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Polarization memory of photoluminescence related with Si nanoparticles embedded into oxide matrix

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Abstract. Investigated in this paper have been polarization properties of photoluminescence in solid and porous nc-Si−SiO_x light emitting structures passivated in HF vapor. These structures were produced by thermal vacuum evaporation of silicon monoxide SiO powder onto polished c-Si substrates. After annealing in vacuum for 15 min at the temperature 975 °C, SiO_x films were decomposed to SiO_2 with Si nanoclusters embedded in the oxide matrix. Comparison of polarizations, inherent to exciting light and that of film photoluminescence, enabled to find the polarization memory effect in the passivated structures. In anisotropic porous nc-Si−SiO_x samples, obtained by oblique deposition in vacuum, there is also well-defined orientation dependence of the PL polarization degree in the sample plane. This dependence is related to the orientation of oxide nanocolumns that form the structure of the porous layer. The above effects are associated with transformation during etching in HF the symmetric Si nanoparticles to asymmetric elongated ones.

Keywords: Si nanoparticle, oxide matrix, photoluminescence, polarized luminescence, polarization memory.

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1. Introduction

Porous silicon and thin-film nc-Si−SiO_x structures containing Si nanoclusters (nc-Si) embedded into the SiO_x matrix attract attention of many researchers, because of their promising applications in advanced electronic and optoelectronic devices. Both materials show an intense and wide photoluminescence (PL) emission peaking in the near-infrared or visible spectrum. However, they essentially differ in polarization of their PL. In porous silicon, the polarization memory effect (PM), that is the correlation between polarization of excited light and polarization property of photoluminescence (PL), was found, and its features and mechanism were studied [1-5]. However, in thin-film nc-Si−SiO_x structures, in which silicon nanoparticles (nc-Si) are embedded into SiO_x matrix, the PM effect was not observed. This result was obtained for nc-Si−SiO_x structures formed by high-temperature annealing of non-stoichiometric silicon oxide SiO_x in inert atmosphere or vacuum. Because of the isotropy of amorphous oxide, silicon nanoparticles formed during annealing are also isotropic, so the effect of PM in these structures does not manifest itself.

In the previous works, it was shown [6, 7] that the treatment of these structures in solution or vapors of hydrofluoric acid can significantly increase the PL intensity and shift the PL peak position to short-wave

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region due to partial etching of nc-Si and passivation of their surface. It can be assumed that this etching can change the shape of symmetric nanoparticles, similarly to that in porous silicon, and leads to the PM effect. Especially effective etching and passivation takes place in developed by us porous nc-Si−SiO_x structures that are formed by oblique deposition of Si monoxide (SiO) in vacuum and the following high-temperature annealing of obtained SiO_x layer [8, 9]. These layers have a porous columnar structure with oxide nanocolumns inclined at a certain angle to the sample surface. During high-temperature annealing of these films, the thermally stimulated formation of Si nanoinclusions occurs in a restricted volume of the SiO_x columns. Because of free space (cavities) between the oxide columns, the structures is more susceptible to chemical treatments, e.g., to etching in HF solution or vapor [10, 11]. These light-emitting structures demonstrate asymmetry in optical properties even before etching [12], so it seems desirable to investigate the polarization properties of their PL.

In this paper, the polarization properties of solid and porous passivated in HF vapour nc-Si−SiO_x light emitting structures were investigated.

2. Experiment

The investigated nc-Si−SiO_x light-emitting structures were produced by thermal evaporation of 99.9% pure silicon monoxide SiO (Cerac Inc.) powder in vacuum ($(1…2)\times10^{-3}$ Pa) onto polished c-Si substrates. The substrates were arranged at the angles (α) of 0° and 60° relatively to the normal to the substrate surface with the direction to the evaporator (normal and oblique deposition). The evaporation rate was monitored *in situ* by the quartz-crystal-oscillator monitor system (КИТ-1). The deposited film thickness was measured using МИИ-4 micro-interferometer and amounted 400 to 950 nm. Because of additional oxidation by residual gases in the vacuum chamber during evaporation of SiO, the obtained SiO_x films were compositionally nonstoichiometric ($x > 1$). The films were annealed in vacuum for 15 min at the temperature close to 975 °C. This high-temperature annealing induces decomposition of SiO_x into Si and SiO_2 and formation of Si nanoclusters embedded in the oxide matrix. Passivation of the nc-Si−SiO_x structures obtained in this manner was carried in the closed cell with HF vapor flow at the temperature 30 °C in the presence of etching-assisting ultraviolet light.

The PL spectra were excited using linearly polarized emission of a semiconductor laser (with the wavelength 415 nm) at nearly normal incidence to the surface of the samples, and emitted light was collected in the direction normal to the surface. Polarization of the exciting light was rotated by a λ/2 phase plate and cleaned by a linear polarizer. Another sheet polarizer (analyzer) was placed in the detection path. PL spectra were measured at room temperature within the wavelength range 500 to 850 nm. These spectra were normalized to the spectral sensitivity of the experimental system and were corrected with respect to the polarization dependent response of the measurement system.

3. Results and discussion

The structure of obliquely deposited SiO_x films was studied by SEM apparatus (ZEISS EVO 50XVP, Oberkochen, Germany) in the previous papers [6, 11]. These films have a porous inclined pillar-like structure with the pillar (column) diameters of 10 to 100 nm. Porosity of the films depends on the angle of deposition and equals to 34% for $\alpha = 60°$ [8], while the inclination of the formed oxide nanocolumns relatively to the normal to the sample surface was 26…29° [12]. High-temperature annealing of these films does not change porosity and pillar-like structure of the samples. Porosity of the normally deposited SiO_x films was less than 10%, these films were isotropic, and after annealing they were practically nonporous [13].

Fig. 1 shows the PL spectra of nc-Si−SiO_x sample deposited in vacuum at the angle 0°, annealed at 975 °C in vacuum, and then etched in HF vapor (curves *1* and *2*). The curve *1* corresponds to the orientation of the analyzer, which selects polarization of PL parallel to polarization of exciting radiation, and the curve *2* − orientation of the analyzer that is perpendicular to polarization of excitation. As seen from the figure, the intensity of PL polarized in parallel to polarization of excitation (curve *1*) is much higher than the PL component polarized in the perpendicular direction (curve *2*), i.e., in the investigated sample the PM effect is really observed.

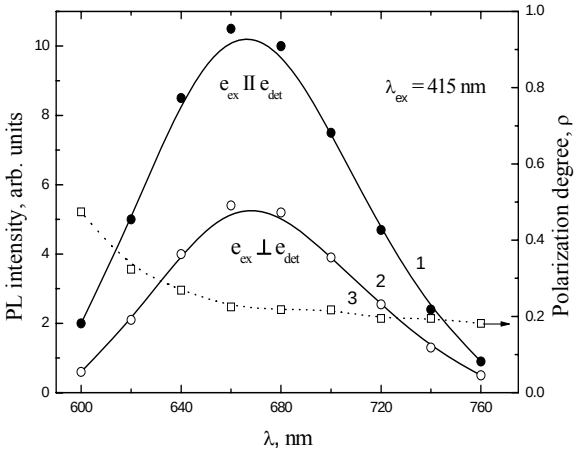

Fig. 1. PL spectra of solid nc-Si−SiO_x sample annealed in vacuum, then treated with HF vapors (*1*, *2*). The curve *1* corresponds to parallel orientation of the analyzer to polarization of the exciting radiation, and the curve *2* − orientation of the analyzer in the perpendicular direction. The curve *3* − value of degree of the linear polarization of PL for this sample.

The effect of PM can be illustrated by the degree of linear polarization of the PL, which is known to be defined with the expression:

$$\rho = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}.$$

Here, $I_{\parallel}$ is the intensity of the photoluminescence polarized in parallel to that of the excited light and $I_{\perp}$ − intensity of photoluminescence polarized in the perpendicular direction. The curve *3* in Fig. 1 corresponds to the ρ value inherent to the investigated sample. Near to the PL maximum, ρ has the value close to 0.2 and increases in the short-wave region of the spectrum, which is similar to the results for porous silicon [2, 3].

Fig. 2 shows the PL intensity dependence on the angle between polarization of the exciting radiation and orientation of the analyzer for the same sample as in Fig. 1, recorded near the PL peak (700 nm). The curves *1* and *2* correspond to two mutually perpendicular orientations of the excitation polarization. For these orientations, the ρ values are equal to 0.23 and 0.22, i.e., they coincide within the measurement errors, which indicates that the PM effect is isotropic in the plane of the sample.

As shown by previous investigations in similar solid nc-Si−SiO_x samples annealed in vacuum or inert gas, but not processed in HF, there is much weaker PL and no PM effect. Thus, within the measurement errors ρ = 0 throughout the investigated range of PL spectra. Similar results were obtained for the sample of porous nc-Si−SiO_x, produced using vacuum deposition of SiO at the angle 60° and annealed for 15 min. The spectral dependence of PL obtained at orientation of the analyzer parallel and perpendicular to the polarization of the exciting radiation coincide, and the ρ value is zero over all the studied spectral range. These results were obtained for any orientation of the excitation polarization relatively to the projection of the inclined SiO_x nanocolumns. Thus, in oblique deposited porous nc-Si−SiO_x structures that exhibit optical anisotropy due to tilting the SiO_x columns [12], the PM effect is not manifested, too.

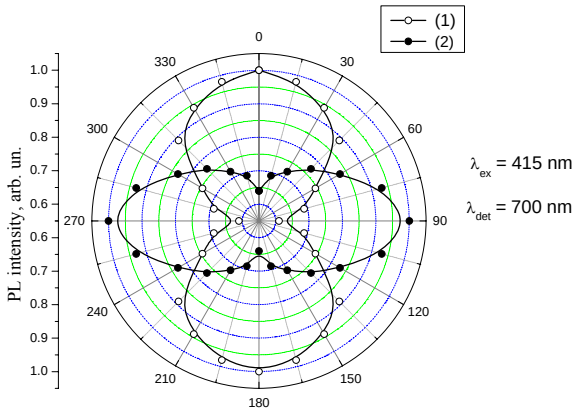

Fig. 2. Polar plot of the PL intensity for nc-Si−SiO_x sample, which spectra are shown in Fig. 1 for two mutually perpendicular orientations of excitation polarization (*1*, *2*). The PL wavelength is 700 nm.

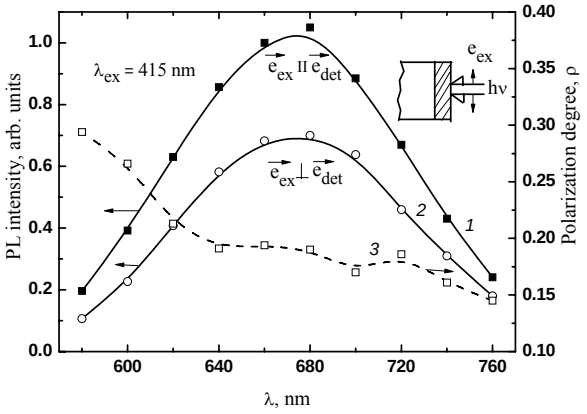

Fig. 3. PL spectra of porous nc-Si−SiO_x sample annealed in vacuum, then treated with HF vapors for parallel (*1*) and perpendicular (*2*) orientations of the analyzer relatively to polarization of exciting radiation, which is oriented in parallel to the projection of SiO_x nanocolumns on the sample plane. *3* − value of the degree of PL linear polarization.

But after treatment in HF vapor, the luminescent properties of nc-Si−SiO_x structures are changed, in particular, there is a significant shift of the PL maximum to the visible part of spectrum and increase in the PL intensity. These changes are explained by decrease in the nc-Si size during etching and passivation of the surface [9]. Besides that, the dependence of PL polarization on excitation polarization direction appears in the porous nc-Si−SiO_x structures, just as in solid samples. Fig. 3 shows PL spectra of the porous nc-Si−SiO_x sample obtained by deposition at the angle 60° and annealed at 975 °C in vacuum for 15 min, then treated with HF vapor. The curves *1* and *2* correspond to orientation of the analyzer parallel and perpendicular to polarization of the exciting radiation, which is oriented in parallel to the projection of the inclined SiO_x nanocolumns on the sample plane. It can be seen that the intensity of PL component polarized in parallel to polarization of the exciting radiation is substantially higher than the intensity of PL polarized in the perpendicular direction. The curve *3* in this figure represents the degree of PL linear polarization.

But unlike results shown in Fig. 1, the PM effect on the porous nc-Si−SiO_x structures has its peculiarities. Fig. 4 shows the PL spectra of the same sample as in Fig. 3, but for the case of excitation polarization perpendicular to the projection of inclined SiO_x nanocolumns on the sample plane. It can be seen that the difference between $I_{\parallel}$ and $I_{\perp}$ is significantly smaller as compared with the case where this sample during measurement was fixed at the position when polarization of the exciting light coincides with the direction of nanocolumns projection.

More clearly, PM anisotropy in the sample plane is manifested in dependences of the PL intensity on the angle between polarization of the exciting radiation and orientation of the analyzer. Fig. 5 shows such

dependences for two orientations of the excitation polarization relatively to the projection of SiO_x nanocolumns. For parallel orientation of the excitation polarization and nanocolumns projection, the PM effect is pronounced much efficiently than for perpendicular orientation, and ρ values at the PL maximum are equal to 0.19 and 0.09, respectively.

This result is similar to that observed in porous silicon formed by electrochemical etching of Si with orientation [100] in the presence of linearly polarized light illumination [2], which indicated the existence of PM anisotropy in the plane of the sample.

It was proposed several mechanisms that determine the PM effect. In [14], PL polarization anisotropy of elongated particles associated with the structure of the valence band due to quantum confinement in two directions − parallel and perpendicular to the longer axis of the particle. More common explanation − within the dielectric model in which porous silicon is considered as a composite that includes elongated and flattened silicon nanocrystals preferentially oriented as elongated nc-Si along the [100] direction [1-3]. The probability of optical absorptions and emission is proportional to the square of the electric field inside the nc-Si and, therefore, nanocrystals with their longest dimensions aligned along the polarization direction of exciting light will preferentially absorb and emit photons. Then PM is the result of selective excitation that part of the nonspherical silicon nanoparticles whose longer axis is parallel to polarization of exciting radiation [1, 4, 15]. Both interpretations as on the basis of quantum size effects and within the dielectric model associate the PM effect with asymmetric, elongated nanoparticles that emit PL.

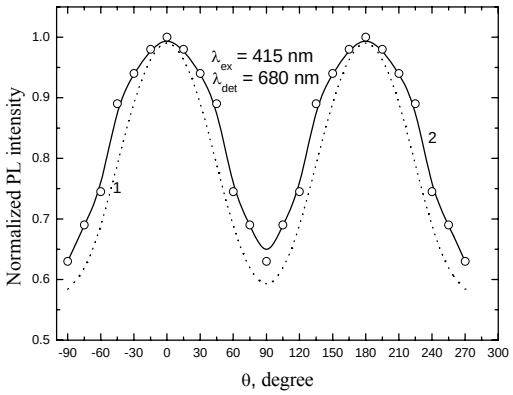

Fig. 6. Dependence of the normalized PL intensity on the angle (θ) between excitation and detection polarizations for continuous nc-Si−SiO_x sample annealed in vacuum, then treated with HF vapor. *1* − simulation results, *2* − experimental values. The PL wavelength − 680 nm.

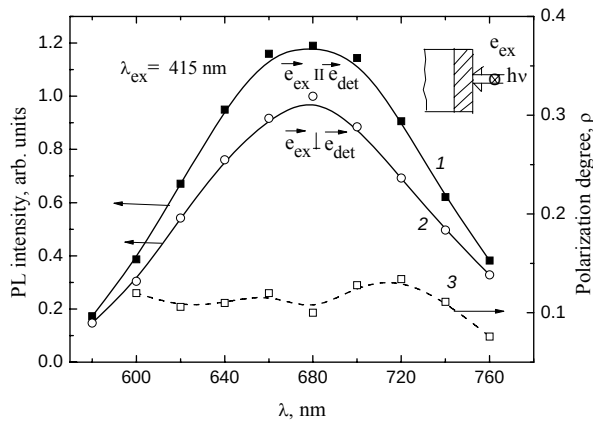

Fig. 4. PL spectra of the same sample as in Fig. 3, but for orientation of excitation polarization perpendicular to the projection of SiO_x nanocolumns on the sample plane.

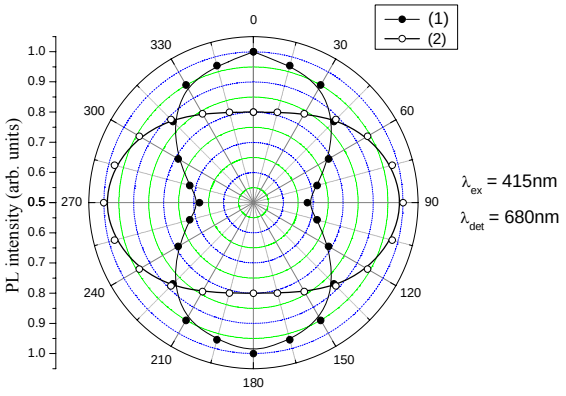

Fig. 5. Polar plot of the PL intensity for nc-Si−SiO_x sample, which spectra are shown in Figs 3 and 4 for two mutually perpendicular orientations of excitation polarization − parallel orientation of the excitation polarization and nanocolumns projection (*1*) and perpendicular orientation (*2*). The PL wavelength is 680 nm.

Another necessary condition to observe this effect is a significant dielectric contrast between the nanoparticles and their environment. As shown experimentally in the work [16] by reducing the dielectric contrast between InP and ZnO nanofiber using Ta_2O_5 deposition, the authors managed to reduce the value of ρ by 84…86%. In the same paper, the model was developed for calculation of the PL intensity dependence on the angle between the directions of exciting light polarization and that of detected one for the structure that contains nanowires (or elongated nanoparticles) randomly oriented in the plane of the sample (similar to our continuous nc-Si−SiO_x structures processed in HF). The main parameters of this model is the dielectric constants of the emitting nanoparticles (or nanofibers) and dielectric environment in which these emitters are embedded. Fig. 6 shows the angular dependence of the normalized PL intensity (points − experimental values, solid line − approximation of the experiment using polynomial) for continuous nc-Si−SiO_x sample annealed in vacuum, then processed in HF vapor, the same as presented in Figs 1 and 2. The dotted curve shows the results of simulation that obtained using the expression [16]:

$$\langle I \rangle = \frac{\pi E^2 L^2 \left[(10\varepsilon_e^2 + 4\varepsilon_e\varepsilon + 2\varepsilon^2)(9\varepsilon_e^2 + 2\varepsilon_e\varepsilon + \varepsilon^2) + (\varepsilon_e - \varepsilon)(2\varepsilon_e + \varepsilon)^2 \cos 2\theta \right]}{4(\varepsilon_e + \varepsilon)^2 (3\varepsilon_e^2 + 2\varepsilon_e\varepsilon + \varepsilon^2)} \quad (1)$$

where ε_e and ε are dielectric functions of environment and emitting nanoparticles, accordingly, θ is the angle between excitation and detection.

The value of the dielectric function ε for silicon nanoparticles was calculated taking into account their size [17] and was equal to 8.8. For SiO_x matrix, if taking into account its porosity and composition, $\varepsilon_e = 1.96$ [13]. One can see minor differences between the experimental and calculated curves, which indicates adequacy of the model and close values of selected parameters to the real values of the dielectric functions for the nanoparticles and matrix.

4. Conclusion

In the samples deposited at the angle 0°, thermostimulated decomposition of SiO_x and formation of nc-Si occur in the isotropic continuous film, therefore nanoparticles also have isotropic (nearly spherical) shape, and the PM effect is not observed. In porous samples deposited at the angle 60°, which are optically anisotropic due to inclination of SiO_x nanocolumns, the PM effect is not observed, too. It means that silicon nanoparticles formed in the SiO_x columns during annealing are also spherically symmetrical, and polarization of PL is mainly determined by the shape of particles that emit light. Anisotropy of the dielectric matrix is not manifested through the dependence of PL polarization on the excitation polarization.

After treatment with HF, the luminescent properties of nc-Si–SiO_x structures are changed. The results obtained in this paper show that this etching leads not only to the reduced sizes of silicon nanoparticles, but also to changes in their shape to the elongated anisotropic one. In the continuous nc-Si–SiO_x structures, in the plane of the sample there are no preferrential orientations of anisotropic silicon nanoparticles. But in the porous matrix, anisotropy of PM is observed in the plane of substrate. It means that anisotropic elongated silicon nanoparticles have preferred orientation in the film, and the projection of this orientation on the plane of the sample coincides with the direction of projection of the SiO_x nanocolumns. It has been assumed that orientation of the longer axes in nc-Si coincides with orientation of SiO_x nanocolumns. This assumption is consistent with the conditions of etching in porous matrix: dissolution occurs starting from the surface of the nanocolumns, so first the side surface of nc-Si is dissolved, since it is closer to the column surfaces, which leads to elongation of nanoparticles along the axis of the column.

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