FABRICATION, TREATMENT, AND TESTING
OF MATERIALS AND STRUCTURES

Effect of High-Temperature Annealing on Photoluminescence of Silicon Nanocluster Structures

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Abstract—Experimental data on the photoluminescence spectra of Si nanocluster structures obtained after high-temperature annealing (1150°C) of SiO_x films deposited onto Si and subsequent low-temperature annealing of the films at the temperature 450°C in different media are reported. It is shown that the photoluminescence intensity substantially increases after low-temperature annealing and the most-pronounced effect is observed after annealing in the oxygen–nitrogen mixture. In this case, the photoluminescence spectrum is shifted to longer wavelengths and shaped as a broad band with a peak around 800 nm. The processes responsible for the increase in the PL intensity on low-temperature annealing in the oxygen–nitrogen mixture are defined by reconstruction of the Si/SiO_2 interfaces and by energy levels formed at the interfaces and involved in recombination of nonequilibrium charge carriers. The quasichemical reactions that bring about the formation of such levels involve oxygen and nitrogen atoms, and the centers, at which the reactions are initiated, are unsaturated valence bonds at the interfaces between Si nanoclusters and the SiO_2 matrix.

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1. INTRODUCTION

The properties of Si nanoclusters (NCs) embedded in insulator matrices (SiO_2, Si_3N_4, silicon oxynitride) have been extensively studied in the last few years [1–3]. The NC samples are fabricated by means of ion implantation of Si into the SiO_2 layers [3] or deposition of SiO_x layers with subsequent high-temperature thermal annealing (1000–1150°C) [4]. In such structures, photoluminescence (PL) in the visible and near-infrared regions of the spectrum is observed, which opens new prospects of application of the structures in optoelectronics and microelectronics. In order to improve the PL efficiency and to control the parameters of the PL spectra, the structures are subjected to additional doping with impurities (nitrogen, carbon, phosphorus, and rare-earth elements) or to low-temperature treatments in different media [7–9].

In the available publications, a number of models are discussed to interpret the mechanisms of radiative recombination in structures containing Si NCs. Some of the models should be specially mentioned. Among these are recombination of nonequilibrium charge carriers in NCs due to the quantum-confinement effect [5, 9], absorption of light in NCs and recombination via energy levels at the Si/SiO_2 interfaces [2, 10], and excitonic recombination [11].

In [7], the effect of low-temperature annealing on PL in structures containing Si NCs was studied and the PL bands were attributed to the formation of various types of thermally induced donor centers.

However, up to the present time, no model has been available to allow an unambiguous interpretation of all of the data on PL in such structures fabricated in different conditions of synthesis and technological treatments.

In this study, we investigate the effect of the medium used for low-temperature annealing on the properties of $Si–SiO_2$ structures containing Si NCs embedded in the insulator. The purpose of this study is to clarify the role of quasi-chemical reactions in the reconstruction of the Si/SiO_2 phase interfaces and in the formation of radiative recombination centers.

2. EXPERIMENTAL

SiO_x films ($x = 1.5$) with a thickness of 320 nm were deposited onto p-Si (100) substrates (with the resistivity 10–20 Ω cm) by thermal sputtering of the SiO_x powder in vacuum (~10^{-4} Pa). The thickness and refractive index of the films were determined by ellipsometry, and the results for the thickness were compared to the thickness determined from profilometry measurements. To form NCs, the films were subjected to annealing at the temperature 1150°C in Ar or N_2 atmosphere. Low-temperature anneals were conducted at the temperature 450°C in vacuum or different media: Ar, N_2, O_2, H_2, and $N_2 + O_2$ mixture (air) at the temperature 450°C. The duration of annealing was varied from 20 min to 6 h. In addition, we conducted several cycles of successive anneals.

The PL spectra of the samples were recorded at room temperature. To excite the PL signal, we used
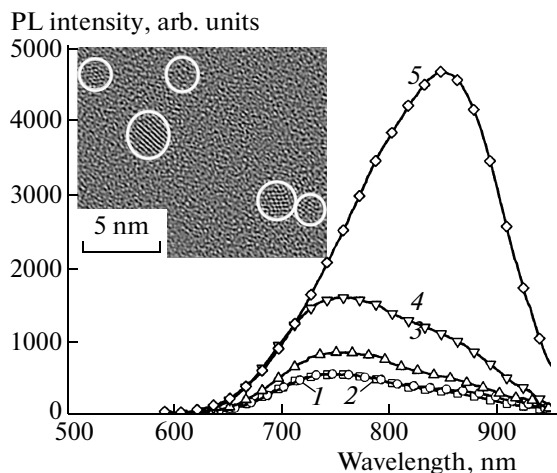
PL intensity, arb. units

Fig. 1. PL spectra of the $SiO_{1.5}$ films after (*1*) HT annealing and (*2–5*) subsequent LT treatments in different media: (*2*) vacuum, (*3*) O_2, (*4*) N_2, and (*5*) air. Inset: TEM image of Si NCs embedded in the SiO_2 matrix.

PL intensity, arb. units

Fig. 2. The dependence of the PL intensity on the duration of LT annealing in (*1*) nitrogen and (*2*) air.

radiation of a solid-state laser at the wavelength 473 nm. The radiation power was ~50 mW.

The structure of the films was studied by transmittance electron microscopy (TEM) with the use of an FEI Titan 80-300 electron microscope providing electrons with the energy 300 keV.

The composition of the films was determined by secondary-postionized-neutral-particle mass spectrometry (SPINMS).

3. RESULTS

Figure 1 shows the PL spectra of the samples after high-temperature (HT) annealing (1150°C, Ar, 20 min) followed by low-temperature (LT) treatments (450°C, 6 h) in different media. In the inset in Fig. 1, the TEM image of Si NCs in the SiO_2 matrix is shown. After HT annealing of the samples, their PL spectrum exhibits a broad asymmetric PL band (curve *1*) that can be approximated with two Gaussian functions with peaks at the wavelengths $\lambda_{max} \approx 750$ nm (1.65 eV) and 880 nm (1.41 eV). Subsequent LT annealing of such samples in vacuum or inert gas atmosphere (Ar) leaves the PL spectrum practically unchanged (curve *2*). At the same time, annealing in O_2 atmosphere induces some increase in the PL intensity (curve *3*); in this case, the shape of the spectrum remains practically unchanged. The LT treatments in the N_2 or H_2 media yield an increase in the PL intensity and a slight change in the shape of the PL band (curve *4*).

A profound increase in the PL intensity is observed in samples annealed in the $N_2 + O_2$ mixture at the temperature 450°C after HT annealing. In this case, the PL intensity becomes several times higher; in addition, we observe a noticeable spectral shift of the PL peak to longer wavelengths (Fig,1, curve *5*).
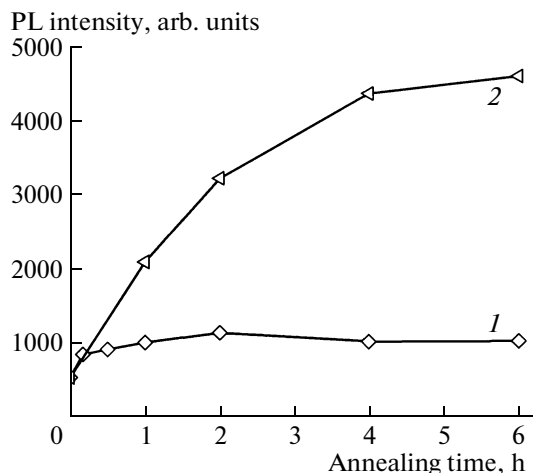
Figure 2 shows the dependence of the PL intensity of the structures, in which NCs were formed, on the duration of LT annealing in N_2 and in the $N_2 + O_2$ mixture. With increasing duration of annealing in the $N_2 + O_2$ mixture to 6 h, the PL intensity increases (curve *2*). At durations of LT annealing longer than 6 h, the PL intensity becomes practically saturated. In this case, with increasing duration of LT annealing, the PL band shifts to longer wavelengths. On long LT annealing in N_2 atmosphere, the PL intensity is found to be several times lower and saturates on annealing during ~1 h (curve *1*).

Figure 3 shows the PL spectra recorded after successive cycles of heat treatments (1150°C, Ar, 20 min) + (450°C, $N_2 + O_2$, 2 h). After the first cycle of (HT + LT) treatments, we observe a broad PL band with a peak at 800 nm (curve *1L*). HT annealing accomplished in the second cycle of treatments of the samples induces a decrease in the PL intensity to the initial level; in this case, the shape of the spectrum is changed in such a manner that the intensity of the short-wavelength component of the PL band (around 700 nm) decreases (curve *2*). Subsequent LT annealing in the second cycle yields an increase in the PL intensity and a broadening of the band towards the long-wavelength region of the spectrum (curve *2L*). Such cyclic change in the PL intensity is observed on threefold repeated annealing; in this case, the PL intensity observed after each LT annealing becomes somewhat higher, and the PL band broadens toward the longer wavelength region (curve *3L*).

Figure 4 shows the results of layer-by-layer analysis of the composition of the $SiO_{1.5}$ films at different stages of successive heat treatments, (I) 1150°C, Ar, 20 min; (II) 1150°C, Ar, 20 min + 450°C, ($N_2 + O_2$), 2 h; and (III) 1150°C, Ar, 20 min + 450°C, ($N_2 + O_2$), 2 h + 1150°C, Ar, 20 min. After the forming HT annealing in Ar atmosphere, the nitrogen content in
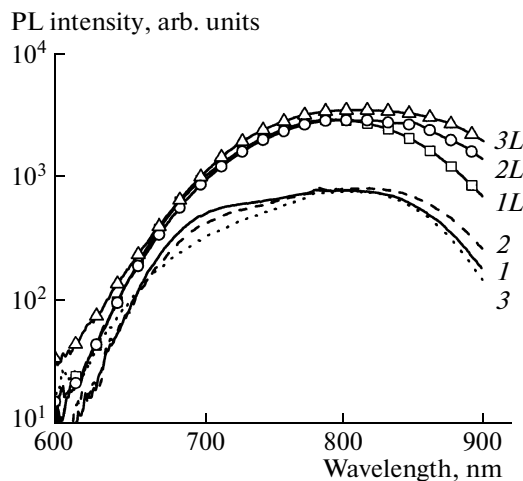
Fig. 3. PL spectra of the $SiO_{1.5}$ films after (*1–3*) HT annealing (1150°C, Ar, 20 min) and (*1L–3L*) subsequent LT annealing (450°C, $N_2 + O_2$, 2 h) in the (*1, 1L*) first, (*2, 2L*) second, and (*3, 3L*) third cycles of heat treatments.
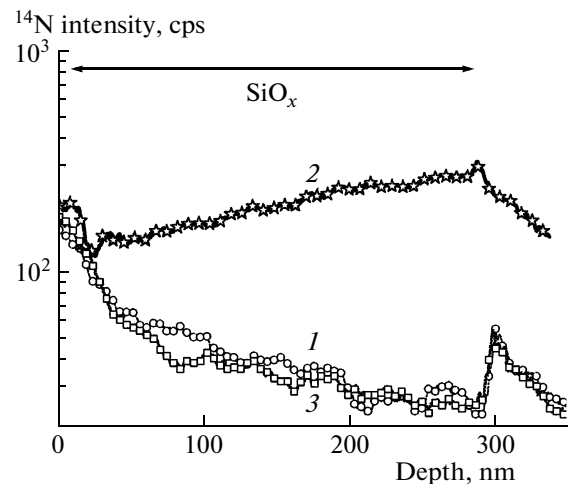

Fig. 4. The depth distribution of nitrogen in the film at different stages of successive heat treatments: (*1*) 1150°C, Ar, 20 min; (*2*) 1150°C, Ar, 20 min + 450°C, $N_2 + O_2$, 2 h; and (*3*) 1150°C, Ar, 20 min + 450°C, $N_2 + O_2$, 2 h + 1150°C, Ar, 20 min.

the film is low (curve *1*). The higher nitrogen content is observed at the film–substrate interface, since nitrogen exhibits the property of being accumulated at the interface [12]. After LT annealing in the $N_2 + O_2$ mixture (II), the nitrogen content in the film becomes substantially higher (curve *2*). The subsequent HT annealing (III) removes nitrogen from the film (curve *3*).

4. DISCUSSION

The TEM studies show that, on HT annealing, single-crystal Si NCs (3 ± 0.4) nm in dimensions are formed in the SiO_2 matrix. These Si NC dimensions and the NC content remain unchanges on all subsequent heat treatments. According to [10], the band gap in such NCs is ~1.7 eV. This gives us grounds to think that the high-energy (1.65 eV) PL band is due to recombination of charge carriers in the NCs. In [7], the 1.7- and 1.5-eV bands in the PL spectrum were attributed to the thermally induced oxygen–silicon donor centers NL_8 and NL_{10}. In the experiments performed in this study, subsequent long-time LT treatments in vacuum or Ar atmosphere do not modify the shape and position of the PL spectral lines. The PL intensity remains unchanged as well. This suggests that the structure of the film is not changed and new PL centers of the type of thermally induced donors are not formed, although the films contain oxygen and silicon.

From our point of view, the mechanism responsible for the 1.5-eV band is the recombination of charge carriers via energy levels at the interfaces between Si NCs and the SiO_2 matrix. We believe that, on LT annealing in the $N_2 + O_2$ mixture, some quasi-chemical reactions proceed and, as a result, the Si/SiO_2

phase interfaces are reconstructed and some energy levels, via which charge carriers radiatively recombine, are formed. At the Si/SiO_2 phase interfaces, there are dangling valence bonds (P_b centers). As shown in [10], the P_b centers are responsible for nonradiative recombination processes. On annealing in oxygen or nitrogen, we observe a slight increase in the PL intensity. This is most probably due to passivation of dangling bonds at the nc-Si/SiO_2 interfaces with these impurities and, hence, some suppression of the nonradiative recombination processes.

The situation is radically changed after LT annealing in the $N_2 + O_2$ mixture: the PL intensity becomes about eight times higher, and the shape of the spectrum is modified. It should be noted that, after LT annealing in the $N_2 + O_2$ mixture, the PL intensity depends on the type of medium, in which the preliminary forming HT annealing is accomplished. If the HT annealing is accomplished in argon, the LT annealing induces a more profound increase in the PL intensity compared to the increase observed for the samples annealed in nitrogen. Subsequent annealing of the samples in hydrogen at the temperature 450°C yields a more substantial relative increase in the PL intensity in the samples preliminarily annealed in argon in comparison with the increase observed in the samples annealed in nitrogen. This observation suggests that, at the Si/SiO_2 phase interfaces in the samples annealed in argon, there are a large number of dangling bonds serving as nonradiative recombination centers. These centers are passivated on annealing in nitrogen, as shown in [9].

On annealing in the $N_2 + O_2$ mixture, a self-catalytic process of formation of PL centers occurs, with

the involvement of both unbound oxygen contained in the film and oxygen penetrating into the film by diffusion from the atmosphere of annealing. An important role in promoting the quasi-chemical reactions is played by dangling bonds located at the phase interfaces. In fact, the dangling bonds serve as centers of initiation of reconstruction of the interfaces. On annealing in nitrogen, nonradiative recombination centers are rapidly passivated by nitrogen that binds to the dangling bonds at the NC/matrix interfaces. In this case, on additional diffusion of oxygen into the film during annealing, new Si_xNO_y centers appear due to the formation of Si−O bonds and subsequent bonding of nitrogen to the bonds. The much slower kinetics of such a process (in comparison to the processes of annealing in nitrogen) suggests that the PL centers are formed with participation of oxygen, the diffusion coefficient of which at the temperatures of annealing is rather small. Thus, the activity in PL is inherent in Si−O−N centers that may be similar to the memory centers in the Si_3N_4−SiO_2−Si structures.

Successive cyclic heat treatments at high (1150°C) and low (450°C) temperatures bring about the formation of recombination-active centers at the phase interfaces and the annealing of the centers; such annealing occurs even at temperatures >650°C. We believe that the Si−O−N PL centers break down because of diffusion of nitrogen from the film, as supported by the profiles of nitrogen in the samples after HT annealing (Fig. 4). After cyclic heat treatments, the PL band with the peak at 1.65 eV becomes lower in intensity and shifted to longer wavelengths. This can be evidence for the increase in the nanocluster dimensions.

Thus, the results of this study show that, with the aim of attaining efficient PL in the SiO_x films, the structures must be fabricated under the following conditions.

(i) The films should be formed with a high concentration of Si NCs embedded in the SiO_2 matrix in order to make the total area of the nanocluster−insulator interfaces larger. This is attained by HT heat treatments. Nitrogen atmosphere used on annealing tends to increase the PL intensity due to passivation of nonradiative recombination centers.

(ii) The films should be subjected to long-time heat treatments (450°C, >2 h) in a mixture of nitrogen with oxygen. Such a type of annealing makes it possible to obtain a high density of Si−O−N centers active in PL. An important role in forming the PL centers is played by dangling bonds located at the nc-Si/SiO_2 interfaces. As shown in the study, the unsaturated valence bonds are formed simultaneously with Si NCs on HT annealing in argon atmosphere.

5. CONCLUSIONS

The effect of high-temperature HT (1150°C) and subsequent low-temperature LT (450°C) treatments of the $SiO_{1.5}$ film structures on the PL spectra is studied. After HT annealing of the Si/$SiO_{1.5}$ structures, their PL spectra exhibit a broad asymmetric PL band that can be approximated by two Gaussian functions with peaks at the wavelengths $\lambda_{max} \approx 750$ nm (1.65 eV) and 880 nm (1.41 eV). The short-wavelength band is attributed to recombination of charge carriers in NCs, whereas the short-wavelength band is related to recombination via energy states at the nc-Si/SiO_2 interfaces. It is shown that LT treatments in vacuum or inert gas atmosphere do not modify the PL spectra. An increase in the PL intensity is observed on LT treatments in nitrogen atmosphere, which is due to passivation of nonradiative recombination centers. A substantial increase in the PL intensity is observed after LT treatments in the mixture of oxygen with nitrogen. In this case, the PL spectrum is shifted to longer wavelengths and shaped as a broad band with a peak at 880 nm. The mechanisms responsible for the increase in the PL intensity on LT annealing in the mixture of oxygen with nitrogen are defined by the annealing-induced reconstruction of the nc-Si/SiO_2 interfaces and by the formation of energy states that participate in recombination of charge carriers. The quasi-chemical reactions of creation of such states involve oxygen and nitrogen atoms. An important role in promoting the reactions is played by unsaturated valence bonds at the nc-Si/SiO_2 interfaces.

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