computer code, we calculated the parameters of the model, where the PL relaxation is described by the expression

$$N_{\rm phot} = \sum_{i=1}^{6} \alpha I N_i d_i^3 t_{\rm pul} \frac{\tau(d_i)}{\tau_r(d_i)} \Big(e^{-T_d/\tau(d_i)} - e^{-T_d+T_s/\tau(d_i)} \Big) \frac{\Gamma(d_i)/2}{(E(d) - E(d_i))^2 + \Gamma(d_i)^2/4},$$

where α is the coefficient of exciting radiation absorption, I the intensity of illumination, and N_i the number of Si NCs with the i-th size. The last multiplier in this formula is a Lorentzian which describes the quantum-mechanical mesoscopic broadening of bands. While carrying on calculations, the broadening Γ and the characteristic times $\tau_r^{\rm ph}$ and $\tau_{\rm nr}$ were considered dependent on the Si NC dimensions as follows:

$$\Gamma(d_i) = \Gamma_0 \left(\frac{d_x}{d_i} \right)^n, \quad \tau_r^{\rm ph} = \mathrm{T}_r^{ph} \left(\frac{d_i}{d_x} \right)^{n1}$$

i $\quad \tau_{nr} = \mathrm{T}_{nr} \left(\frac{d_i}{d_x} \right)^{n2}$,

where $d_x = 3$ nm.

The dependence of the nonradiative lifetime on the Si NC dimensions is governed by the mechanism of nonradiative Auger-recombination assisted by a deep local center. As the Si NC size decreases, one should expect for the growth of this recombination probability, owing to the increase of the overlapping integral of the exciton wave function and the wave function of a deep surface energy level.

The parameters of the model are the value of the relative occurrence of each discrete Si NC dimension $A_i = N_i/N_{\max}$ and the quantities that govern the mesoscopical broadening factor and the characteristic times, namely, Γ_0, n, $T_r^{\rm ph}$, n_1, $T_{\rm nr}$, and n_2.

4. Experimental Results and Their Discussion

Figure 2 exposes the time-resolved PL spectra of two films (panels *a* and *b*) and the experimental integrated-in-time PL spectra of the same films together with the calculated ones (panels *c* and *d*).

Panels *a* and *b* demonstrate that the spectra of both films are multimodal and differ by shape: the intensity of the low-energy band of the first film is lower than that of the second. The PL relaxation times are also different: 1 μs for the first film and 12 μs for the second.

Panels *c* and *d* demonstrate that the experimental and calculated spectra are close to each other. A satisfactory agreement was achieved by a proper selection of bands contributing to the experimental PL spectra. There exists some ambiguity in the determination of the model parameters, because the amplitude of a band is governed by two factors: $A_i = N_i/N_{\max}$ and the function of characteristic times, with those two cannot be determined unequivocally together.

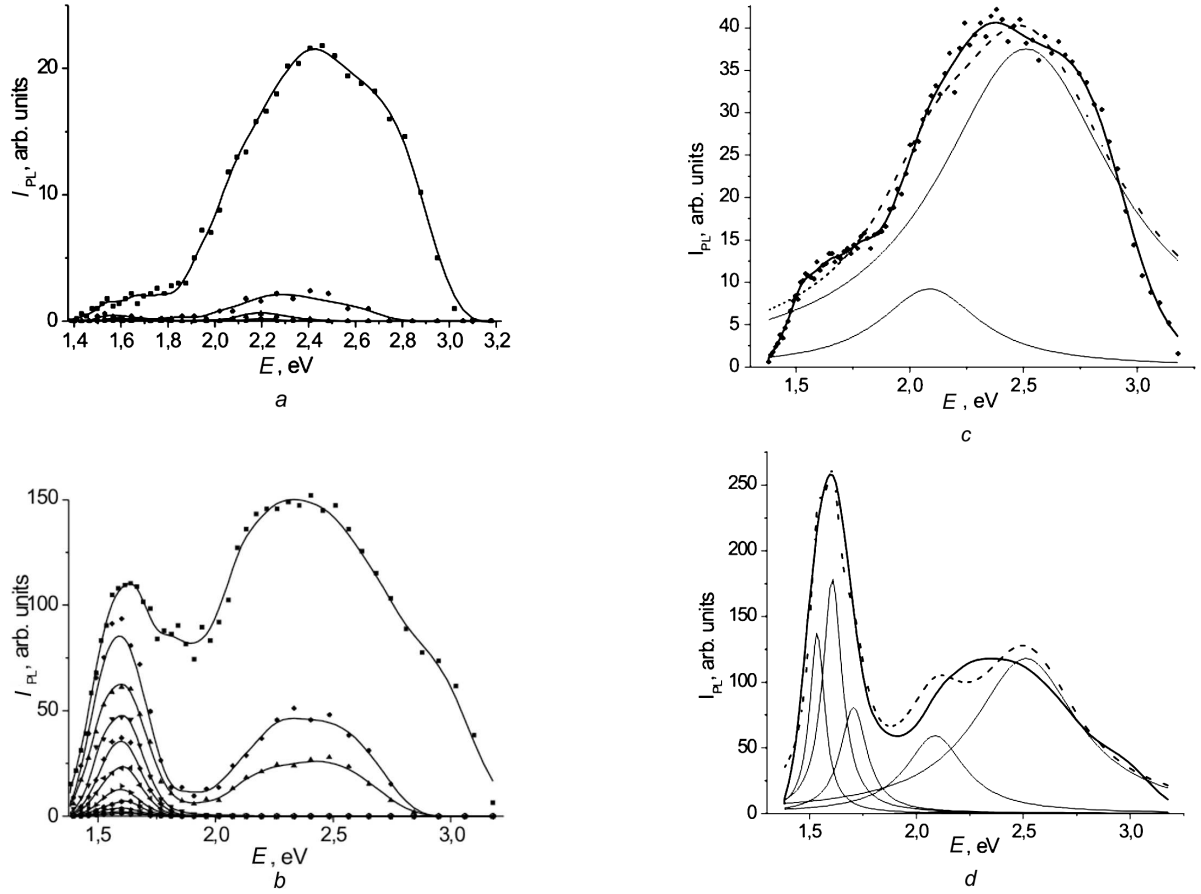

Fig. 2. (*a*) and (*b*) Time-resolved PL spectra of two films (points); solid curves serve as eye-guides. (*c* and *d*) Integrated-in-time experimental (solid curves) and calculated (dashed curves) PL spectra of the same films. Thin solid curves demonstrate the decomposition of the experimental PL spectra into separate PL bands

Calculated model parameters of decomposed Si QD PL spectra

Film	d_i, nm	1.95	2.59	3.23	3.87	4.51	5.15
	E_i, eV	2.51	2.09	1.85	1.71	1.61	1.54
N1	$A_i = \frac{N_i}{N_{\max}}$	1	0.06	—	—	—	—
	$\Gamma_i = 0.4\left(\frac{3}{d_i}\right)^2$, eV	0.95	0.54	—	—	—	—
	$\tau_r^{\rm ph} = 10^{-5}\left(\frac{d_i}{3}\right)^{3,93}$, s	1.84×10^{-6}	$5.61 \times$ ‘10^{-6}	—	—	—	—
	$\tau_{nr} = 1.99 \times 10^{-7}\left(\frac{d_i}{3}\right)^{4.17}$, s	3.3×10^{-8}	1.08×10^{-7}	—	—	—	—
N2	$A_i = \frac{N_i}{N_{\max}}$	1	0.37	—	0.24	0.44	0.24
	$\Gamma_i = 0.25\left(\frac{3}{d_i}\right)^2$, eV	0.59	0.34	—	0.15	0.11	0.08
	$\tau_r^{\rm ph} = 1.28 \times 10^{-5}\left(\frac{d_i}{3}\right)^{5.97}$, s	9.79×10^{-7}	$5.33 \times 10^{-}6$	—	5.86×10^{-5}	1.46×10^{-4}	3.23×10^{-4}
	$\tau_{nr} = 1.92 \times 10^{-7}\left(\frac{d_i}{3}\right)^{2.69}$, s	6.03×10^{-8}	1.29×10^{-7}	—	3.81×10^{-7}	5.75×10^{-7}	8.21×10^{-7}

But the adopted set of the values obtained for the model parameters is acceptable (see Table).

It is evident from the table that, in the case of the first film, practically only the smallest Si NCs with

dimensions of about 2 nm emit. At the same time, in the case of the second film, the portions of Si NCs, which emit in either high- or low-energy ranges of the spectrum, are comparable; their dimensions fall within the size interval 2—5 nm. The quoted amplitudes of quantum-mechanical mesoscopic broadening testify that this effect is more pronounced for the first film with smaller Si NCs and grows strongly enough as the Si NC dimensions diminish. The values of the characteristic radiative lifetimes of excitons for phonon-assisted transitions fall within the interval 2×10^{-6}—3×10^{-4} s and the corresponding nonradiative lifetimes within the interval 2×10^{-8}–1×10^{-7} s. In this case, the maximum of the internal quantum yield reaches 1–6%, which agrees with the experimentally determined values.

5. Conclusions

A capability to analyze the complicated PL spectra of films with Si QDs in the framework of the exciton model has been demonstrated. The analysis is based on the discreteness of Si QD dimensions with an increment of 0.64 nm, which is originated from the indirect-band-gap nature of silicon. The model parameters of the excitonic PL of Si QDs fabricated by pulse laser deposition have been determined.

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АНАЛІЗ СПЕКТРІВ ЕКСИТОННОЇ ФОТОЛЮМІНЕСЦЕНЦІЇ ПЛІВОК З КРЕМНІЄВИМИ КВАНТОВИМИ ТОЧКАМИ

А.В. Саченко, І.О. Соколовський, Е.Б. Каганович, Е.Г. Манойлов

Р е з ю м е

У рамках моделі екситонної фотолюмінесценції (ФЛ) розглянуто спектри ФЛ плівок з кремнієвими квантовими точками (Si КТ) — системи "кремнієвий нанокристал / $SiO_x(x \to 2)$-матриця". В розрахунках припускали дискретність розмірів випромінюючих кремнієвих нанокристалів, яку визначали за мінімумами осцилюючої залежності випромінювального часу життя екситонів від розмірів кремнієвих нанокристалів (Si НК), а також квантово-мезоскопічне розширення смуг ФЛ. Одержано задовільне узгодження розрахованих та виміряних спектрів ФЛ.