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Effect of low-temperature annealing on light-emitting properties of na-Si/SiO_x porous nanocomposite films

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Abstract. The effect of low-temperature annealing on light emitting properties of na-Si/SiO_x porous column-like nanocomposite films has been studied. Influence of type of chemically active gas or inert ambient on PL characteristics is shown. Existence of meta-stable defects in such structures is shown. A temperature interval for healing the meta-stable defects is defined. Mechanisms to reduce a non-radiative recombination channel depending on the gas ambient are proposed.

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

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1. Introduction

The task to optimize light emitting properties of silicon nanocomposite system with Si inclusions imbedded into oxide matrix remains currently important. An effective mean to enhance the luminescence intensity is, in particular, low-temperature annealing of nc-Si/SiO_2 system in the ambient of hydrogen, oxygen, nitrogen, and so on [1, 2]. Passivation of surface inherent to nc-Si inclusions with corresponding gas atoms leads to noticeable reduction of nonradiative recombination channel. In the case of porous nanocomposite films that have a column-like structure with highly developed effective surface, influence of such a treatment should be substantially specific.

2. Experiment

Porous nanocomposite system, which contains amorphous Si nanoparticles (na-Si/SiOx) were produced by high temperature treatment (975 ºC, 15 min, vacuum) of porous SiO_x ($x \approx 1.78$) films obtained by the method of oblique (60 º) deposition of thermally evaporated SiO particles in vacuum. Our earlier investigation has shown that this nanocomposite has column-like structure with silicon nanoinclusions imbedded into silicon oxide [3, 4]. The samples were annealed in vacuum ($\sim 10^{-3}$ Pa) or in ambient air, argon, nitrogen or hydrogen within the temperature range of 100–550 ºC. The spectra of IR-absorption were measured using a Fourier spectrometer Spectrum BXII PerkinElmer. The photoluminescence (PL) spectra were measured at room temperature in the wavelength interval from 550 to 1000 nm under the excitation by the beam of a semiconductor laser with a wavelength of 473 nm. The emission power was about 50 mW. The obtained PL spectra were corrected with regard for the spectral sensitivity of the measuring setup.

3. Results and discussion

High temperature (975 ºC) forming heat treatment of SiO_x films in vacuum lead to appearance of remarkable PL band with peak position at ~830 nm, which is inherent to Si nanoinclusions (Fig. 1). The data of Raman spectroscopy show that these silicon inclusions have an amorphous structure (Fig. 2). Subsequent low-temperature heat treatments considerably enhanced the PL band (~850 nm), intensity and the efficiency of this effect depended on type of gas ambient – it was maximal (up to 8 times) for nitrogen atmosphere.

Fig. 3 demonstrates influence of isochronous annealing in Ar ambient ($\Delta T = 50$ ºC, $\Delta t = 10$ min) on the PL intensity. It is seen that the PL intensity begins to increase at the temperatures larger than 100 ºC. Within the temperature range of 100-250 ºC, PL intensity grows up to ~2 times, and then the dependence of I_{PL} saturates. At temperatures higher than 450 ºC, I_{PL} rapidly decreases and at $T \approx 500$ ºC it becomes less then that for initial sample. PL band position and full width at half maximum value (160–170 nm) during heat treatment did not practically change, however in some cases a certain red shift is observed. It should be noted that in the latter case PL intensity has never been changed for solid SiO_2 films with imbedded Si nanocrystals.

Results obtained on the samples treated at low-temperature annealing in chemically active gases ambient are similar to those observed earlier in the case of nc-Si/SiO_2 structures with solid matrix [1, 2]. Hence, these data may be explained in the framework of commonly adopted model – at elevated temperatures molecules (atoms) of nitrogen, hydrogen or oxygen passivates broken bonds of silicon on the surface of silicon nanoinclusions. As a result the concentration of centers of non-radiative recombination is diminished and PL intensity increases. It should be noted that optimal temperatures for passivation process are in the vicinity of 400 to 450 ºC [1, 2].

For the case of low-temperature heat-treatments in vacuum or in argon ambient such a model can not explain the facts observed. In this case some following mechanisms may be involved:

1) Growth in the concentration of silicon inclusions due to thermally induced phase separation at low temperatures.

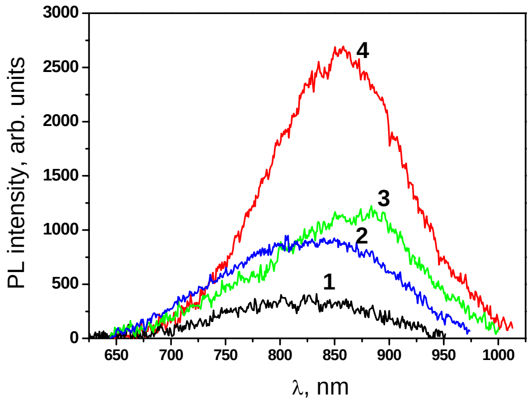

Fig. 1. Influence of type of gas ambient on PL spectra (1 – initial sample without low-temperature annealing, 2 – after annealing in H_2 ambient, 3 – in Ar and 4 – in N_2).

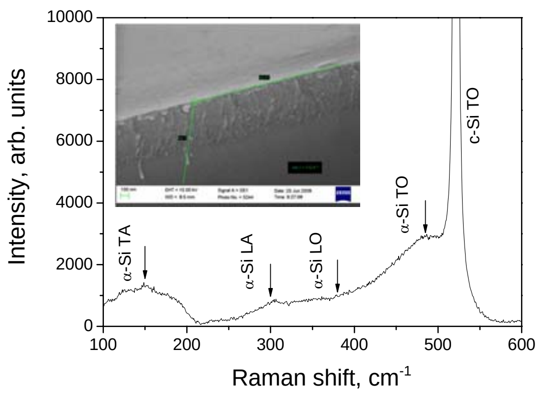

Fig. 2. Raman spectra and SEM micrographs (insert) of na-Si/SiO_x porous column-like nanocomposite films

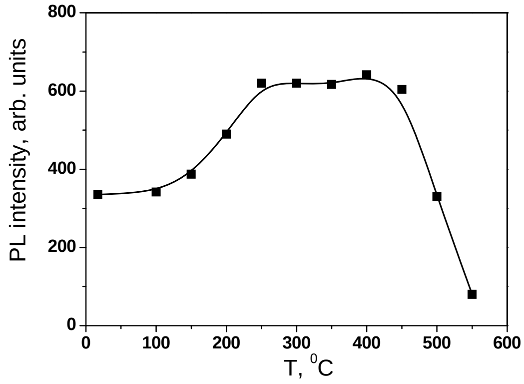

Fig. 3. Influence of isochronous annealing in Ar ambient on the PL intensity of na-Si/SiO_x porous column-like nanocomposite films.

2) Passivation of broken bonds on silicon nanoinclusion surface with participation of molecules (for example, H_2O, CO_2) or radicals (such as OH, H), which were adsorbed on the advanced surface of porous matrix during storage of the samples in room atmosphere.

3) The same as (2), but impurities appeared in the matrix in the process of SiO_x film deposition.

4) Thermal elimination of thermodynamically nonequilibrium (meta-stable) defects, which were generated on the surface of silicon nanoinclusions in the process of thermally induced phase separation.

IR-spectra measurements has shown that low-temperature treatments did not affect on the maximum position or intensity of Si-O vibration absorption band (~1080cm^{-1}). This fact means that the process of phase separation and, respectively, formation of new silicon nanoinclusions under action of heat within the temperature range 100 to 450 ºC was absent. Participation of molecules or radicals adsorbed on film surface in the process of broken-bond passivation is incredible – under vacuum heat treatments at low temperatures desorption of these components is more probable. Moreover, IR-spectra of both initial and heat-treated nanocomposite structures demonstrated absence of the bands connected with such impurities as carbon, hydrogen or water. Therefore, scenarios (2) and (3) should be also excluded from consideration. One may conclude that in our case at interface of amorphous Si – porous SiO_x meta-stable (thermodynamically nonequilibrium) defects exist, and these defects are the centers of nonradiative recombination. These defects are generated due to process of silicon nanoinclusions formation. Their origin may be, for example, connected with an action of mechanical stresses that exist in thin (10–100 nm) oxide columns of porous matrix. Thermal annealing of meta-stable defects is similar to the case when elimination of radiation defects leads to enhancement in the PL intensity.

Hence, PL intensity enhancement is the most likely caused by structural transformations in oxide matrix near the surface of silicon nanoinclusions. Two mechanisms, at least, may be involved. For the samples annealed in vacuum or in Ar atmosphere, elevated temperatures (100–250 ºC) lead to healing the meta-stable defects (e.g. dangling bonds of silicon and oxygen) at the na-Si–SiO_x interface. In fact, this temperature interval is characteristic for annealing the radiation defects both in planar Si/SiO_2 structures [5] and in nanocomposites nc-Si/SiO_2 [6]. Existence of these defects may be associated with an oxide strained structure in porous film nanocolumns. If gas ambient is chemically active, mainly passivation of more stable broken bonds of silicon and oxygen with corresponding gas molecules may additionally take place, i.e., reinforcing process of elimination of nonradiative recombination centers may be observed.

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