

INFLUENCE OF NITROGEN IMPURITY ON PHOTOLUMINESCENCE OF SILICON NANOCLUSTERS IN SiO₂ MATRIX

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Photoluminescence (PL) spectra of SiO_x layers ($x = 1.4\text{--}1.6$) have been investigated. It is determined that the maximum intensity of PL is observed after the thermal annealing in SiO_x films with $x = 1.5$. The dependence of the photoluminescence spectra of SiO_{1.5} layers on the concentration of nitrogen introduced by ion implantation and annealing in the N₂ ambient is investigated, and the depth profiles of the nitrogen distribution in SiO_x films are studied as well. The results obtained are explained within the framework of a model of the origin of radiative recombination centers on Si nanocrystal/matrix interfaces under the participation of nitrogen and the passivation of centers of non-radiative recombination.

1. Introduction

The high-temperature annealing of SiO_x films fabricated by different ways is the known method of creation of the structures with Si nanoclusters (nc) [1–3]. Such an approach allows one to create nano-structures (NS) which give stable intense PL in the long-wavelength (700 to 1100 nm) spectral region [4, 5]. Advantages of the formation of silicon NS by using SiO_x films are as follows: 1) low cost of a technological process; 2) homogeneity of the concentration of excess silicon over the film thickness; 3) possibility to obtain films with different thicknesses.

Interpretation of experimental results on PL is based on a few basic models related to the presence of isolated silicon nanoclusters in a SiO₂ matrix: model of the quantum-size effect [1, 5, 6], when light absorption and radiative recombination of electron-hole pairs or excitons take place in a nanocrystal; model of the localized electronic states at the ncSi–SiO₂ interfaces [2–5]: light is absorbed in a nanocrystal, and recombination takes place at interfaces; luminescence of defect and impurity complexes of different nature in SiO₂, depending on the technology of fabrication or modification of structures.

Reduction of the nanocrystal sizes causes not only a change of their band structure, but also a modification of Si–SiO₂ interface properties [3–5, 7–9] (surface

energy, concentration of Si–O–Si bonds, mechanical deformation, width of a transitional region on the ncSi–SiO₂ interface). This leads to an ambiguity in the choice of a model of photoluminescence mechanisms in such structures. For example, it was shown in [2] that a PL spectrum is displaced to the short-wavelength region depending on the duration of the oxygen-involved annealing of the structures implanted by silicon ions. This confirms the quantum-size model, because the nanocluster sizes diminish under oxidation. But the subsequent annealing of such structures in nitrogen results in a displacement of the PL spectrum to the opposite direction, that cannot be related to the increase of nc sizes, and it is probable that a modification of the nanocrystal–matrix interfaces takes place, and PL occurs due to the recombination of charge carriers through energy levels at the interfaces.

Incorporation of impurities to the SiO_x matrix by implantation or diffusion enables one to efficiently govern the radiative properties of ncSi [10, 11]. The use of such an approach allows one to control the concentration and sizes of silicon nanocrystals in the SiO₂ matrix and to modify the ncSi/SiO₂ interfaces (to change the density and the energy spectrum of electronic states).

In a number of papers [7, 8, 12–14], the influence of the nitrogen impurity on luminescent properties of structures with silicon nanoclusters was investigated. Studies of the influence of the annealing ambient on the PL spectra of SiO_x–Si structures have shown that the annealing in nitrogen substantially increases the PL intensity in a region of ~ 800 nm [7]. It was also shown that the PL band of the samples annealed in Ar is shifted to the long-wavelength region in comparison with the samples annealed in N₂. It is indicated that the annealing in argon results in the annealing of defects, while the annealing in nitrogen is a combination of the thermal annealing of defects with chemical reactions of silicon, nitrogen, and oxygen.

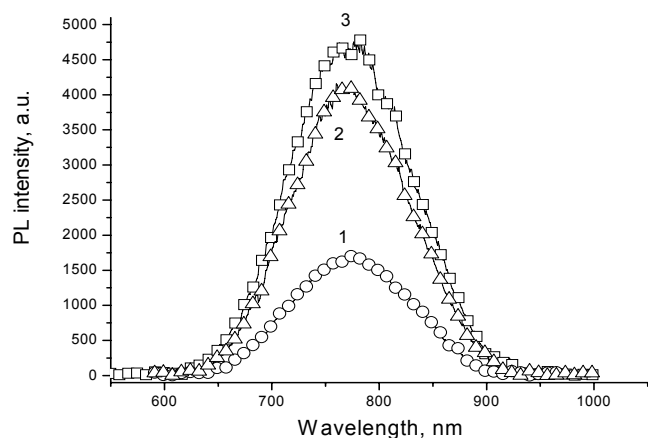


Fig. 1. PL spectra of the SiO_x layers annealed during 20 min: 1 – in argon; 2 – in nitrogen; 3 – in argon or in nitrogen after the N_2^+ ($D = 1.7 \times 10^{16} \text{ cm}^{-2}$) implantation

As was shown in [12], the successive implantation of N^+ and Si^+ ions to the SiO_2 matrix promotes an increase of the PL intensity and a displacement of the spectrum to the short-wavelength region. It was shown in [13, 14] that, at the ion implantation of nitrogen, the 330- and 430-nm PL bands attributed to Si–N–O defect complexes arise.

The mechanism of the nitrogen influence on the luminescent properties of Si nanoclusters in the SiO_2 matrix is not finally established. In particular, the dependence of photoluminescent properties on the concentration of introduced nitrogen is not explored. The purpose of the given work was to find out the mechanisms of the nitrogen influence on the radiative properties of nanoclusters in the SiO_2 matrix depending on its concentration and the method of insertion.

2. Experimental

SiO_x ($x = 1.4$ to 1.6) films of 380 nm in thickness were deposited onto Si (100) substrates using the thermal evaporation of a SiO_x target in vacuum ($\sim 10^{-4}$ Pa). Nitrogen was incorporated by two methods: using the thermal annealing in the nitrogen ambient at a temperature of 1150 °C (the annealing duration changed from 1 to 65 min) or the successive implantation of N_2^+ ions with energies of 70 and 140 keV and with the total dose in an interval of 1.2×10^{15} to $2.5 \times 10^{16} \text{ cm}^{-2}$. In the first case, the equilibrium concentration of nitrogen which depend on many factors (temperatures, annealing time, and also on the initial state of the matrix) was introduced in a SiO_x film. In the case of the implantation, nitrogen is introduced with the

exactly established concentration that can be increased in comparison with a value available at the thermal annealing.

Measurements of PL spectra were made at room temperature. A solid-state laser with a wavelength of 473 nm was used for PL excitation. The excitation power was ~ 50 mW. The component composition of the layers and the atom distribution over the sample depth were determined by SIMS and XPS measurements. The thicknesses of the layers before and after the annealing were measured by the profilometry method.

3. Results

The PL spectra of initial SiO_x layers, as well as the spectra of nitrogen-implanted samples annealed in the argon and nitrogen ambient are given in Fig. 1. The PL intensity depended on the parameter x and had a maximum for the SiO_x layers with $x = 1.5$, both under the annealing in argon and nitrogen. Therefore, in what follows, we give the results obtained for the SiO_x matrix with $x = 1.5$.

The PL spectrum for unimplanted samples depends on the annealing ambient. For example, the annealing of such samples in the nitrogen ambient (curve 2) exceeds almost three times the PL intensity in comparison with that under the annealing in argon (curve 1). In addition, for the samples annealed in nitrogen, a small shift of the PL band maximum to the short-wavelength region is observed: for the samples annealed in Ar and in N_2 , the PL maxima are near 777 nm and 766 nm, respectively. The PL intensity of the samples implanted by nitrogen with the dose $D = 1.7 \times 10^{16} \text{ cm}^{-2}$ (curve 3) exceeds thrice the PL intensity of unimplanted samples annealed in the Ar ambient (curve 1). In addition, for the nitrogen-implanted samples in the dose interval of 1.2×10^{16} to $1.8 \times 10^{16} \text{ cm}^{-2}$, the PL spectrum does not depend on the annealing ambient.

The dependence of the PL intensity of annealed samples on the dose of implanted nitrogen is given in Fig. 2. One can see that, with increase in the implanted nitrogen dose, the PL intensity of SiO_x layers increases and achieves the maximum at $D \sim 1.7 \times 10^{16} \text{ cm}^{-2}$, which corresponds to a nitrogen bulk concentration of ~ 3.5 –4 at. %.

At the nitrogen concentration > 4 at. %, the PL intensity drops sharply.

With the purpose of a more detailed study of the influence of the annealing on the luminescence intensity, we varied the annealing duration in nitrogen for unimplanted samples from 1 to 65 min. It is

established that, with increase in the annealing duration to 65 min, the PL intensity grows slightly. In addition, with increase in the annealing duration in nitrogen, we observe a shift of the PL maximum (λ_{\max}) to the short-wavelength region (Fig. 3,*a*). Such a displacement is observed for the annealing duration of up to 60 min, and the subsequent increase in the annealing duration does not change the spectral position of a PL band. A similar displacement of the PL band maximum to the short-wavelength region is observed under an increase of the implanted nitrogen dose (Fig. 3,*b*).

Depth profiles of the nitrogen atom distribution for the samples under study are shown in Fig. 4. The nitrogen distribution over the thickness of an unimplanted sample annealed in N_2 is almost regular and corresponds to a concentration of ~ 2 at. %. The depth distribution of implanted nitrogen in the film after the annealing in Ar is also practically regular, except for the area adjacent to a substrate (250–280 nm). In the samples annealed in argon, no nitrogen impurity is detected.

4. Discussion

Our experimental data testify that the presence of nitrogen atoms in a film during the nc-Si structure formation leads to a substantial increase in the photoluminescence intensity. This effect does not depend on the method of introduction of nitrogen but substantially depends on its concentration. In addition, the dependences of the position of the PL band maximum on the annealing duration in the N_2 ambient (an increase of the nitrogen concentration due to diffusion) and on the dose of implanted nitrogen are identical. The data of measurements of the film thickness before and after the annealing show a considerable “shrinkage” of the structure (~ 20 %), which testifies that the deposited film is not compact. This facilitates the penetration of nitrogen into such a structure during an annealing. The nitrogen diffusion causes its uniform distribution over the film thickness, which is confirmed by the results of SIMS measurements of unimplanted SiO_x films annealed in the nitrogen ambient (Fig. 4). An increase in the nitrogen concentration at a depth of ~ 270 nm is caused by its accumulation at the SiO_2/Si interface [15].

The improvement of radiative properties of the nc-Si structures under the introduction of nitrogen can be related to

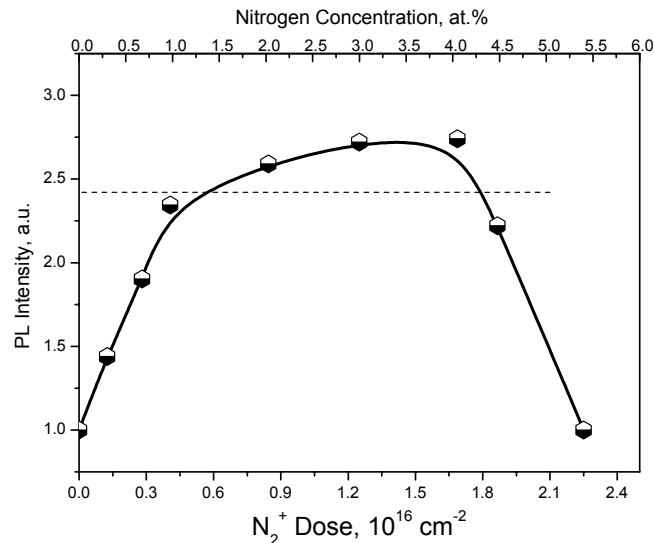


Fig. 2. PL intensity versus the dose of implanted nitrogen for the samples annealed in the argon ambient during 20 min. The dashed line shows the PL intensity of an initial SiO_x layer annealed during 20 min in nitrogen

i) an increase of the amount of nanoclusters [12] and/or

ii) a reduction of the concentration of non-radiative recombination centers [7, 15].

We consider that exciting light is absorbed in nanoclusters, and radiative recombination takes place through the energy levels at SiO_2 –Si interfaces (in particular, Si=O bonds) [16].

The role of nitrogen in this process consists in the following. As the enthalpy of the silicon nitride phase formation is substantially less than that of the silicon oxide formation [17, 18], Si–N bonds are quickly formed under the thermal annealing and the break of silicon bonds, which retards the diffusion of silicon in a SiO_x film. This restricts the diffusion-limited stage of cluster growth and suppresses the processes of cluster oxidation due to the autocatalytic mechanism [19]. Consequently, the presence of nitrogen stabilizes the structure of ncSi– SiO_2 and conserves a high concentration of nanoclusters. Under annealing in the N_2 ambient, nitrogen diffuses gradually to the SiO_x film, so that the crystallization of Si into nanoclusters inside the film on initial stages of the annealing goes without the participation of nitrogen.

Under the annealing of nitrogen-implanted samples, the formation of clusters over the whole film thickness occurs with the participation of nitrogen. As a result, we have observed an increase of the luminescence intensity in implanted samples even at small nitrogen

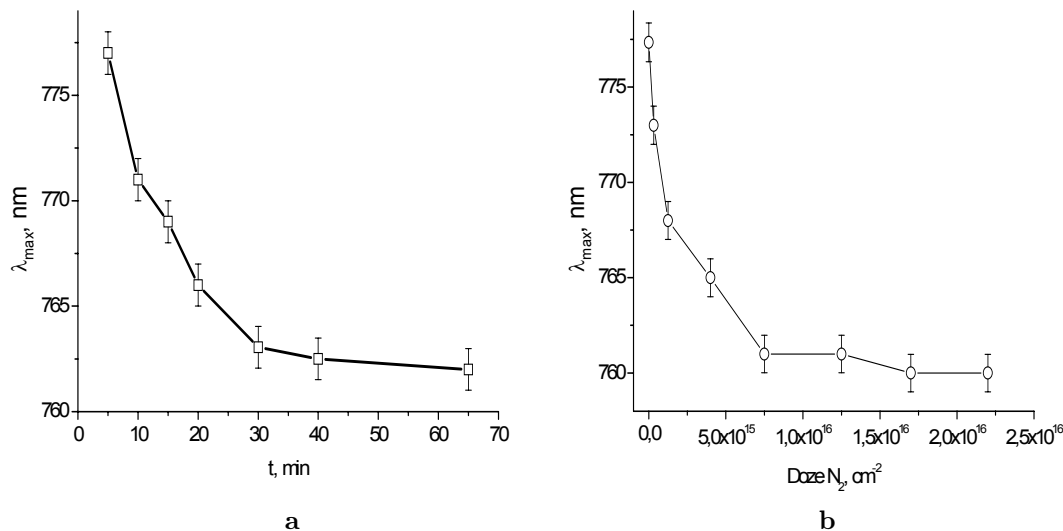


Fig. 3. PL band maximum position versus the annealing time for unimplanted SiO_x samples annealed in nitrogen (a) and versus the implanted nitrogen dose for the samples annealed in argon during 20 min (b)

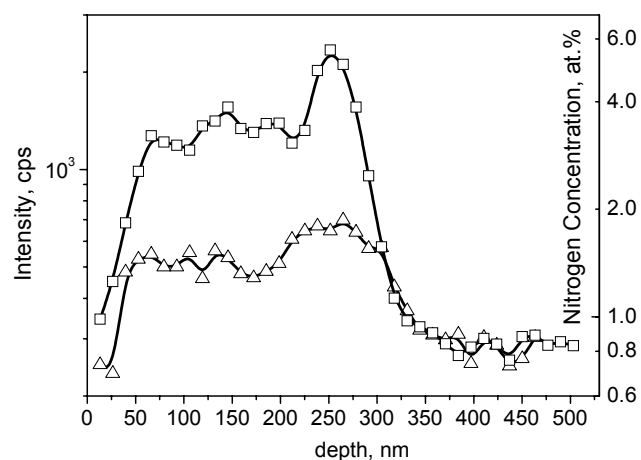


Fig. 4. SIMS profile of the nitrogen distribution in a SiO_x film after the annealing during 20 min: Δ – in the atmosphere of nitrogen; \square – in the atmosphere of argon with N_2 implantation, $D = 2.2 \times 10^{16} \text{ cm}^{-2}$

concentrations (~ 1 at.%). During the annealing, nitrogen is accumulated at the oxide/nc-Si interfaces and passivates silicon dangling bonds. This leads to a reduction of the concentration of non-radiative surface states at the oxide/silicon interface [7]. Thus, during a thermal annealing, a high concentration of nanoclusters surrounded by the SiO_2 phase (dangling bonds in the nanoclusters are passivated by nitrogen) is conserved.

Shifts of the PL spectrum maximum to the short-wavelength region with increase in the annealing duration in nitrogen or with increase in the nitrogen

concentration under a growth of the nitrogen implantation dose are related to a modification of the nanocrystal- SiO_2 interfaces under the participation of nitrogen. On the stage of the diffusion-limited cluster growth, nitrogen can also induce a reduction of average nanocrystal sizes due to the formation of the oxynitride phase, which will also cause a shift of the PL spectrum maximum to the short-wave length region. At the same time, at a nitrogen concentration of ~ 2 at.%, a change of the PL maximum achieves ~ 15 nm, and a subsequent increase of the nitrogen concentration does not result in a PL maximum change, although the PL intensity continues to grow. This testifies that the PL mechanism is not related to the quantum-size effect in Si nanoclusters, because, in this case, an increase of the concentration of nanoclusters and a reduction of their size would result in a simultaneous increase of the PL intensity and a monotonous (depending on the nitrogen concentration) spectral shift.

The PL intensity falls sharply with increase in the nitrogen concentration from 4 to 5.5 at.% (see Fig. 2). This is related to the appearance of the oxynitride phase at cluster surfaces, a reduction of the concentration of radiative interface electronic states, and, respectively, a reduction of the radiative recombination intensity. Estimations show that, at maximal nitrogen concentrations used in the given work, its amount is sufficient for the creation of a continuous superficial oxynitride layer at the surface of Si nanoclusters, but it is insufficient for the dissolution

of clusters in the oxynitride phase. This confirms the model of radiative recombination via interface centers.

5. Conclusions

We have studied the dependence of the photoluminescence spectra of $\text{SiO}_{1.5}$ layers on the concentration of nitrogen incorporated into layers by the ion implantation method, as well as the influence of the annealing ambient (argon and nitrogen) on the PL spectra.

It is shown that the PL intensity depends on the nitrogen concentration and grows with the nitrogen content in a film up to 4 at.%. The increase of the nitrogen concentration higher than the optimum value results in the break of Si=O bonds, appearance of the oxynitride phase on cluster surfaces, reduction of the radiative interface electron state concentration, and, accordingly, reduction of the intensity of radiative recombination. Thus, the samples under study demonstrate the radiative recombination mainly via local surface centers at the Si nanocluster–matrix interfaces rather than the recombination inside quantum-size nanoclusters.

The analysis of the experimental results obtained and data of the literature testifies that the influence of the nitrogen impurity on the PL spectra of ncSi/SiO₂ nanocluster structures consists in the stabilization of silicon nanocluster sizes, increase in their concentration, and a modification of nanocluster–matrix interfaces due to the passivation of centers of non-radiative recombination and the creation of additional centers of radiative recombination (Si=O bonds), which allows one to increase the PL intensity of such samples in a certain range of the nitrogen concentration.

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ВПЛИВ ДОМШКИ АЗОТУ НА ФОТОЛЮМІНЕСЦЕНЦІЮ КРЕМНІЙОВИХ НАНОКЛАСТЕРІВ В МАТРИЦІ SiO_2

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Резюме

Проведено дослідження спектрів фотолюмінесценції (ФЛ) плівок SiO_x ($x = 1, 4-1,6$). Встановлено, що максимальна інтенсивність ФЛ спостерігається після термічного відпалу в плівках SiO_x з $x = 1,5$. Досліджено спектри фотолюмінесценції плівок $\text{SiO}_{1.5}$ залежно від концентрації азоту, введеного іонною імплантацією та відпалом в атмосфері N_2 . Досліджено профілі розподілу азоту по глибині плівки SiO_x . Отримані результати пояснюються в рамках моделі виникнення за участі азоту центрів випромінювальної рекомбінації на межах поділу нанокристал Si/матриця та пасивації центрів безвипромінювальної рекомбінації.