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Effect of chemical and radiofrequency plasma treatment on photoluminescence of SiO_x films

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Abstract. Effect of hydrogen radiofrequency plasma and chemical treatment on photoluminescence (PL) spectra of SiO_x layers containing Si nanoparticles are investigated. Considerable PL intensity growth in the samples containing Si nanocrystals (nc-Si-SiO_x) after plasma treatment is observed. The process saturates for time of 15 minutes. Chemical treatment in ammonia and acetone vapour before thermal annealing of SiO_x layers leads to the considerable changes in PL spectra effecting both on the band shape and on the intensity. The possibility of controlled changes in PL spectra in nc-Si-SiO_2 layers is shown.

Keywords: nanocrystals, silicon oxide, photoluminescence, thin film.

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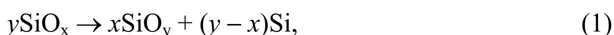
1. Introduction

Since the discovery of visible light emission from porous silicon and silicon nanocrystals (nc-Si), the number of investigations on SiO_x thin films containing silicone nanoinclusions [1-3] has increased, because of its promising applications in Si-based optoelectronics. Photoluminescence (PL) observed in such structures in visible and near infrared range is connected with quantum-confinement effect of silicon nanoclusters in SiO_x films annealed at high temperatures.

Several techniques are used to fabricate silicon suboxide films, namely: chemical vapor deposition, ion implantation, laser ablation, magnetron sputtering, thermal evaporation in vacuum and others. All these methods allow to fabricate amorphous SiO_x films with required *x*. Formation of nc-Si is thermostimulated process that is often described by reaction:



$$y\mathrm{SiO}_x \rightarrow x\mathrm{SiO}_y + (y - x)\mathrm{Si}, \quad (1)$$

where $y > x$. The annealing temperature determines the structure of inclusions: annealing at 500 to 900 °C favors coagulation of Si atoms into amorphous clusters, at higher temperatures nanocrystalline Si particles are formed [1, 2].

To provide controlled emission in nc-Si-SiO_x layers, it is necessary to study factors that influence on PL spectra. Although the mechanism of light emission in such structures is still under discussion, it is known that emission energy depends on the nanoparticle size. As for control of the size and volume density of Si nanoinclusions, it seems to be useful to control the structure of deposited SiO_x layers by changing the conditions of their deposition. The size control in these systems is usually realised by varying the silicon content in SiO_x layers [3], or by introducing a superlattice-like structure into the synthesis process [4]. Another method for size-controlled silicon nanocrystal synthesis, using oblique deposition and thermal annealing of SiO_x layers, was proposed in our previous paper [5]. Thermal evaporation of silicon monoxide on the substrate obliquely oriented to the direction of the evaporated substance flow leads to the formation of the porous SiO_x films with the columnar structure [6]. Depending on the angle of evaporation and other parameters of the technological process, the diameter of deposited columns varies from 10 to 30 nm. Thermostimulated formation of Si nanoinclusions in such films takes place in a limited volume of SiO_x columns, which can result in smaller dimensions of nc-Si than in continuous films with the same content (*x*).

PL of deposited films depends also on the temperature, time and atmosphere of annealing. It was shown [7] that the choice of annealing environment during the formation of silicon nanocrystals in the oxide matrix may have a significant effect on their PL. Hydrogen and nitrogen treatment have a passivating

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effect on nonradiative defects at the nc-Si-oxide interface: annealing in forming gas (5 % H_2 in N_2) at 500 °C [7] leads to several times growth in PL intensity. Annealing of SiO_x films in nitrogen atmosphere leads to slow growth in PL intensity up to 16 hours of its duration [8, 9].

A more effective method of defect annealing in the silicon structure is the low-pressure RF plasma treatment [10, 11]. This paper presents the results of investigation of PL in nc-Si/SiO_2 structures being passivated using hydrogen plasma and chemical treatments.

2. Experiment

Thin SiO_x layers were obtained by thermal evaporation of SiO (Cerac Inc., purity of 99.9 %) in vacuum at the residual pressure of 1…2×10^{-3} Pa. The angle (β) between the vapor flow and the substrate normal was 0 and 75° for different samples. Two-sided polished Si wafers and silica plates were used as the substrates. The substrate temperature during deposition was 150 °C.

The rate of deposition onto the normally oriented substrate was 1.5 nm/s and decreased with increasing β. The time of deposition was chosen to provide the deposition of the same mass on the same area of the samples, independently on substrate orientation. Thickness of the films were monitored *in situ* by the quartz-crystal-oscillator monitor system (КИТ-1) and measured after deposition by a microinterferometer МИИ-4. The thickness of normally deposited films was equal to 250-300 nm, for oblique deposited films – about 600 nm. The density (ρ) of investigated samples was determined by comparing the thickness of the films deposited at different angles with the films deposited normally. The density of normally deposited film was measured early and was equal to 1.90 g/cm^3 [12].

Portions of obliquely deposited samples were exposured to acetone and ammonia saturated vapor atmosphere for 48 hours at the room temperature. After that, all the samples were annealed in vacuum (10^{-3} Pa) at 700 and 950 °C to obtain amorphous and crystalline Si inclusions in the oxide matrix. Chemically non-treated films were passivated by the radiofrequency (RF) plasma treatment in hydrogen atmosphere (20 % H_2 in N_2), diode type reactor, frequency 13.6 MHz.

PL spectra were measured at room temperature using SPM2 monochromator with nitrogen-cooled ФЭУ-62 photomultiplier. The 488 nm line of an Ar^+ laser was used for excitation.

3. Results and discussions

3.1. RF plasma treatment

Main characteristics of prepared samples are summarized in Table.

As it can be seen from Table, the density of films decrease greatly for oblique deposited samples, which is the evidence of a porous structure of such layers (under annealing, the density does not practically change). The porosity of samples with the same mass of deposited SiO_x on the same substrate area was determined as (d(75) – d(0))/d(75), where d(75) is the thickness of film deposited at angle 75°, d(0) is the thickness of the normally deposited film, and porosity was equal to 52 %.

To estimate the oxide composition of both as-deposited (*x*) and annealed (*y*) samples, we used monotonous dependence [13] of the maximum position for the main IR absorption band for SiO_x in the range 1000 – 1100 cm^{-1} (which corresponds to the asymmetric stretching vibration of the oxygen atom in its two-fold coordinated bridging bonding site) on the oxide composition.

The as-evaporated SiO_x films show rather weak photoluminescence in the visible range. After annealing at 700-950 °C, the intensive wide band appears in the near IR range with the peak position that depends on the deposition angle and temperature. Normalized PL spectra of normally and oblique deposited as well as annealed at 950 °C are given in Fig. 1. It can be seen that position of PL band for obliquely deposited film is

Table. Characteristics of deposited films.

Deposition angle	*x* As-deposited	*y* Annealed		ρ, g/cm^3	Peak position in the IR absorption band, cm^{-1}		
		700 °C	950 °C		As-deposited sample	Annealed sample	
						700 °C	950 °C
0	1.27	1.41	1.91	1.90	1023	1040	1073
75°	1.51	1.60	1.92	0.88	1052	1063	1076

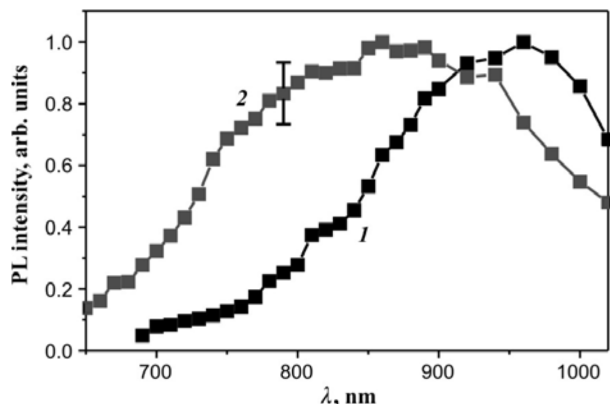

Fig 1. Normalized PL spectra of normally (1) and obliquely (2) deposited and annealed at 950 °C SiO_x films.

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blueshifted, and the maximum position is equal to 860 nm, when for the normally deposited film it is about 960 nm. This blue shift in PL spectra is explained by decreasing the nc-Si size that depends on the deposition angle and is the result of the porous (columnar) structure of the film [5]. In columns of small diameter (less than 10 nm) at high-temperature annealing, the Si nanoparticles of smaller sizes are formed, in columns of greater diameter the size of particles is the same as in continuous SiO_x films. With increasing the deposition angle, porosity of the deposited films is increased, and the average diameter of columns decreases. It enables to control the light-emitting characteristics of nc-Si-SiO_x structures by changing the deposition angle.

The normally and obliquely deposited and annealed films were treated with RF hydrogen plasma. No changes in PL spectra for samples annealed at 700 °C were observed. As for the samples annealed at 950 °C, this RF plasma treatment leads to significant growth of PL intensity (about 10 times) for both types of the samples. Fig. 2 shows the evolution of the room-temperature PL spectra obtained for normally deposited samples annealed at 950 °C after 5, 10, 15 and 20 min plasma treatments. It can be seen (e.g., in the inset) that the intensity-time dependency is linear for times 5 to 15 min, and for larger times it reaches saturation. Further treatments do not lead to enhancement of the PL intensity. The same results were obtained for obliquely deposited films.

The position of the PL peak doesn't change after this plasma treatment both for porous and solid samples.

Results obtained for plasma treatment can be interpreted as follows. There exist several factors capable to influence on treated samples [10, 11]: 1) low energy ion and electron bombarding; 2) X-ray and UV irradiation over a wide spectral range; 3) RF electromagnetic field; 4) thermal heating. Atoms and ions of hydrogen penetrate inside the nc-Si-SiO_x film causing the following changes: neutralization of fixed charges, relaxation of mechanical strains, annealing of defects and reduction of surface states at the Si/SiO_2 interface. In our opinion, the latter process is determinative in the growth of PL intensity. Most of authors recognised the critical role of P_b centres – nonradiative centres at the Si/SiO_x interface. P_b centres are the dangling bonds of silicon that cause nonradiative quenching and can be passivated by hydrogen. It was shown using electron spin resonance (ESR) experiments that the PL intensity in these nc-Si-SiO_x films inversely correlates with the amount of P_b centers [7]. Consequently, annealing of the nc-Si-SiO_x samples in hydrogen environment (forming gas), or plasma treatment enhance the PL intensity due to a reduction in the P_b concentration, without modifying the spectral shape of the PL emission.

It should be noted that enhancement of the PL intensity in the case of treatment by plasma considerably exceeds influence of annealing in hydrogen atmosphere (in our experiments the maximal enhancement of intensity was 30-fold). That is protons and atomic hydrogen, which penetrate in oxide during the plasma treatment, together with electric recharging the defect states cause considerably more effective annealing of the surface states on the nc-Si-SiO_x interface [10, 11] than the standard hydrogen annealing [7]. Plasma treatment not only passivates Si dangling bonds but also anneals structural defects in silicon and its oxide, that is orders structure of material.

As for samples annealed at 700 °C where growth of the PL intensity was not observed, it can be explained by the following assumption. Annealing of the SiO_x films at lower temperatures leads to formation of silicon particles with an amorphous structure [1]. Passivation of such particles is not enough effective because of the absence of a sharp interface between silicon and the matrix. Moreover, the concentration of P_b centers in films

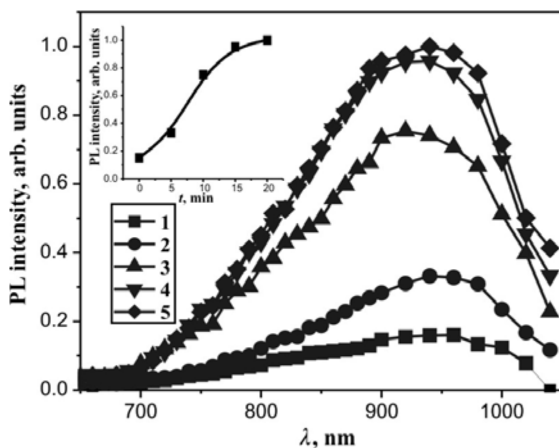

Fig 2. PL spectra of normally deposited samples annealed at 950 °C and treated with RF plasma for various times: non-treated (curve 1), treated for 5 min (2), 10 (3), 15 (4), and 20 min (5). In inset: the dependency of the PL peak intensity on the time of a plasma treatment.

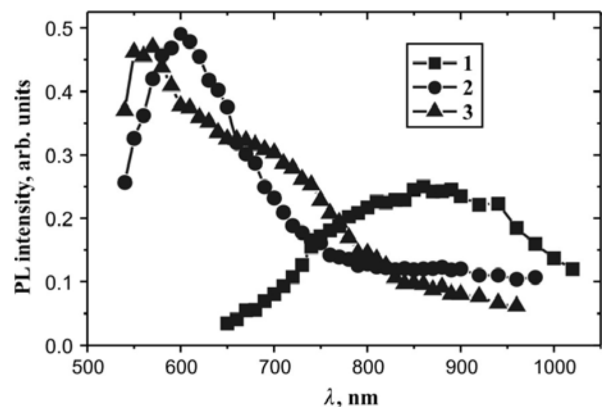

Fig. 3. PL spectra of obliquely deposited samples: non-treated (curve 1), exposured to acetone (2), ammonia (3) and annealed after the chemical treatment at 950 °C.

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annealed at 200…700 °C decrease by more than one order of its magnitude relatively to the as-deposited film [4]. More high-temperature annealing induces a growth of the P_b center density. Therefore, in samples with amorphous Si nanoinclusions influence of P_b centers on PL will not be substantial because of their considerably smaller concentration, and passivation of these layers practically does not increase the PL intensity.

3.2. Chemical treatment

PL spectra of obliquely deposited samples non-treated (curve 1), exposured to acetone (2), ammonia (3) and annealed at 950 °C are shown in Fig. 3. It can be seen that PL band for the samples chemically treated before annealing is shifted to shorter wavelengths. The PL intensity in these samples significantly grows, too. It should be noted that the samples being treated after annealing do not demonstrate any noticeable changes in PL spectra. Maximum of PL for samples exposed to ammonia (NH_3) is about 560 nm. The PL band for samples exposured to acetone (CH_3COCH_3) vapour has the peak position near 610 nm.

This essential shift of the maximum and enhancement of the intensity can be caused by two reasons. First, owing to reduced sizes of Si nanocrystals. In paper [14], it is shown that nitrogen can hinder aggregation of crystal nuclei and growth of larger Si nanocrystals at high-temperature annealing. Therefore, adsorption of the ammonia containing nitrogen, can promote growth of smaller nanocrystals during annealing and a shift of the PL spectrum to the short wave range.

The second reason can be associated with restrictions that are imposed by the oxide matrix. Availability of oxygen causes the formation of silicon-oxygen double bonds at the nc-Si-SiO_x interface. Due to these bonds, nc-Si in oxide matrix has localized levels in the band gap and emit light only in the near-infrared range even when the size of nc-Si was controlled to below 2 nm [15]. To overcome this restriction, it is possible if using passivation of nc-Si surface by other atoms, for example nitrogen or carbon (that is to change the oxide matrix, at least at nc-Si surface, by another one). In some recent works, short wave radiation (up to 400 nm) from nc-Si structures in silicon nitride [16, 17] and carbon doped matrix [18] is received.

Our samples have a porous structure and adsorb ammonia or acetone during chemical treatment. In our opinion, the presence of ammonia or acetone in porous oxide layers promotes passivation of nc-Si surface and prevents formation of Si=O bonds during annealing in vacuum and further exposure on air. Moreover, the presence of acetyl and methyl effect on oxidation (or oxicarbonization) of silicon and formation of nc-Si with smaller sizes takes place. To make this assumption more obvious, the process of acetone and ammonia exposure needs further investigations. So, chemical treatments of porous SiO_x films in ammonia and acetone vapour atmosphere with further annealing allow to change shape and intensity of PL band in nc-Si-SiO_x structures.

4. Conclusions

RF hydrogen plasma treatments of both normally and obliquely deposited nc-Si-SiO_x samples allow to increase the PL intensity. But the position of PL peak doesn't change after plasma treatment. Enhancement of the PL intensity in the case of treatment by plasma considerably exceeds influence of the standard hydrogen annealing, because of the plasma treatment not only passivates Si dangling bonds on the nc-Si-SiO_x interface but also anneals structural defects in silicon and its oxide.

As for samples annealed at 700 °C when amorphous nanoclusters are formed, no changes in PL spectra were observed.

Chemical treatments by ammonia and acetone vapor of porous SiO_x layers before annealing allow to effect on PL spectra, too. The PL band in these samples is shifted to shorter wavelengths and the intensity of PL significantly grows. The PL peak position for samples exposed to ammonia is about 560 nm, for samples exposed to acetone – near 610 nm. It is assumed that nitrogen in ammonia, and carbon in acetone promotes passivation of nc-Si surface by nitrogen or carbon and prevents formation of Si=O bonds.

RF plasma and chemical treatments by ammonia and acetone vapor are efficient methods that allow to increase the PL intensity of silicon nanocrystals embedded in the oxide matrix and vary the PL peak position in a wide spectral range.

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