*Semiconductor Physics, Quantum Electronics & Optoelectronics. 2004. V. 7, N 4. P. 400-403.*

PACS: 76.70.Hb, 78.55.Hx, 78.66.Sq

# Paramagnetic defects related to photoluminescence in $SiO_x$ films

**G.Yu. Rudko, I.P. Vorona, I.Z. Indutnyy, S.S. Ishchenko, P.E. Shepeliavyi, V.O. Yukhymchuk**

*V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, 41, prospect Nauky, 03028 Kyiv, Ukraine*
*Phone: (38 044) 525-63-42; Fax: (38 044) 525-83-42*
*E-mail: g_rudko@yahoo.com*

**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 $\bullet Si \equiv Si_yO_{3-y}$. The annealing at 750 ºC causes the formation of amorphous silicon inclusions in $SiO_x$ matrix, appearance of the photoluminescence peaked at ~ 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.

Manuscript received 10.09.04; accepted for publication 16.12.04.

## 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 anticorrellation 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 $P_{b0}$-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 $P_b$-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 $2 \cdot 10^{-3}$ 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 ºC. $SiO_x$ layers were deposited at the rate of 1.6 nm/s, the thickness being monitored *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, $d = 1166 \pm 12$ nm, in order to get intense EPR signals.

To carry out the thermally stimulated structural transformation of the $SiO_x$ layers, the samples were annealed at 750 ºC 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 $Ar^+$ 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 $Ar^+$ 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 $MgO:Mn^{2+}$ 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 $SiO_x$ films subjected to thermal treatment demonstrated that the annealing in the temperature range 700…900 ºC causes phase separation in the film into $SiO_x$ phase and amorphous silicon phase. The latter forms clusters of nanoscale sizes in $SiO_x$ 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 $SiO_x$ layers exhibit no photoluminescence. After the annealing at 750 ºC the wide photoluminescence band appears (Fig. 1). This band lies in the range from 650 to 850 nm. Due to interference in the thick $SiO_x$ 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 $SiO_x$ layers.

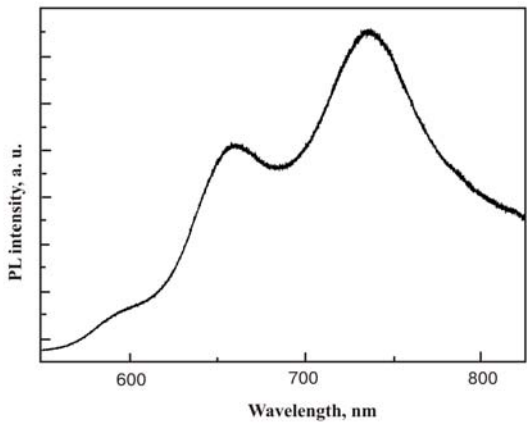


**Fig. 1.** Photoluminescence spectrum of the $SiO_x$ film annealed at 750 ºC.

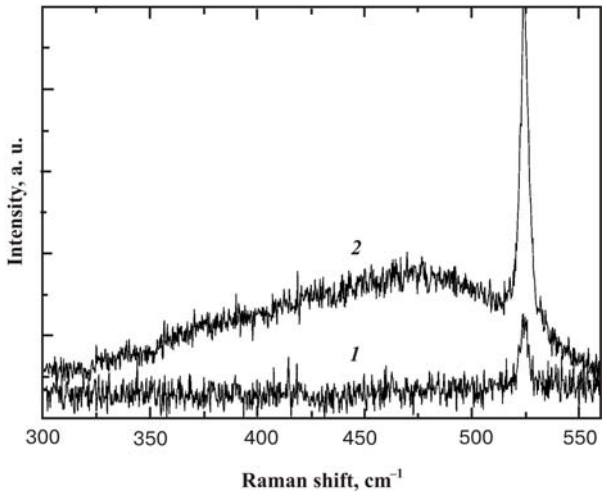


**Fig. 2.** Raman spectra of the as-deposited (1) and annealed at 750 ºC (2) $SiO_x$ films.

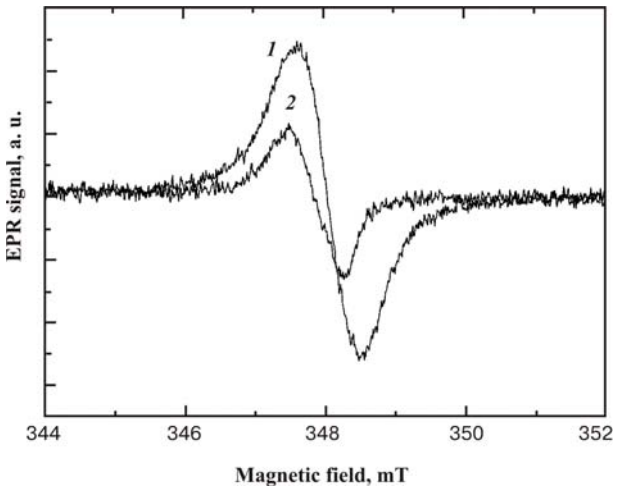


**Fig. 3.** EPR spectra of the as-deposited (1) and annealed at 750 ºC (2) $SiO_x$ films.

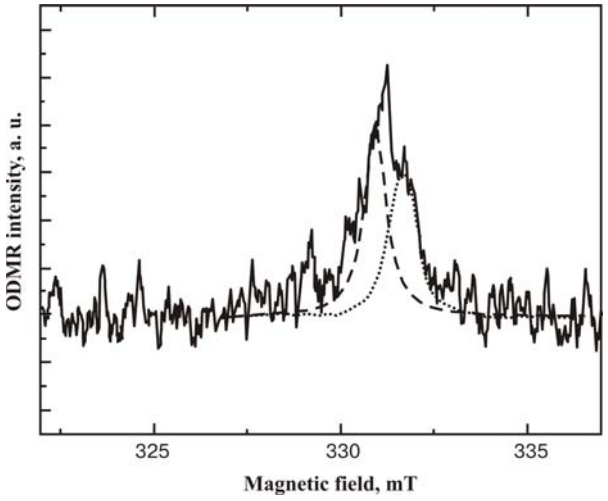


**Fig. 4.** ODMR spectrum of the $SiO_x$ film annealed at 750 ºC (solid curve), integrated EPR spectrum (see curve 2, Fig. 3) and the Lorentzian with $g \sim 2.013$ and linewidth 0.7 mT (dashed curve).

Fig. 2 shows the Raman spectra of the as-deposited $SiO_x$ film and the film annealed at 750 ºC. The intense line at 521 $cm^{-1}$ corresponds to the signal from the silicon substrate. After annealing, the wide structureless band at 490 $cm^{-1}$ appears in the Raman spectrum. This band corresponds to the scattering by TO phonons in amorphous silicon. Thus, the observation of 490 $cm^{-1}$ band evidences the presence of the amorphous silicon clusters in the sample.

Fig. 3 shows the EPR spectra of the as-deposited $SiO_x$ layers and of the $SiO_x$ layers annealed at 750 ºC. The spectrum of the as-deposited film is the wide featureless line with *g*-factor equal to 2.0040. The annealing at $T = 750$ ºC causes the decrease of the signal intensity and the shift of the spectrum to the range of lower field values. The *g*-factor of the latter spectrum is equal to $g = 2.0058$.

The shift of the EPR spectrum after the annealing can be explained assuming that the EPR signal of the as-grown film is the superposition of several EPR lines that are related to different paramagnetic defects. We suppose that this spectrum can be identified with the dangling bonds of silicon in the tetrahedrons $Si–Si_yO_{4–y}$ ($0 \le y \le 4$). These dangling bonds can be described as $\bullet Si \equiv Si_yO_{3–y}$ where the symbol • denotes the unpaired electron. The total EPR signal is the superposition of several individual components corresponding to the silicon dangling bonds surrounded by different nearest neigbours (with different *y* values: $\bullet Si \equiv O_3$, $\bullet Si \equiv SiO_2$, $\bullet Si \equiv Si_2O$ и $\bullet Si \equiv Si_3$). These individual components are characterized by different *g*-factor values, and their contribution to the intergated EPR spectrum reflects statistical distribution of the corresponding defects in the $SiO_x$ film. The most known among these defects are the dangling bonds of silicon in silicon ($\bullet Si \equiv Si_3$) and of silicon in quartz ($\bullet Si \equiv O_3$) with *g*-factors equal to 2.0055 and 2.0005, respectively.

Thus, it can be supposed that the EPR line of $SiO_x$ is a superposition of the signals from silicon dangling bonds surrounded by various kinds of nonstoichiometric silicon suboxide clusters. The highly-oxydized clusters give the high-field EPR lines, while the clusters with smaller content of oxygen contribute the low-field components to the total EPR signal. The overlap of all these signals forms the wide line with an averaged *g*-factor that is measured experimentally.

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 $SiO_x$ 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 $g \sim 2.013$ and $\Delta H_{1/2} = 0.7$ mT, where $\Delta H_{1/2}$ 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

them. The fact that the intensity of the ODMR line of these defects is larger than the intensity of the dangling bond line can be caused by a higher efficiency of the former centers in the PL-related recombination processes. Another way to explain why the $g = 2.013$ defect is seen in ODMR and not seen in EPR spectra is the optical excitation of the sample during the ODMR experiments. The incident light generates free electrons and holes that can be trapped and can form new paramagnetic centers. Thus, without the illumination these defects cannot be seen by the EPR method.

Additional measurements have shown that this ODMR signal has the negative sign. It means that the ODMR signal plotted in Fig. 4 corresponds to the decrease of the PL intensity under spin resonance conditions. Thus, the both types of paramagnetic centers that cause the ODMR are 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 $SiO_x$", 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 $P_b$-like (or $P_{b0}$) 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 ºC 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 ºC. 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 $\bullet Si\text{-}Si_yO_{3-y}$. The annealing causes the decrease of the EPR spectrum intensity and the shift to $g = 2.0058$ (750 ºC). 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.

**Acknowledgments**

The authors are grateful to Prof. W.M. Chen and Prof. I.A. Buyanova for the possibility to carry out the ODMR experiments.

This study was funded by the Programs of the National Academy of Sciences of Ukraine "Optical and spectroscopic investigations of semiconductors and semiconductor structures" and "Magnetic resonance and optical study of defects in semiconductors and dielectrics".

*References*

1. L.T. Canham, Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers // *Appl. Phys. Lett.* **57** (10), p. 1046-1048 (1990).
2. D. Goguenheim, M. Lannoo, Theoretical calculation of the electron-capture cross-section due to a dangling bond at Si <111>-$SiO_2$ interface // *Phys. Rev. B* **44** (4) p.1724-1733 (1991).
3. H.J. von Bardeleben, M. Chamarro, A. Grosman, V. Marazzani, C. Ortega, J. Seika, S. Rigo, $P_b$-defects and visible photoluminescence in porous silicon *// J. Lumin.* **57**, p. 39-43 (1993).
4. S.M. Prokes, W.E. Carlos, Oxygen defect center red room temperature photoluminescence from freshlyetched and oxydized porous silicon // *J. Appl. Phys.* **78** (4), p. 2671-2674 (1995).
5. M.S. Brandt, M. Stutzmann, Spin-dependent effects in porous silicon // *Appl. Phys. Lett.* **61** (21) p. 2565-2571(1992).
6. B.K. Mayer, D.M.Hofman, W. Stadler, V. Petrova-Koch, F. Koch, P. Omling, P. Emanuelson, Defects in porous silicon investigated by optically detected and by electron paramagnetic resonance techniques // *Ibid.* **63** (15) p. 2120-2122 (1993).
7. V.Ya. Bratus', V.A. Yukhimchuk, L.I. Berezhinski, M.Ya. Valakh, I.P. Vorona, I.Z. Indutnyi, T.T. Petrenko, P.E. Shepelyavyj, I.B. Yanchuk, Structural transformations and silicon nanocrystallite formation in $SiO_x$ films // *Semiconductors* **35** (7), p. 821-826 (2001).
8. I.P. Lisovskyy, I.Z. Indutnyy, B.N. Gnennyy, P.M. Lytvyn, D.O. Mazunov, A.C. Oberemok, N.V. Sopinskyy, P.E. Shepeliavyi, Structural-phase transformations in the $SiO_x$ films in the course of vacuum heat treatment // *Ibid.* **37** (1), p. 97-102 (2003).
9. R.A. Street, Localized states in doped amorphous silicon // *J. Non-Cryst. Solids* **77-78**, Part 1, p. 1-16 (1985).