Abstract. The correlation between the photoluminescence and paramagnetic defects is studied in SiO$_x$ films grown by vacuum thermal deposition and annealed at 750 ºC. The as-grown samples exhibit a wide structureless EPR line centered at $g = 2.0040$, which is explained by the presence of a variety of dangling bonds $\cdot\cdot\cdot\text{Si} \equiv \text{Si}_y\text{O}_{3-y}$. The annealing at 750 ºC causes the formation of amorphous silicon inclusions in SiO$_x$ matrix, appearance of the photoluminescence peaked at $\sim 1.8$ eV and shift of the EPR line to the low field range. The latter implies the preferable annealing of the paramagnetic defects in the regions of the sample with higher concentration of oxygen. The optically detected magnetic resonance studies show that these defects are not responsible for the luminescence; they are the centers of nonradiative recombination, but the efficiency of photoluminescence quenching due to these defects is rather low.

Keywords: paramagnetic defects, photoluminescence, optically detected magnetic resonance, SiO$_x$ films.

1. Introduction

Observation of visible photoluminescence (PL) in porous silicon [1] has initiated an intense search for silicon-based materials for optoelectronics. Later the similar luminescence was also found in composite materials formed by introducing silicon clusters or nanocrystals into a dielectric SiO$_x$ matrix. These materials are more mechanically and chemically stable as compared with porous silicon, and the processes of their production are compatible with modern silicon technology.

Mechanisms of luminescence in both porous silicon and composite materials are still under the debate. The radiative recombination of confined electron-hole pairs (excitons), luminescence of various surface centers and chemical compounds have been discussed. There is also still a lot of contradiction as to the nonradiative processes in these materials. In [2, 3], porous silicon was studied using the PL and electron paramagnetic resonance (EPR) techniques. The anticorrelation between the intensity of the visible photoluminescence and the amount of the interfacial silicon dangling bond defects, the so-called $P_b$-centers, was observed. These defects were supposed to be the centers of nonradiative recombination in porous silicon. On the other hand, there are experimental data that show the correlation between some other paramagnetic defects and PL intensity (see, e.g. [4]). Thus, the role of paramagnetic defects in the PL of porous silicon is not clear.

This problem was also studied by optically detected magnetic resonance (ODMR) which can give the direct evidence of participation of the centers in radiative or nonradiative processes. In [5], the $P_{60}'$-centers were found to decrease the intensity of the 1.5 eV PL band, but this decrease was fairly small, of the order of $10^{-5}$. On the contrary, the authors of the paper [6] observed the enhancement of the PL intensity in 1.5 eV and the decrease of 1 eV band.

While the paramagnetic centers in porous silicon were widely studied, little is known about the role of paramagnetic centers in the composite materials. In [7], the dominant paramagnetic centers in heat-treated SiO$_x$ were shown to be various silicon dangling bonds. The concentration of these defects correlated with the PL intensity. The $P_{\theta}$-centers related to chaotically oriented Si nanocrystalites in SiO$_2$ were also observed, but no evidence was obtained about the influence of these defects on PL.

In this paper, we study the composites containing amorphous silicon nanoclusters in SiO$_x$ matrix in order to clarify the role of paramagnetic defects in the photoluminescence of these materials.

2. Experimental

SiO$_x$ ($x \approx 1.3$) layers were obtained by thermal evaporation of SiO (Cerac Inc., purity of 99.9 %) in vacuum at the residual pressure of 2·10$^{-3}$ Pa. One-sided polished $n$-Si wafers (2…3 kOhm-cm) were used as the
substrates. The substrate temperature during the deposition was equal to 150 °C. SiO\textsubscript{x} layers were deposited at the rate of 1.6 nm/s, the thickness being monitored \textit{in situ} by the quartz-crystal-oscillator monitor system. After the deposition, it was measured with the MII-4 microinterferometer. We have grown the films of comparatively large thickness, \( d = 1166 \pm 12 \text{ nm} \), in order to get intense EPR signals.

To carry out the thermally stimulated structural transformation of the SiO\textsubscript{x} layers, the samples were annealed at 750 °C in nitrogen atmosphere during 15 min. This treatment is known [7, 8] to cause the formation of amorphous Si nanoclusters in the oxide matrix.

The photoluminescence was measured at room temperature under the excitation with 514.5 nm line of the Ar\textsuperscript{+} ion laser. The spectra were recorded by MDR-23 grating spectrometer with cooled FEU-62 photomultiplier and lock-in registration system.

Raman spectra were measured at room temperature under the excitation with 514.5 nm line of the Ar\textsuperscript{+} ion laser using DFS-24 double grating monochromator with photon counting system for registration.

The EPR spectra were measured using X-band EPR spectrometer with 100 kHz magnetic field modulation at room temperature. The number of paramagnetic defects and \( g \)-factor were determined relatively to the MgO:Mn\textsuperscript{2+} sample. The ODMR investigations were carried out using a modified X-band Bruker spectrometer at liquid helium temperature. The luminescence was excited by the 532 nm line of solid state laser.

3. Results and discussion

Recent investigations [7, 8] of the vacuum-deposited SiO\textsubscript{x} films subjected to thermal treatment demonstrated that the annealing in the temperature range 700...900 °C causes phase separation in the film into SiO\textsubscript{x} phase and amorphous silicon phase. The latter forms clusters of nanoscale sizes in SiO\textsubscript{x} matrix. The resulting composite material exhibits rather intense photoluminescence in the visible and near infrared ranges depending on a thermal treatment.

In the present study, we apply the same treatment to obtain the material with bright photoluminescence in order to ascertain the role of the paramagnetic defects in radiative recombination.

The as-deposited SiO\textsubscript{x} layers exhibit no photoluminescence. After the annealing at 750 °C the wide photoluminescence band appears (Fig. 1). This band lies in the range from 650 to 850 nm. Due to interference in the thick SiO\textsubscript{x} layer the PL intensity is modulated and, hence, it is difficult to estimate the precise PL band peak position. Nevertheless, the comparison of the spectra obtained with the results of [7] shows that this is the typical PL band observed previously in thermally treated SiO\textsubscript{x} layers.
The total EPR signal is the superposition of several EPR lines. The observed 490 cm⁻¹ band corresponds to the scattering by TO phonons in SiOₓ film. The most known among these defects are the statistical distribution of the corresponding defects in the SiOₓ layers and of the SiOₓ layers annealed at 750 ºC.

The behavior of EPR spectrum at the annealing shows that the paramagnetic defects are partly destroyed by the annealing and that those species that are destroyed are characterized by lower g-values. This corresponds to the annealing of the centers in the oxygen-rich regions of the layer, i.e., in SiOₓ with larger x parameter. On the other hand, relative contribution to the total EPR spectrum of the paramagnetic defects with higher g-values increases in the course of annealing. This shows that the thermal stability of defects is higher in those regions of the layer which have lower local concentration of oxygen. The appearance of the PL band correlates with the disappearance of the paramagnetic defects with lower g-factors but can not be ascribed to the defects with higher g-factors.

To check this assumption, we have carried out the ODMR measurements of the annealed samples. The typical ODMR spectra are shown in Fig. 4. The intensity of the spectrum is rather low, therefore it is difficult to carry out thorough analysis of the line shape. Nevertheless, it is seen that the ODMR signal is the superposition of two lines with g-factors close to 2.006 and 2.013. To identify the defects that are related to these signals, one has to compare the ODMR and EPR spectra. For this comparison, we integrated the EPR line shown in Fig. 3 because this EPR spectrum is the derivative of the microwave absorption signal. EPR and ODMR spectra were normalized to the same frequency so that they could be directly compared. The result is shown by the dotted line in Fig. 4. It is seen that this integrated EPR spectrum describes the high-field part of the ODMR spectrum pretty well. Thus, it can be concluded that the defects responsible for the EPR spectrum contribute mainly to this part of the ODMR line. It means that the high-field part of the spectrum results from the silicon dangling bonds. The remaining part of the ODMR spectrum can be rather well described by the Lorentzian with g = 2.013 and linewidth 0.7 mT, where DH₁/₂ is the linewidth at the half of the maximum. The similar signal have been previously observed in the ODMR spectra of porous silicon [6] and EPR spectra of amorphous silicon [9]. There in [9], it has been assigned to a self-trapped hole. It should be noted that this defect is not observed in EPR spectra. In our opinion, it can be explained in two ways. One possible reason is that the concentration of these defects is small, and the sensitivity of the EPR spectrometer is too low to detect...
Photoluminescence quenching is rather low. Recombination, but the efficiency of the centers of nonradiative recombination. The low intensity of the ODMR signal indicates that these centers do not quench the PL effectively. Since the EPR spectra indicate that there is a large amount of defects in the samples that are identified as “a dangling bond in SiOx”, one can conclude that these defects do not efficiently influence the photoluminescence. As to the trapped hole defects, their weak influence on the photoluminescence can be caused simply by a low concentration of these defects in the sample.

It is worth noting that \( P_g \)-like (or \( P_{g0} \)) defects that are, according to [6], the efficient quenching centers of the PL in porous Si are not observed in our samples. Most probably the reason is that the composite films annealed at 750 °C contain nanoclusters of amorphous Si that do not have an abrupt interface crystalline silicon/silicon dioxide which is necessary for the formation of these defects.

4. Conclusion

Complex investigations of SiO\(_x\) films by EPR, ODMR, Raman and photoluminescence spectroscopy are reported. The films were grown by vacuum thermal deposition of SiO\(_x\) and annealed at 750 °C. The annealed samples contain amorphous clusters of silicon and exhibit the wide photoluminescence band in the range 650 to 850 nm. The EPR spectrum of the as-grown films is a wide line with \( g = 2.0040 \). It is interpreted as a superposition of the signals from the dangling silicon bonds Si-SiO\(_{2-x}\). The annealing causes the decrease of the EPR spectrum intensity and the shift to \( g = 2.0058 \) (750 °C). This shift is caused by the preferable annealing of the paramagnetic defects in the regions with the higher concentration of oxygen. The ODMR studies show that these defects are the centers of nonradiative recombination, but the efficiency of the photoluminescence quenching is rather low.

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References