Absorption Cross Section and Photoluminescence Lifetime of Silicon-Based Light-Emitting nc-Si-SiOₓ Structures

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The spectral dependence of the photoluminescence (PL) decay kinetics at room temperature have been studied in porous nc-Si-SiOₓ nanostructures. Investigated samples were obtained by oblique evaporation of SiO with following annealing at 975 °C in vacuum and treating in the HF vapor at 50 °C. PL decay in these structures described by a stretched exponential and the average lifetime of the PL decrease exponentially with increasing energy of photons. PL lifetime values is in microsecond range that point out on phonon participation in radiative recombination. Dispersion parameter β do not depend on emission energy and tends to 1 with increasing porosity, which is consistent with the model of noninteracting nc-Si. It was established, that the absorption cross section σ of the nc-Si particles increase with decreasing of nc-Si dimensions and increasing of emission energy.

This result is consistent with the quantum confinement effects, where the smaller nc-Si with larger energy gaps are characterized by a short radiative lifetime and the corresponding radiative recombination process take place within the individual nc-Si.

Keywords: Si nanocrystals, Photoluminescence, Decay time.

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1. INTRODUCTION

The creation of light-emitting structures on the basis of developed silicon technology for advanced electronic and optoelectronic devices is actual problem now. Porous silicon [1], Si nanoclusters (nc-Si) embedded in the SiO_2 matrix [2, 3], Si/SiO_2 superlattices [4], etc. structures of the most intensively investigated in recent years. On the basis of nano-silicon has created electronic and optoelectronic devices (lasers, photodetectors, etc.) [5, 6], now it is a promising candidate for next-generation flash memory silicon technology [7].

Some of the most promising silicon light-emitters are structures containing Si nanoclusters (nc-Si) embedded in the SiO_x matrix. Recently we have developed new porous light-emitting nanocomposite nc-Si-SiO_x structures obtained by thermal evaporation of silicon monooxide and oblique deposition with following high temperature annealing in a vacuum [8-10]. HF vapor treatment of such structures results in significant (more than 100 time) photoluminescence (PL) intensity increasing and essential shift (up to 210 nm) of PL maximum from infrared to visible spectral range, that can explained by modification of nc-Si and nanocluster-SiO_x matrix interface. But, mechanism of photoluminescence (PL) in such structures is discussed yet.

The present paper continues investigations of PL properties of thin films porous nc-Si-SiO_x structures, where nc-Si clusters are situated in suboxide SiO_x columns (e.i. on the surface or near surface area). The main objective of this work is the elucidation of the mechanism of recombination of excited carriers in these structures by studying the kinetics of luminescence decay.

2. EXPERIMENT

Investigated samples were obtained by thermal evaporation of silicon monoxide SiO (Cerac Inc., 99.9 % purity) in a vacuum (residual pressure $1\text{-}2\cdot10^{-3}$ Pa) and oblique deposition onto two-side polished silicon substrate. The angle (α) between the vapor stream and the substrate normal was 60° and 75° for different samples (samples I and II, correspondently). The rate of deposition was controlled by the calibrated quarts monitor. The film thicknesses measured with the use of an MII-4 microinterferometer after deposition were 400–600 nm. Because of additional oxidation by residual gases during evaporation of SiO, the compositionally nonstoichiometric SiO_x (x > 1) films were deposited in the vacuum chamber.

The structure of the obliquely deposited SiO_x films was studied by transmission electron microscopy (TEM) with the use of a ZEISS EVO 50XVP high-resolution electron microscope. The film structure presents well-defined columns characterized by a certain orientation of growth; the column diameter varies in the range 10–100 nm. The dimensions of the columns, their orientation, and the porosity (the relative volume of pores) of the films depend on the angle of deposition. The porosity of the film (specific pore volume) for deposition angles 60° and 75°, calculated from the change of its thickness in comparison with that of normally deposited film [9], was 34 and 53 %, respectively. Due to the presence of free space (pores) between the oxide columns, porous films of SiO_x easily amenable to chemical treatment, and additional oxidation in air compared with the same solid SiO_x films, which allowed to specifically change the luminescence properties of these structures by modifying the interface nc-Si/oxide matrix [8] .

After the deposition the porous SiO_x films were annealed in vacuum chamber at 975° C for 15 min. For

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such annealing the thermally stimulated formation of the nc-Si occurs in the SiOx columns thus forming nc-Si–SiOx structures. Before PL measuring annealed nc-Si–SiOx samples were treated in the HF vapor at 50° C and than they were maintain for a month in air atmosphere for characteristic stabilization.

Time-resolved PL was investigated at room temperature under exitation of a pulsed nitrogen laser (337 nm). The excitation photon flux density was $3 \cdot 10^{22}$ cm^{-2}s^{-1} and can was changed by using of optical aperture and neutral density filters. PL signal was analyzed by monochromator and was detected by a photomultiplier in conjunction with a pulse oscillograph. Time-resolution of our system was 0.5 µs. Obtained PL spectra were corrected on setup spectral sensitivity.

3. RESULTS AND DISCUSSION

Fig. 1 shown normalized room temperature PL spectra of nc-Si-SiOx structures (curves 1 and 2 correspond on samples obtained at α = 60° and 75°). There is a broad band in the spectral range of 1.25 – 2.0 eV and the band shapes are similar for both types of samples. PL band maximum are situated at 1.44 and 1.51 eV, and their widths on half of maximum consists of 0.4 and 0.37 eV, correspondently.
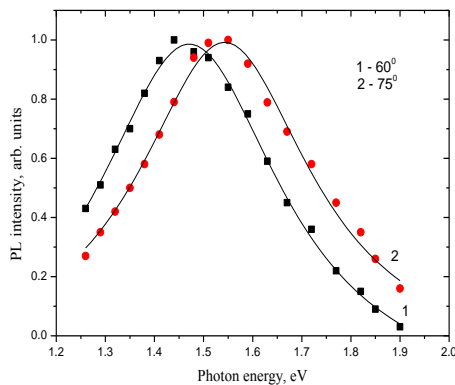

Fig. 1 – PL spectra of porous nc-Si-SiOx structures (curves 1 and 2 correspond on samples deposited at α = 60° and 75°)

The comparison of obtained PL spectra with early known literature data [11, 12] allows to suggest that PL of nc-Si-SiOx structure is connected with silicon nanoparticles. The short-wavelength shift of PL maximum in 75° sample (curve 2) is explained by nanoparticles Si size decreasing (are forming during high temperature annealing) with increasing of deposition angle. Such size decreasing depend on (in the first line) changing of film composition (x rise when α increase).

Fig. 2. shows experimental PL decay for sample deposited at α = 60° measured at registration energies 1.48, 1.59, 1.72 and 1.87 eV (curves 1, 2, 3, and 4, correspondently). PL relaxation is more quickly for more short-wavelength emission. It correlates with probability rise of radiative recombination in smaller Si nanoparticles. In consistent with the quantum confinement effect (e.g. size dependent phenomena), when nc-Si size decrease then nc-Si energy gap increase and radiative recombination rate growths [13, 14].
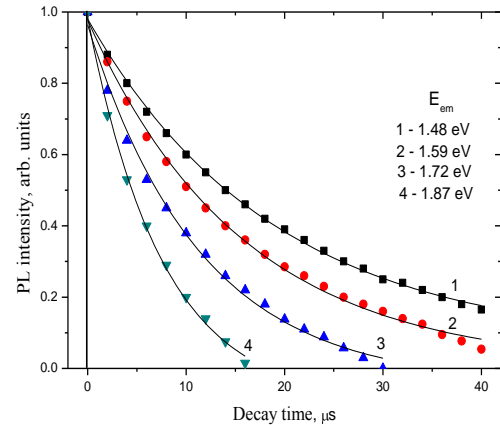

Fig. 2 – PL decay time for nc-Si-SiOx structure deposited at α = 600

Decay PL curves (and their main characteristics) for the samples deposited at α = 75° are qualitatively similar to curves shown on Fig. 2.

In order to analyze the kinetics of PL decay we have fitted the experimental date (Fig. 2) to a stretched-exponential decay function that is frequently used to describe dispersive processes in disordered systems with a distribution of relaxation times [15, 16]:

$$I_{PL}(t) = I_0 \exp[-(t/\tau)^{\beta}], \qquad (3.1)$$

where τ – is the PL average decay time, $I_{PL}(t)$ and I_0- are current and at $t = 0$ PL intensity values, $0 \leq \beta \geq 1$ is the dispersion exponent.

We used our experimental data and eq. (3.1) to calculate τ and β of investigated samples. The least-squares fit of the eq. (3.1) to experimental data brings values of τ and β. Fig. 3 presents the dependence of average decay time τ of PL from emission energy E_{em} in semilogarithmic plot.

It may seen that the τ obtained for sample (II) (at the same emission energies) are smaller in comparison with the one for sample (I), that, given the smaller size of nc-Si in them, consistent with the results [8, 14, 17]. Moreover, as in the most structures, contained silicon nanoparticles, our experimental dependence τ on photon energy (E_{em}) can be described by exponential function: $\tau = 1/k \infty \exp(-E_{em}/E_0)$. The experimental line slope ($1/E_0$) allowed to determine a value of characteristic energy E_0. For sample (I) value $E_0 = 0.33$ eV almost coincide with difference between energy position of PL maximum and massive silicon gap ($E_c = 0.31$ eV). Rather well correlation is observed between these values ($E_0 = 0.36$ eV and $E_c = 0.39$ eV) in sample (II) too.

Dispersion parameter β do not depend on emission energy E_{em} (within experimental errors) in both samples (I and II) and its average values are equal to 0.85 (I) and 0.90 (II). As was pointed out, increasing of deposition angle is accompanied by growth of obtained SiOx film porosity, decreasing of silicon content and the nc-Si concentration after high temperature annealing. So nc-Si-SiOx structures formed on the base of SiOx films with smaller silicon content may be consider as a ensemble of non interacting nc-Si. In that case parameter β increasing ($\beta \rightarrow 1$) is typical, and its behavior characterize the local properties of oxide matrix surrounded nanoincludi-

ons nc-Si. This conclusion is proved by value $\beta = 0,76$ for samples obtained at deposition angle $\alpha = 45°$ (results on these films not shown).
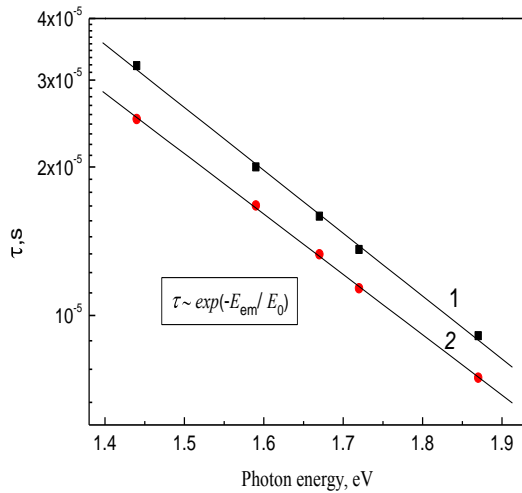

Fig. 3 – Spectral dependence of average PL decay time τ. Curves 1 and 2 correspond on samples deposited at $\alpha = 60°$ (sample I) and $75°$ (sample II)

Assuming the nc-Si can be represented by a quasi-level system, the following rate equation can be written:

$$dN^*/dt = \sigma\Phi(N - N^*) - N^*/\tau, \qquad (3.2)$$

where N, N^* σ, τ and Φ are the total number of the nc-Si, the number of the nc-Si in the exited state, the nc-Si absorption cross section at 3.68 eV (wavelength of excitation), the lifetime of the nc-Si excited state, and the excitation photon flux, respectively. If the PL intensity is defined by $I_{pl} \approx N^*/\tau_{rad}$, where τ_{rad} is the nc-Si radiative lifetime, solving (1) for steady state conditions gives the following expression of the PL intensity:

$$I_{pl}(E_{em}) \approx A\sigma(E_{em})\tau(E_{em})\Phi/1 + \sigma(E_{em})\tau(E_{em})\Phi, \quad (3.3)$$

where A is constant.

Fig. 4 presented of the dependence of the PL intensity from the excitation flux at the different emission energy E_{em}. The data are normalized with respect to the PL intensity measured at the maximum of the laser power used. The lines represent the fit of the experimental data by expression (3.3). Using the obtained data we have calculated absorption cross section σ on one nc-Si particle. It was established that σ increase from $5 \cdot 10^{-18}$ to $1.34 \cdot 10^{-17}$ cm^2 when the emission energy varies from 1.48 to 2.06 eV.

Since σ is defined as the product of electron states density and oscillator force of optical transition then we

observed monotonic rise σ when E_{em} increase. It is mean, that the increase of the oscillator force, when the size of emitting nc-Si decrease, predominate over the reduction of electronic state density in little particles.
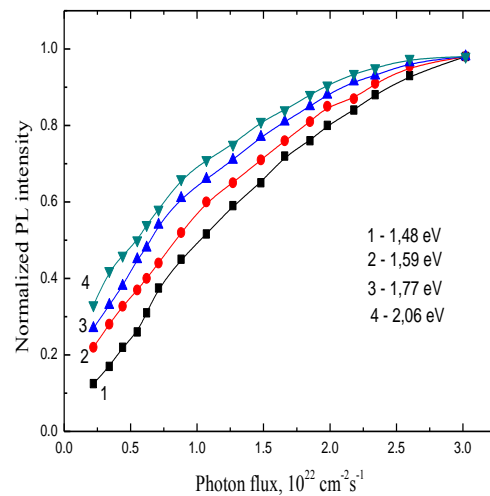

Fig. 4 – PL intensity dependence on photon flux for sample (I). Curves 1, 2, 3, and 4, correspond to registration energies 1.48, 1.59, 1.77 and 2.06 eV.

4. CONCLUSIONS

In this work we carried out investigation of photoluminescence decay kinetics of the samples of porous nc-Si-SiO$_x$ nanostructures obtained by oblique deposition (at angles of $60°$ and $75°$) and annealed in vacuum followed by treatment with HF vapor at $50°$ C. At room temperature photoluminescence decay kinetics in these structures described by a stretched exponential and the average lifetime of the PL decrease exponentially with increasing energy of photons. The parameter β tends to 1 with increasing porosity, which is consistent with the model of noninteracting nc-Si. It was established, that the absorption cross section σ of the nc-Si particles increase with decreasing of nc-Si dimensions and increasing of emission energy.

The results of spectral and kinetics investigations allowed suppose that PL of porous light-emitting nc-Si-SiO$_x$ structures in the 1.25-2.0 eV region is originated from radiative recombination of carriers (excitons). The recombination take place in nc-Si, moreover emission energy depend on nc-Si sizes. The room temperature PL lifetime values are in microsecond range that point out on phonon participation in radiative recombination.

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