

INFRA-RED SPECTROSCOPY OF A BARRIER PHASE OF PHOTOLUMINESCENT NANOCOMPOSITE Si/SiO_x FILMS

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Infra-red (IR) transmission spectra of Si/SiO_x nanocomposite films obtained by a pulsed laser deposition have been measured, and the shapes of lines that correspond to stretching vibrations of bridging oxygen have been analyzed. The content of Si—O_y—Si_{4-y} (1 ≤ y ≤ 4) molecular complexes in the structural network of SiO_x films has been determined versus their formation conditions. The correlation between photoluminescent properties of the films and the composition and the structure of the barrier phase is reported.

pulsed laser deposition (PLD). This is necessary both for the confirmation of the proposed PL model and the optimization of the formation conditions of PL Si/SiO_x films [3 — 5].

1. Introduction

Nowadays, the photoluminescence (PL) nature of many nanocomposite Si/SiO_x structures in the range 1.2—3.2 eV at room temperature is usually related to the quantum confinement effect and to the formation of a potential well for charge carries and excitons. Such a well is formed by Si nanocrystals (nc-Si) with dimensions 1—5 nm with the SiO_x (x → 2) barrier phase that provides a high (above a quantization level) potential barrier and a low permittivity ε. The exciton concentration in the well increases with the binding exciton energy, which increases in turn with the rise of a potential barrier and with a decrease of permittivity ε of the barrier phase. Therefore, the PL intensity related to the radiative exciton annihilation in a potential well depends on the composition, structure of the SiO_x barrier phase, its porosity, etc. Among other optical methods, namely IR transmission is successfully used to analyze the SiO_x composition. In works [1,2], the approach was proposed to the analysis of the Gaussian line deconvolution of the main absorption band of SiO_x within the random bond model, which allows the determination of the content of Si—O_y—Si_{4-y} (1 ≤ y ≤ 4) complexes in the SiO_x phase.

The goal of this work was to determine the composition and the structure of the SiO_x barrier phase of PL NC Si films using the above-mentioned approach in the analysis of IR spectra and to determine how the SiO_x phase structure and the efficiency of visible PL are related to the formation conditions of films during the

2. Experimental Technique

Nanocomposite films of Si/SiO_x were obtained by the PLD method using a vacuum chamber and a Si monocrystal target that was illuminated by a YAG:Nd³⁺ laser beam at a wavelength of 1.06 μm, which was operating in a modulated quality mode with a pulse energy ≈0.2 J, pulse duration of 10 ns, and repetition rate of 25 Hz [3—5]. The deposition was carried out on c-Si substrates. The films of type I were obtained by the deposition of a direct flux of high-energy particles from the erosion jet on the substrate placed at a distance of 20 mm along a normal to the target, in the atmosphere of a residual gas of a vacuum chamber (10⁻⁴ Pa) with addition of oxygen at pressure P: 0, 6.5, and 16 Pa (for samples 1, 2 and 3, respectively). The films of type II were deposited from a backward flux of low-energy particles of the erosion jet on the substrate placed in the target plane in the inertial gas (argon) atmosphere at a pressure of 13 Pa (samples N 4). Some films of type II during the deposition process were doped with gold (samples N 5). It was assumed that gold atoms act as a catalyst and help the formation of the SiO₂ phase in place of the SiO_x phase. The thickness of films was within the range 50—500 nm.

Time-resolved PL spectra were measured in the energy range 1.4—3.2 eV at room temperature. PL was excited by a nitrogen laser with a wavelength of 337 nm and a pulse duration of 8 ns. The stroboscopic signal registration was carried out in the photon counting mode.

IR transmission spectra were measured in the range 800—1350 cm⁻¹ using an automatic spectrometer IRS-25M. As a reference sample, a silicon substrate without

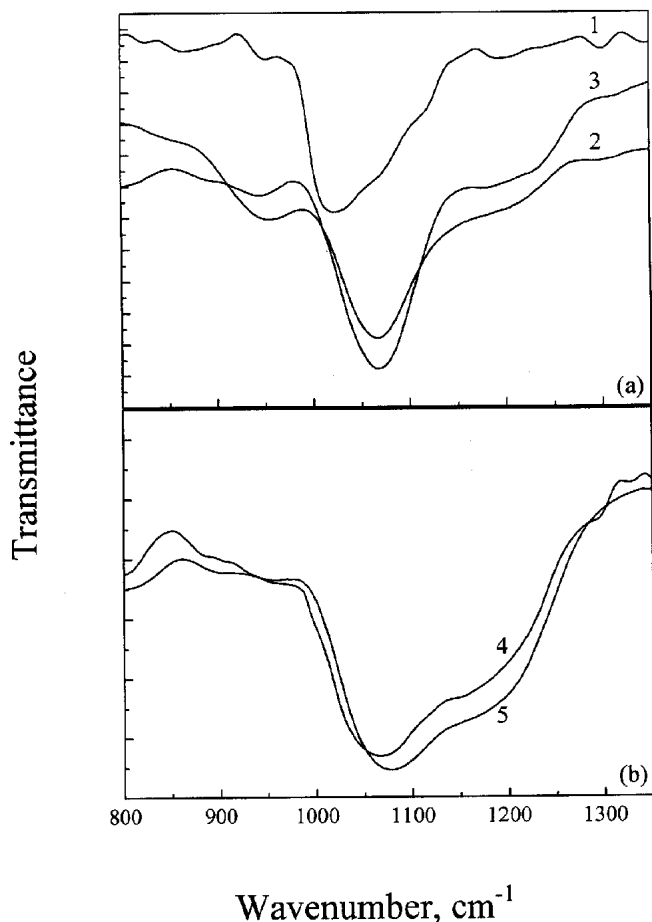


Fig. 1. IR transmission spectra of nanocomposite Si/SiO_x films: *a* – type I, *b* – type II. Numbering of curves is the same as numbering of samples

an oxide film was employed. It is known that, in this spectral range, there is an absorption band of antisymmetric stretching vibrations of bridged oxygen atoms. The maximum of this band ν_{\max} is located approximately within 1000–1100 cm⁻¹, depending on the composition and the structure of the silicon-oxygen phase. This band was decomposed into Gaussian lines, whose characteristics (the peak positions and the intensities) were analyzed using the model of random bonds. For the non-stoichiometric silicon-oxygen SiO_x phase, the goal of this analysis was to determine the content of Si–O_y–Si_{4–y} ($1 \leq y \leq 4$) molecular complexes, and, for the stoichiometric SiO_x phase, we tried to determine the configuration of SiO₄ tetrahedron rings. The reliability of the mathematical deconvolution of spectral bands is a serious issue. This problem was studied before by different authors, including us, for the films of thermic silicon dioxide [6,7] and for the

films of non-stoichiometric silicon oxides obtained by thermic SiO spraying [8, 9] or by the CVD-method [1, 2]. As a criterium of the deconvolution uniqueness in the above-cited works, the Alentsev–Fock approach [10] was used that allowed quite a good consistency of main characteristics of elementary components, which demonstrates a reliability of the obtained deconvolution results. Thus, in this work, the mathematical treatment of the absorption spectra was carried out with the use of the obtained earlier parameters of Gaussian (peak positions and half-width of lines), and these parameters were corrected for each sample. The deconvolution accuracy was estimated by the mean square deviation of the sum of Gaussians from the experimental spectrum. In our experiments, this deviation did not exceed 10⁻².

3. Results and Discussion

Fig. 1,*a* shows the transmission spectra of the films of type I obtained from the direct particle flux of the erosion jet at various oxygen pressures P . It can be seen that the shape and the position of the transmission band strongly depend on pressure P . In particular, the value of ν_{\max} changes from ~ 1021 cm⁻¹ (sample N 1) to ~ 1070 cm⁻¹ (sample N 3). For sample N 1, the absorption occurs in quite a narrow spectral range (1000 – 1150 cm⁻¹), while the spectra reveal a high-frequency tail for samples obtained at higher P , which indicates the presence of a longitudinal vibration mode of the Si–O bond. These characteristic features allow us to make conclusion that, at low pressures, we obtain SiO_x films with the low oxygen content, while, at higher P , we obtain films that are close by content to silicon dioxide. The oxygen content in the samples can be evaluated by using the known function ν_{\max} for films obtained by thermic spraying on silicon monoxide [11]. These estimates give the following results: $x \sim 1.2$ (sample N 1) and ~ 1.8 (samples N 2 and N 3). The increase of the oxygen content with pressure observed in the films seems quite natural and indicates that, at high P , the silicon particles sprayed from a target undergo strong oxygenation.

Fig. 1,*b* shows the transmission spectra of the films of type II obtained from a backward flux of particles of the erosion jet. It can be seen that although the shapes of the absorption bands are similar for two samples, the values of ν_{\max} are quite different, namely, 1066 cm⁻¹ (sample N 4) and 1078 cm⁻¹ (sample N 5). These facts indicate that both films have the SiO_x composition, but the doping with gold helps the formation, at equal other conditions, of

silicon oxygen films of the almost stoichiometric composition. Indeed, the estimate of the oxygen content in these samples gives the values $x \sim 1.8$ and 2 for samples N 4 and N 5, respectively.

The data on the structure of SiO_x films can be obtained from the deconvolution of the main absorption band. The example of such a deconvolution is presented in Fig. 2, and the parameters of elementary lines are given in the table. It should be noted that the deconvolution results were almost the same for both the model of a uniform SiO_x phase and the model of a mixture of the SiO_x and SiO_2 phases. For films of type I, the main band is composed of 4–6 profiles corresponding to shear and longitudinal stretching vibrations of bridging oxygen in $\text{Si}-\text{O}_y-\text{Si}_{4-y}$ complexes. With increase in the oxygen concentration in a vacuum chamber, the share of vibrations corresponding to the bridging oxygen in $\text{Si}-\text{O}_3-\text{Si}$ and $\text{Si}-\text{O}_4$ complexes also increases. In these films, $\text{Si}-\text{O}-\text{Si}_3$ complexes disappear, and the share of $\text{Si}-\text{O}_2-\text{Si}_2$ complexes essentially decreases.

For the films of type II doped with gold, a characteristic feature is a noticeable increase of the content of vibrations related to the bridging oxygen incorporated in $\text{Si}-\text{O}_4$ complexes. On the basis of a significant increase of the share of the 1094-cm^{-1} band, we can conclude that the dominant share in the SiO_2 phase in these films is created by 6-fold rings of $\text{Si}-\text{O}_4$ tetrahedra, which should relax mechanical stresses and reduce the number of electrically active defects [12].

The shape of absorption bands of the films of type I is essentially different from that of the films of type II. In the latter case, the high-frequency tail is more pronounced (Fig. 1, *a, b*). This fact deserves a more detailed discussion. At present, the high-frequency tail of the absorption band related to stretching vibrations of oxygen atoms in $\text{Si}-\text{O}-\text{Si}$ “molecules” is usually attributed to a longitudinal mode of optical phonons in films of the silicon-oxygen phase [6, 13, 14]. However,

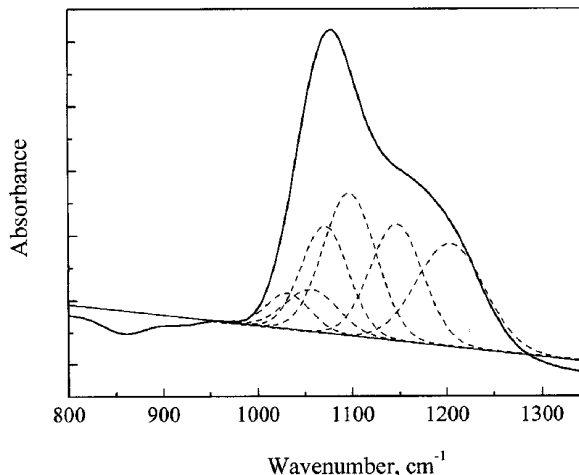


Fig. 2. Example of the optical density spectrum deconvolution into Gaussian profiles for sample N 5

such phonons appear in the film-substrate system only in the case where the electric field vector of a light wave has a component normal to the film plane [15]. That is, the ray should be directed at an angle to the film. In our experiments, the spectra were measured at the normal incidence of light onto samples. Therefore, the appearance of longitudinal phonons can be explained by light scattering by various inhomogeneities of the film, in particular, by pores.

Earlier investigations of a surface morphology of films with the use of atomic-force microscopy (AFM) revealed its dependence on deposition conditions [3]. The surfaces were found to present nanograin complexes which were strongly inhomogeneous for the films of type I and were composed from clusters of lateral dimensions of 100–300 nm and with a broad dispersion in height, spreading from 1.5 to 13 nm. The films of type II were characterized by a more homogeneous surface and smaller average grain sizes, but these films also revealed

Parameters of elementary lines of IR absorption of the SiO_x barrier phase of Si/SiO_x films

Line	Maximum position, cm^{-1}	Half width, cm^{-1}	Vibrational mode	Structural component	Content of structural component, %				
					Samples N				
					1	2	3	4	5
1	1005 ± 2	48 ± 2	TO	$\text{Si}-\text{O}-\text{Si}_3$	23	—	—	—	—
2	1033 ± 3	44 ± 3	TO	$\text{Si}-\text{O}_2-\text{Si}_2$	40	6	11	11	5
3	1053 ± 3	55 ± 2	TO	$\text{Si}-\text{O}_4^*$	—	14	14	6	8
4	1067 ± 2	50 ± 2	TO	$\text{Si}-\text{O}_3-\text{Si}$	20	40	39	26	21
5	1094 ± 3	54 ± 2	TO	$\text{Si}-\text{O}_4^{**}$	17	17	10	19	29
6	1145 ± 3	55 ± 2	TO	Linear fragment $\text{Si}-\text{O}-\text{Si}$	—	9	13	19	21
7	1200 ± 3	62 ± 3	LO	$\text{Si}-\text{O}_2-\text{Si}_2$	—	14	13	19	16

Note. * — 4-fold rings; ** — 4- and/or 6-fold rings of SiO_4 tetrahedra of the SiO_2 phase.

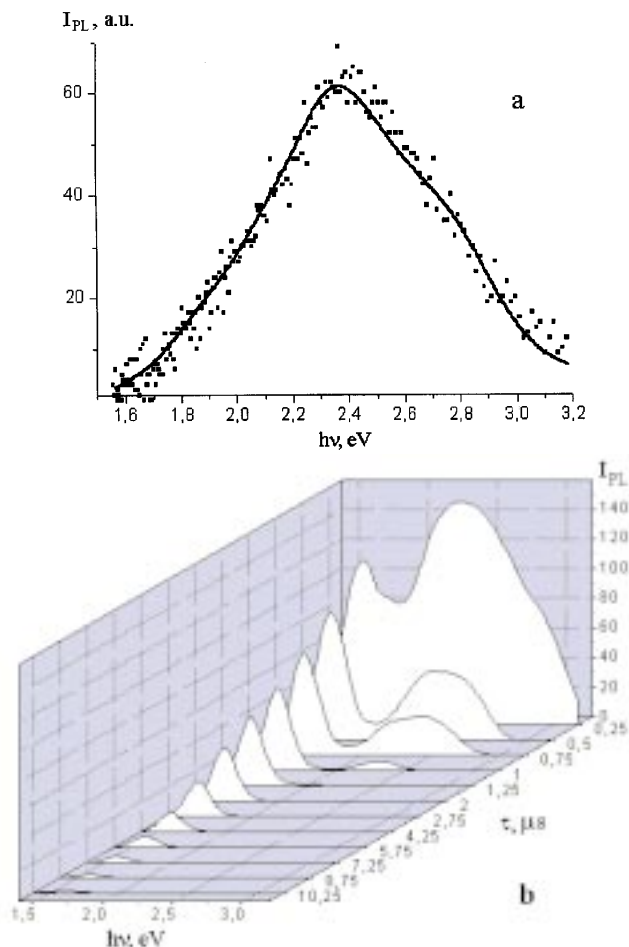


Fig. 3. Time-resolved PL spectra of nanocomposite Si/SiO_x films: *a* – type I, samples N 2; *b* – type II (samples N 5)

pores. The films of type II doped with gold had the bigger grains at the surface, but the film roughness was the same. Taking into account the results of the AFM study of the film structures, the appearance of longitudinal phonons in the IR transmission spectra for the films of type I can be related to a wider dispersion of grain sizes and to the grain clusterization, while to the presence of pores for the films of type II.

The results of the band deconvolution correlate with a shift of the total absorption band to the high-frequency region, which can be observed in Fig. 1, *a, b* by comparing the data for all samples.

Among films deposited from a direct flux of particles of the erosion jet, only samples N 2 obtained at the optimal oxygen pressure $P=6.5$ Pa revealed visible PL. The PL spectrum of samples N 2 was located in the energy range 1.4–3.0 eV, and PL relaxation times were less than 50 ns (Fig. 3, *a*). All films of type II deposited from the backward flux of particles of the erosion jet

also revealed visible PL. The spectrum of samples N 4 (non-doped) was in fact the same as that of samples N 2. At the same time, in samples N 5 (doped with gold), the PL intensity strongly increased, and the relaxation times increased by three orders of magnitude and reached tens of microseconds. These samples also exhibited a low-energy band at 1.6 eV (Fig. 3, *b*) [4, 5].

Thus, it is shown that the increase of the PL intensity and the relaxation time and also the PL red shift correlate with the composition change of the barrier SiO_x phase from the weakly oxygenated molecular silicon-oxygen complexes to the strongly oxygenated ones. The strongest PL is observed in the films doped with gold, in which the barrier layer has almost stoichiometric composition with a dominated content of 6-fold rings of SiO₄ tetrahedra, which provides the highest potential nc-Si/SiO₂ barrier and, in addition, strongly decreases the concentration of electroactive defects related to non-radiative recombination.

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ІЧ-СПЕКТРОСКОПІЯ БАР'ЄРНОЇ
ФАЗИ ФОТОЛЮМІНЕСЦЕНТНИХ
НАНОКОМПОЗИТНИХ ПЛІВОК Si/SiO_x

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Резюме

Проведено вимірювання ІЧ-спектрів пропускання та проаналізовано форми смуг, які відповідають валентним коли-

ванням місткового кисню в нанокompозитних плівках Si/SiO_x, одержаних імпульсним лазерним осадженням. Визначено вміст молекулярних комплексів Si—O_y—Si_{4-y} ($1 \leq y \leq 4$) в структурній сітці SiO_x-плівок в залежності від умов їх формування. Спостерігається кореляція фотолюмінесцентних властивостей плівок та складу і структури їх бар'єрної фази.