STRUCTURAL COMPOSITION OF A SILICON-OXYGEN INTERLAYER IN PHOTOLUMINESCENT Al_2O_3 FILMS WITH Si NANOCRYSTALS

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Photoluminescent Al_2O_3 films with Si quantum dots were obtained by the method of pulsed laser deposition. The silicon-to-aluminum ratio in the target was varied. The photoluminescence spectra in the range 1.4–3.2 eV and the infrared absorption ones in the range 850–1400 cm^{-1} were measured. For all specimens, the infrared band associated with the absorption by Si–O bonds was observed, which testified to a presence of an intermediate silicon-oxygen phase at the Si nanocrystal–Al_2O_3 interface. Molecular complexes Si–O_y–Si_{4-y} ($1 \leq y \leq 4$) were analyzed in the framework of the random bond model. Interrelations among the target composition, the structural composition of silicon-oxygen interlayer, and the photoluminescence properties of the films were determined.

1. Introduction

Researches of photoluminescent films with silicon quantum dots (QDs) are intensively carried out now. Such an activity is associated with the development of our understanding of quantum dimensional effects in those films, the development of their formation technology, and still existing difficulties of the aimed control of their properties. Recently, a tendency to substitute the conventional silicon oxide matrix that contains Si for aluminum oxide has been observed [1–3]. Since Al_2O_3 is characterized by a higher value of the dielectric permittivity in comparison with SiO_2, the quantum-mechanical confinement of charge carriers in Si nanocrystals is reached at smaller dimensions of the barrier layer, which allows one to increase the concentration of Si QDs. The Al_2O_3 matrix also possesses higher stability and higher heat conductivity. These facts are associated with a reduction of photoluminescence instability in and a possibility for higher currents to pass through instrument structures that are constructed on the basis of those systems.

If an Al_2O_3 matrix is used, there emerges a silicon oxide interlayer with a complicated structure at its interface with Si nanocrystals. The composition of this interlayer is responsible for the dielectric permittivity, the energy gap width, and other parameters of the barrier layer in Si QDs, which govern the energy states of the system and, respectively, the photoluminescent properties of the films. The structural state of this interlayer is poorly studied.

The aim of this work is to produce photoluminescent films, which contain Si QDs in an Al_2O_3 matrix, making use of the pulsed laser deposition method, and to carry out infrared (IR) spectroscopy studies of the variations in the structural composition of the silicon oxide interlayer connected with the fraction of aluminum in the Si target.

2. Experimental technique

Photoluminescent films with Si QDs were formed by depositing aluminum and silicon oxides, as well as Si nanocrystals, onto a silicon substrate polished from both sides [3]. A wafer of single-crystalline silicon was used as a target, with some part of its surface being covered with an aluminum film. The aluminum fraction on the target surface, K, was changed within the range from 0 to 1. The substrate was arranged in the target plane. The film was deposited using particles obtained from the

inverse low-energy flux of an erosive torch in an argon atmosphere of 10–15 Pa. The target was scanned by a beam of IAG:Nd^{3+} laser (the wavelength was 1.06 μm, the pulse energy 0.2 J, the pulse duration 10 ns, and the pulse frequency 25 Hz), which operated in the Q-switched mode. The time of film deposition was about 60 min. The film thickness, which was measured with the help of a Dektak 3030 profilometer, ranged from 1.5 to 2.5 μm.

Photoluminescence spectra with time resolution were measured in the energy range 1.4–3.2 eV. They were excited by nitrogen laser irradiation with a wavelength of 337 nm and a pulse duration of 8 ns. The signal was stroboscopically registered in the photon count mode. The strobe width was 250 ns. By our estimates, the accuracy of measurements of the photoluminescence spectra presented below is equal to several per cent, which is sufficient to analyze the nature of photoluminescence. Such an accuracy is determined, first, by positioning the wavelength of a monochromator and equals 1-2 nm. Second, the photoluminescence intensity given in arbitrary units is obtained by the comparison of the photoluminescences from experimental specimens and the control one. In this case, the relative error of measurements was at most 5%. Such an accuracy was attained due to the procedure of measurement of the photoluminescence spectra in the photon counting mode. The stability of photoluminescence was estimated by a change in its intensity during the storage of specimens in air, as well as under the action of the emission of a nitrogen laser on them.

The IR transmission spectra were measured with the help of an IKS-25M automated spectrometer in the wave number range 850–1400 cm^{-1}, where the main absorption band of silicon oxide is located. The film spectra were determined relatively to the silicon substrate. The results of optical density measurements were corrected taking the film thickness into account. In the measurement of the spectra, the absolute error of a spectrometer was at most ±0,5%. The main absorption band, associated with absorption by valence vibrations of bridge oxygen atoms in an oscillating Si–O–Si molecule, was deconvoluted into Gaussian components. The positions, half-widths, and areas of the peaks were used to estimate the structural state of oxygen, i.e. the kind and the relative content of molecular complexes $Si–O_y–Si_{4-y}$ $(1 \le y \le 4)$, in the framework of the random bond model and according to the known approach [4, 5]. The results obtained allowed us to draw a conclusion on the variations of both the silicon oxide composition and the structural state of oxygen in it, which depend on the aluminum content in the target.

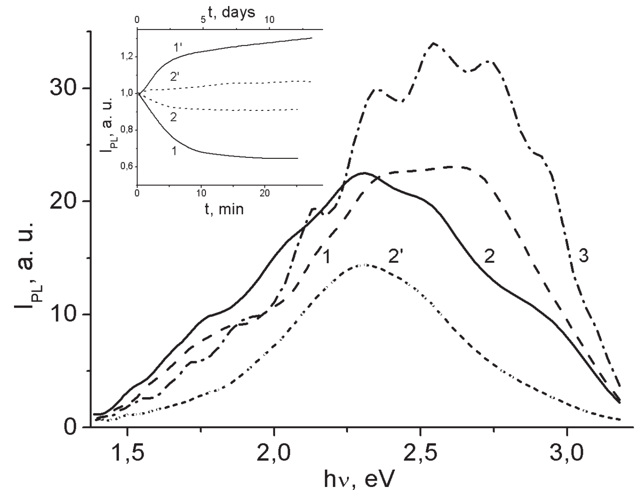

Fig. 1. Photoluminescence spectra of the films obtained without introducing Al into the target: as-deposited (*2*) and held in air (*2′*), and with introducing Al to the fraction $K = 0.2$ (*3*) and 1 (*1*). The inset illustrates the instability of photoluminescence intensity of the films obtained with introducing Al into the target ($K = 0.2$, dotted curves) and without it (solid curves): the films were held in air (curves *2′* and *1′*) or irradiated by an N_2-laser (curves *2* and *1*). The photoluminescence relaxation time $t < 250$ ns (curves *1–3*) and 250 ns $< \tau <$ 500 ns (curve *2′*)

3. Results and Their Discussion

3.1. Photoluminescence spectra

The film photoluminescence spectra fall within the energy interval 1.4–3.2 eV. They are wide, multimode, and contain several bands. As a rule, the band maxima in the spectra lie in the range 2.2–2.4 eV for films that do not contain the Al_2O_3 phase, and in the range 2.3–2.7 eV for Al_2O_3 films. In Fig. 1, the film photoluminescence spectra registered for an Al (curves *1* and *1′*) and a Si (curves *2* and *2′*) target, and a target that contains both Si and Al (curve 3) are depicted. The relaxation time for as-deposited films of the system nanocrystalline Si/SiO_x was shorter than 250 ns. If such films were held in air for several hours, not only the first strobe was filled, but also the second one became well pronounced (curve *2′*), i.e. the relaxation times became four times longer; the photoluminescence intensity also grew (the inset in Fig. 1, curve *1′*). Since the films are porous, diffusion of air oxygen promotes additional oxidation of the SiO_x phase formed in the torch, thus passivating broken bonds of silicon both at the nanocrystalline Si/SiO_x interface

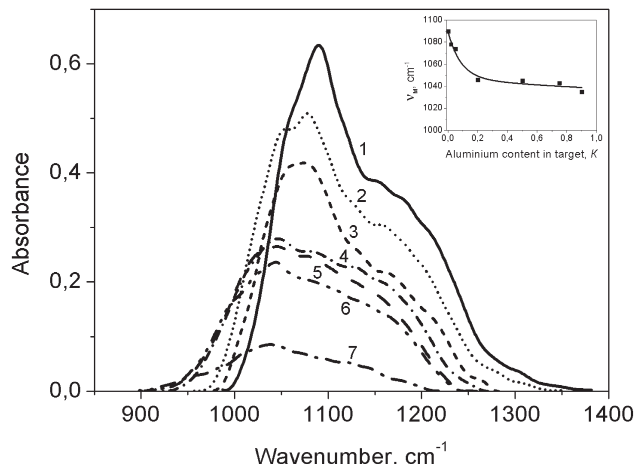

Fig. 2. Optical density spectra of films with various contents of aluminum in the target $K = 0$, 0.02, 0.05, 0.2, 0.5, 0.75, and 0.9 (curves 1 to 7, respectively). The insert shows the position of the absorption band maximum versus the Al content in the target K

and in the SiO_x matrix bulk. In so doing, the radiationless channel of recombination is inhibited, and the relaxation time and the photoluminescence intensity increase. The films were unstable: the photoluminescence intensity decreased by 40–45% after the films had been irradiated by the nitrogen laser for no more than 25–30 min (the inset in Fig. 1, curve *1*). Photoluminescence in those films occurs due to the radiative annihilation of excitons in Si QDs. The large band width is determined by the dispersion of Si QD dimensions and the quantum-mechanical mesoscopic broadening of high-energy bands [6].

Photoluminescence of films obtained making use of the Al target was characterized by shorter relaxation times (usually less than 100 ns). Being held in air, they preserved high photoluminescence stability. Under the influence of nitrogen laser irradiation, the photoluminescence intensity decreased, but by no more than a few percent (the inset in Fig. 1, curve *2*). The origin of photoluminescence in Al_2O_3 films is associated with the radiation emission by oxygen-deficient centers (F-centers) – aggregate centers of the F_2 type in various charge states [7].

The photoluminescence intensity for films obtained using Si+Al targets was somewhat higher than that for Al_2O_3 films. The photoluminescence relaxation times did not exceed 250 ns. The high dielectric permittivity of Al_2O_3 confines the manifestation of the dielectric enhancement effect. The Al_2O_3 layer prohibits the diffusion of environmental oxygen and the passivation of broken bonds; therefore, it interferes with the inhibition of radiationless recombination channel. A distinctive feature of those films is a fine structure of their photoluminescence spectra. Such a fine structure was observed for films of low-dimensional silicon; it was associated with the interface states of $Si_{4-n}O_n$ ($n = 0, 1, 2, 3, 4$) [2,8]. The introduction of Al into the target gave rise to an enhancement of photoluminescence stability (the inset in Fig. 1, curves *2* and *2′*). The nature of photoluminescence in those films is determined by both the Si QDs and the oxygen vacancies in oxides. The availability of Si nanocrystals results in an increase of defectness of both oxides. On the one hand, Al_2O_3 prohibits oxygen from penetrating into the matrix, thus protecting Si nanocrystals from complete disappearance, and stabilizes the barrier phase composition. On the other hand, it promotes the appearance of all variety of structural states at the nanocrystalline Si/Al_2O_3 interface.

3.2. IR transmission spectra

In Fig. 2, the spectra of film optical density obtained at various Al contents in the target are depicted. For every film, a band with the maximum at $1035\ cm^{-1} \leq \nu_m \leq 1090\ cm^{-1}$ associated with the absorption at Si–O bonds is observed, which evidences for the presence of the silicon-oxygen phase. Figure 2 demonstrates that the fraction of Al in the target affects the band intensity, the maximum position, and the band shape.

The insert in Fig. 2 exhibits the dependence of the absorption band maximum position ν_m on the fraction K of Al in the target. The value of ν_m substantially decreases with the growth of K. In particular, for a film obtained without introducing Al into the target, $\nu_m = 1090\ cm^{-1}$, whereas for a film obtained at $K = 0.9$, $\nu_m = 1035\ cm^{-1}$. This implies, according to [9], that the introduction of Al into the target enhances the nonstoichiometry of the SiO_x phase, namely, the x-value diminishes from 2 to 1.4. Note that two sections are distinctly observed in the dependence $\nu_m(K)$: an abrupt one at $K < 0.15$ and a smooth one at $K > 0.15$. Therefore, the growth of Al content in the target is accompanied by a reduction of the concentration of oxidized Si atoms and a reduction of their oxidation degree. The structural state of oxygen in the silicon-oxygen phase, i.e. the type and the concentration of molecular complexes $Si–O_4–Si_{4-y}$, where $1 \leq y \leq 4$, also changes [10, 11].

This fact is confirmed by the analysis of the shape of the main absorption band. The results of the analysis of Gaussian components for the specimens of films that

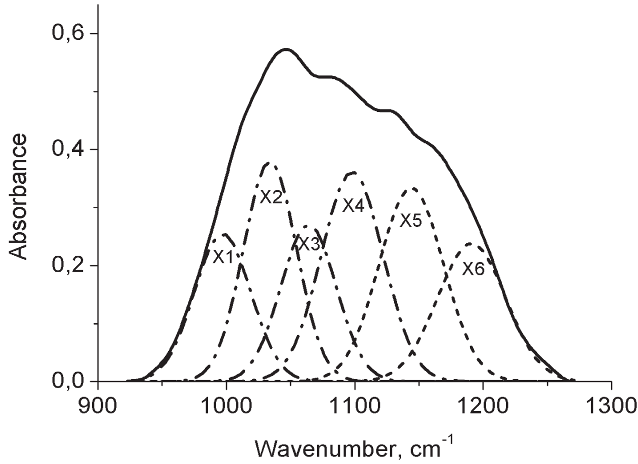

Fig. 3. Deconvolution of the absorption band into Gaussian components for a film obtained with the introduction of Al in the target at $K = 0.2$

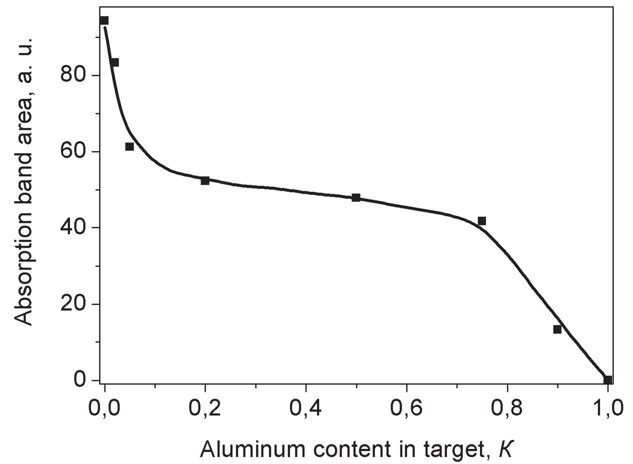

Fig. 4. Dependence of the area under the absorption band on the Al fraction in the target K

did not contain Al_2O_3 and were held in air, as well as for films obtained at the Al content in the target $K = 0.2$, are given in Tables 1 and 2, respectively. In Fig. 3, we present the example of the deconvolution of the absorption band into Gaussian components for films obtained at the Al content in the target $K = 0.2$. The data of Table 1 testify that the absorption band of a film free of Al_2O_3 is described by a sum of components associated with the oscillations of transverse (TO) and longitudinal (LO) optical phonons, which are characteristic of the SiO_2 phase [4,12]. The introduction of Al into the target is accompanied by the appearance of components that are characteristic of the SiO_x phase [5,13] in the film absorption band (see Table 2). At low Al contents in the target ($K < 0.15$), the intensity of those components is small, but they dominate, if $K > 0.15$. Hence, in the case of Si+Al target composition, the silicon-oxygen phase in the films is either the phase mixture SiO_2+SiO_x or the phase SiO_x.

Figure 4 demonstrates the influence of Al content in the target on the area under the film absorption band. Owing to the fact that the area of the main absorption band of silicon oxide films is proportional to the oxygen concentration in vibrating "molecules" Si–O–Si [14], the presented curve determines the dependence of the concentration of bridging oxygen in the silicon-oxygen phase on the Al fraction in the targets. From Fig. 4, it follows that the concentration of "molecules" Si–O–Si diminishes substantially – by almost an order of magnitude – if K increases. In this case, three sections with different K can be distinguished: $0 < K < 0.15$, $0.15 < K < 0.75$, and $0.75 < K \leq 1$.

In the film free of Al_2O_3, the surface of Si clusters becomes actively oxidized, so that the film contains Si nanocrystals in the SiO_2 matrix. In the interval $0 < K < 0.15$, a drastic reduction of bridge oxygen concentration

T a b l e 1. Parameters of elementary absorption bands of SiO_2 films free from Al, $K = 0$

Band	Maximum position cm^{-1}	Half-width cm^{-1}	Vibration type	Si–O–Si bond angle deg.	Structure type
1	1054±4	58±3	TO	132	4-member ring SiO_4
2	1090±5	43±3	TO	144	4- and 6-member rings
3	1147±3	52±3	TO	180	linear fragments Si–O–Si β-crystabolite
4	1200±3	68±3	LO	126	the same as 1
5	1252±3	44±3	LO	142	the same as 2
6	1300±3	57±3	LO	180	the same as 3

T a b l e 2. Parameters of elementary absorption bands of SiO_x films at $K = 0.2$

Band	Maximum position cm^{-1}	Half-width cm^{-1}	Vibration type	Si–O–Si bond angle deg.	Structure type
X1	1000±10	50±2	TO	116	Si–O–Si_3
X2	1033±3	45±2	TO	127	Si–O_2–Si_2
X3	1067±4	50±2	TO	136	Si–O_3–Si
X4	1092±7	55±1	TO	145	Si–O_4
X5	1141±2	56±1	LO	114	the same as X1
X6	1195±3	60±5	LO	124	the same as X2
X7	1246±2	50±1	LO	140	the same as X4

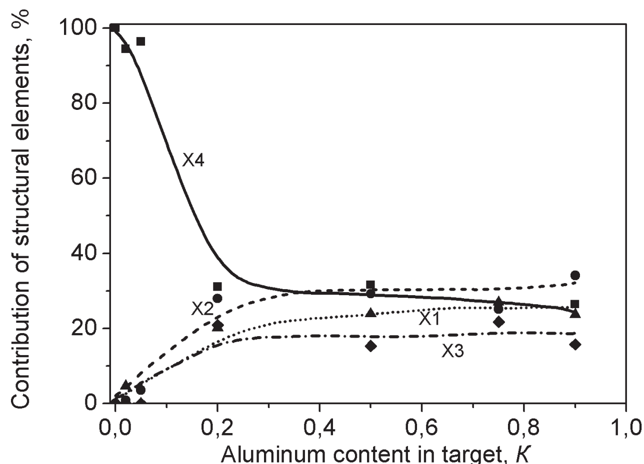

Fig. 5. Variation of the structural state of oxygen with the change of Al fraction in the target: (X1) Si–O–Si_3, (X2) Si–O_2–Si_2, (X3) Si–O_3–Si, (X4) Si–O_4

is observed, and the structural state of oxygen in this phase changes considerably (see Fig. 5, where the contribution of components associated with TO vibrations to the main absorption band is illustrated). Figure 5 also demonstrates that the introduction of Al into the target even in low concentrations ($K < 0.15 \div 0.2$) gives rise to a drastic decrease of concentration of Si–O_4 tetrahedra and an appearance of Si–O_y–Si_{4-y} complexes ($1 \leq y \leq 3$). This phenomenon is explained by the fact that Al atoms are oxidized more effectively than Si ones. The former capture oxygen atoms, so that some Si atoms remain oxidized incompletely, and the fraction of those atoms increases as K grows.

If the Al content is high ($0.75 < K \leq 1$), a drastic reduction of bridge oxygen concentration in the silicon-oxygen phase is also observed. Taking into account that the number of sputtered Si particles is relatively small in this region and that the oxidizing activity of aluminum is high, this region contains a small amount of silicon oxide; moreover, the latter is mainly available in the form of weakly oxidized molecular clusters $SiOSi_3$ and SiO_2Si_2. In the absence of silicon in the target, the band associated with Si–O bonds disappears from IR spectra.

In the range $0.2 \leq K \leq 0.75$, the reduction of bridge oxygen content in the silicon-oxygen phase with the growth of K slows down sharply. This phenomenon can be explained by the fact that the increase of silicon content in the target is accompanied by an emergence of the SiO_x phase on the surface of Si nanocrystal, which protects its bulk from oxidation and, in that way, reduces the efficiency of silicon oxidation. It is logical to admit that the increase of the silicon content in the target stimulates the dimension growth of silicon nano-inclusions, which has to induce the photoluminescence band shift towards low-energy range. Such a phenomenon was really observed in the experiment (cf. curves *2* and *3* in Fig. 1)

4. Conclusions

1. The method of pulsed laser deposition of particles from the inverse flux of an erosive torch was used to obtain photoluminescent films of Al oxide with Si nanocrystals. The silicon-to-aluminum ratio in the target was varied.
2. The analysis of the main IR absorption band of the silicon–oxygen phase and its dependence on the Al content in the target allowed us to determine—in the framework of the random bond model—the content variation of the molecular complex Si–O_y–Si_{4-y} ($1 \leq y \leq 4$) in the barrier phase of Si QDs. In the case of low aluminum fractions ($K < 0.15$), the composition of the oxide phase drastically changed from SiO_2 to a mixture of SiO_2 and SiO_x. If the Al fraction increased from 0.15 to 0.75, the composition of silicon oxide changed weakly, approaching to that of the phase $SiO_{1.4}$.
3. The spectra of film photoluminescence were shown to lie in the radiation emission energy range 1.4–3.2 eV, and the photoluminescence relaxation times to extend from tens to hundreds of nanoseconds. The introduction of Al_2O_3 into the film enhanced the photoluminescence stability. An agreement between practically identical photoluminescence spectra and the stability of silicon oxide phase composition in the films obtained at the Al fraction in the target $0.15 < K \leq 0.75$ was observed. In this case, the photoluminescence spectra were determined by the system Si QD/SiO_x.

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СТРУКТУРНИЙ СКЛАД КРЕМНІЙ-КИСНЕВОГО ПРОШАРКУ ФОТОЛЮМІНЕСЦЕНТНИХ ПЛІВОК Al_2O_3 З Si НАНОКРИСТАЛАМИ

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Р е з ю м е

Фотолюмінесцентні плівки Al_2O_3 з Si квантовими точками отримано методом імпульсного лазерного осадження при варіюванні співвідношення частинок кремнію і алюмінію в мішені. Вимірювали спектри фотолюмінесценції в інтервалі 1,4–3,2 еВ та інфрачервоного поглинання в діапазоні 850–1400 см$^{-1}$. На всіх плівках спостерігали смугу інфрачервоного поглинання на Si–O-зв'язках, що свідчить про наявність проміжної кремній-кисневої фази на межі поділу Si нанокристал – Al_2O_3. Аналіз молекулярних комплексів Si–O_y–Si_{4-y} ($1\leq y \leq 4$) виконано в рамках моделі випадкового зв'язку. Установлено взаємозв'язки між складом мішені, структурним складом кремній-кисневого прошарку та фотолюмінесцентними властивостями плівок.