PARAMAGNETIC DEFECTS IN PHOTOLUMINESCENT SiO_x COMPOSITE FILMS WITH SILICON NANOINCLUSIONS

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The SiO_x composite films which contain the nanosize inclusions of amorphous and crystalline silicon have been studied by means of the paramagnetic resonance methods. It is shown that the dominating paramagnetic defects in these materials are the Si dangling bond centers located in various surroundings. A role of these defects in the recombination processes occurring under the optical excitation is specified.

1. Introduction

A number of works devoted to the research of a visible photoluminescence (PL) in the structures which contain nanodimensional inclusions have been recently published. The research interest in this topic is conditioned by the opportunity to create the optoelectronic equipment on the basis of a well-advanced silicon technology. To date, a number of materials which display PL in a visible, mainly red spectral region have been created on the basis of silicon. It is porous silicon [1], nanocrystalline silicon films [2], and SiO_x composite films [3] that belong to such structures among others. In spite of a great deal of the works on this topic, the mechanisms of the visible PL in the materials under consideration remain controversial. Up to now, two types of models have been prevailing: a model of quantum confinement [1] and models which consider the visible PL as originating from the surface of silicon nanoclusters (see, for example, [4—6]). It is the latter models that are concentrated on the studies of the emission of various surface structures such as, for example, siloxen [4], Si=O [6, 7], and various surface defects [5].

However, for the above materials, a role of defects in the processes of carrier recombination is not established exactly. It is shown in a series of works (see, for example, [3,8]) that the most widespread defects are the silicon dangling bond centers located in a silicon matrix, on a silicon surface, or in a silicon oxide matrix. Moreover, it is found that there exists the anticorrelation between the number of P_b-centers (a P_b-center is a silicon dangling bond located at the Si/SiO_2 boundary) determined by means of the electron paramagnetic resonance (EPR) method and the PL intensity [9]. At the same time, it is shown by means of the optically detected magnetic resonance (ODMR) that the P_b-centers are the centers of nonradiative recombination [10]. By contrast, the quantity of shallow donors and defects (E'-center, nonbridging oxygen) in silicon oxide correlates with the PL intensity [5, 8, 11].

It is well known that the as-prepared SiO_x composite films don't display PL. After annealing, two PL bands dependent on the annealing temperature appear with the maxima near 650 and 750 nm, where the latter one is related to the formation of nanosize silicon inclusions in the process of annealing (see, for example, [3]). In this paper, the results of the EPR and ODMR investigations of paramagnetic defects are presented, and their role in the recombination processes of photoexcited carriers is discussed.

2. Materials and Methods

SiO_x films were prepared by the method of thermal evaporation of SiO (SiO, Cerac Inc., 99.9%) in vacuum with a pressure of residual gases $(1 \div 2) \times 10^{-5}$ Torr. Silicon wafers were used as the substrates. During the deposition, the substrate temperature was 150°. The film growth rate equaled 1.6 nm/s. The films with a thickness of (1.16 ± 0.01) μm were used for investigations. To create the nanoinclusions of amorphous and crystalline silicon, the films were annealed in the nitrogen atmosphere for 15 min at temperatures 750 and 1050°, respectively (according to the procedure described in [13]). The Raman spectroscopy was used as a tool indicative of nanoinclusion formation. It is known that the formation of the nanoinclusions of amorphous and crystalline silicon is accompanied by the appearance of

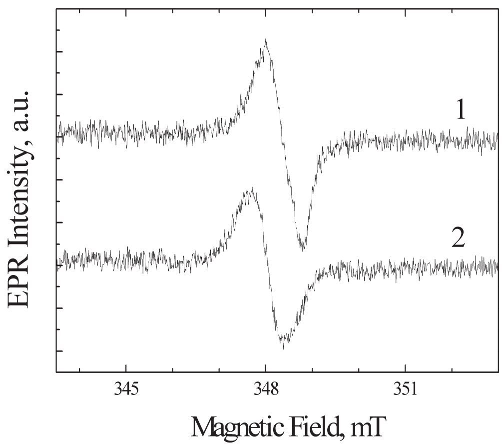

Fig. 1. EPR spectra of the SiO_x composite films annealed at 750 (*1*) and 1050 °C (*2*)

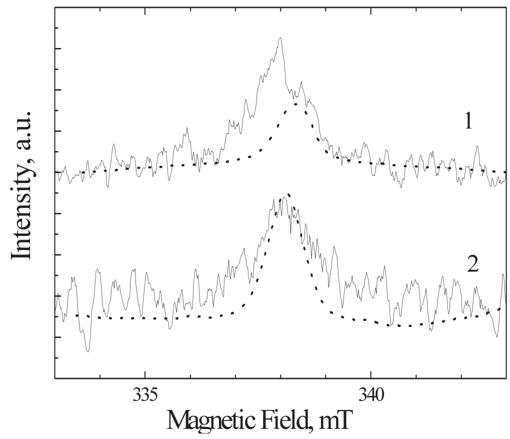

Fig. 2. ODMR spectra (solid lines) and integrated EPR spectra (dotted lines) of the SiO_x composite films annealed at 750 (*1*) and 1050 °C (*2*)

characteristic Raman bands near 490 and 512 cm^{-1}, respectively. Raman and PL spectra were measured at room temperature with the use of a DFS-24 monochromator and FEU-62, respectively. 514.5 nm line of an argon laser was used for excitation.

The EPR spectra were registered at 77 K with the use of a Radiopan SE/X 2547 spectrometer operating in a three-centimeter wavelength range (9.97 GHz). For the measurements, a high-frequency (100 kHz) modulation of magnetic field with an amplitude of 0.1 mT and a non-saturating microwave power (2 mW) were used.

The ODMR spectra were registered at 4.2 K with the use of a modified X-band Bruker ER 200 D spectrometer (an operating frequency — 9.3 GHz). A solid state laser with a wavelength of 532 nm was used as an excitation source. A PL signal was detected with the use of a germanium detector which was cooled by liquid nitrogen. The integral intensity of the PL band with a maximum at 750 nm was detected. The ODMR signal was registered as a change in the PL intensity caused by a spin resonance. The amplitude modulation (2.8 kHz) of a microwave radiation with a typical power of 200 mW was used in the experiments.

3. Results and Discussion

Fig. 1 shows the EPR spectra for the SiO_x composite films containing the nanosize inclusions of amorphous (the specimen annealed at 750°) and crystalline (the specimen annealed at 1050°) silicon. For each of the composites, the EPR spectrum consists of a structureless line which is characterized by $g \approx 2.0050 \pm 0.0005$ for the former composite and by $g \approx 2.0060 \pm 0.0005$ for the latter one.

In the previous studies [3], the EPR spectra of SiO_x composite films were considered as a superposition of the signals originating from the Si dangling bond in $\bullet Si \equiv Si_xO_{3-x}$ tetrahedra with various x values (with various numbers of oxygen in the nearest neighborhood of a Si dangling bond). It was noted that, in this case, the annealings gave rise to a healing of the defects with a higher oxygen content in the nearest neighborhood. It is known that the silicon dangling bond of a $\bullet Si \equiv Si_3$ kind is characterized by $g = 2.0055$, whereas the substitution of silicon atom by oxygen in the nearest neighborhood of the given silicon atom leads to a reduction in the g-factor. It is due to this fact that, after the annealing of SiO_x composite films, a shift of the EPR spectra towards the low magnetic field side (towards the greater g-factors) is observed.

Basing on these facts, it can be assumed that, for the composite containing silicon nanoinclusions, the Si dangling bonds of $\bullet Si \equiv Si_2O$ and $\bullet Si \equiv Si_3$ kinds are the dominant defects. In Fig. 2, the integrated experimental EPR spectra for the composites with silicon inclusions are shown by the dotted lines. The solid lines in this figure reflect the experimental ODMR spectra. Both the EPR and ODMR spectra were normalized to the same microwave frequency, to make their comparison be possible.

The ODMR signal intensity is too small to allow a detailed analysis of its shape. It is seen, however, that the positions of the EPR and ODMR lines are close to one another for the composites with the crystalline silicon nanoinclusions, i.e. for the specimen annealed at 1050°. A somewhat greater width of the ODMR line can be caused, for example, by higher power (by two orders) of microwave field at ODMR measurements, which can lead to the saturation of the magnetic resonance signal and, respectively, to a broadening of the magnetic resonance line.

For the composite containing the inclusions of amorphous silicon (the specimen annealed at 750°), the picture is more complicated. The ODMR spectrum has an asymmetric shape and can be represented as a superposition of two lines. One line with $g \approx 2.005 \pm 0.001$ coincides (within the limits of an experimental error) with the EPR spectrum for a Si dangling bond. Another line can be described with a Lorentzian with $g \approx 2.010 \pm 0.002$ and $\Delta B_{1/2} = (0.70 \pm 0.05)$ mT, where $\Delta B_{1/2}$ is a line halfwidth. A similar signal of the Lorentzian shape with a somewhat greater value of g-factor (≈ 2.013) was observed previously in the ODMR spectra of a porous silicon [10] and in the EPR spectra of an amorphous silicon [13]. It was identified as that originating from self-trapped holes [13]. On the other hand, the total ODMR signal is similar to the EPR signal from the P_{b0}-centers of a powder specimen, but the presence of these interface defects in the given specimen seems to be unlikely, as the Si/SiO_2 boundary is unlikely sharp.

It should be noted that, for the specimen annealed at 750°, the defects that give a low-field contribution to the ODMR signal don't contribute to the EPR spectra. In our opinion, this can be caused by several reasons. First, it is possible that the concentration of these defects is too small for a signal to be detected by an EPR spectrometer. Their greater contribution to the ODMR spectra, in comparison with the signal from the Si dangling bond, can result from their greater efficiency in the recombination processes inducing the PL which was used for the ODMR registration. Another reason can lie in the fact that this signal originates from a shallow level which is ionized at 77 K, i.e. at the temperature, at which the EPR spectra were registered.

Additional measurements showed that all the ODMR signals registered were negative, i.e., under the conditions of paramagnetic resonance, a decrease in the PL intensity occurred. As follows from the examination of all the ODMR mechanisms described in the literature (see, for example, [13—15]), the above situation becomes most likely when the magnetic resonance originates from the luminescence quenching centers, similarly to the situation occurring in porous silicon [10].

4. Conclusions

The complex investigations of the EPR and ODMR spectra of the SiO_x composite films containing the nanosize inclusions of amorphous and crystalline silicon have shown that paramagnetic defects in these films play the role of the luminescence quenching centers. For the films annealed at the temperatures that ensure the crystallization of silicon inclusions (1050°), it is the Si dangling bond of $\bullet Si\equiv Si_2O$ and $\bullet Si\equiv Si_3$ kinds that predominantly serve as the paramagnetic centers of luminescence quenching. For the films annealed at lower temperatures (750°), in which the silicon inclusions are in the amorphous state, other centers with close values of the g-factor are observed in addition to the above centers of nonradiative recombination.

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ПАРАМАГНІТНІ ДЕФЕКТИ В ФОТОЛЮМІНЕСЦЕНТНИХ КОМПОЗИТНИХ ПЛІВКАХ SiO_x З КРЕМНІЄВИМИ НАНОВКЛЮЧЕННЯМИ

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Р е з ю м е

Методами парамагнітного резонансу досліджено композитні плівки SiO_x, що містять нанорозмірні включення аморфного та кристалічного кремнію. Виявлено, що домінуючими парамагнітними дефектами в таких матеріалах є обірвані зв'язки кремнію з різним оточенням. Встановлено роль цих дефектів у процесах рекомбінації носіїв при оптичному збудженні.