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VISIBLE PHOTOLUMINESCENCE FROM ANNEALED POROUS SiO_x FILMS

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Porous light-emitting SiO_x films have been prepared by oblique thermal vacuum evaporation of SiO and thermal post-annealing in vacuum. A thermally stimulated (annealing temperatures – 700 and 950 ^oC) transformation of the SiO_x layers, which leads to the formation of amorphous and crystalline Si nanoinclusions, was investigated using photoluminescence and infrared spectroscopy. The size of Si nanoparticles and their volume fraction depend on film's porosity. Conclusion is drawn about possibility to control the structure, composition and, hence, light-emitting characteristics of nc-Si-SiO_x structures by changing of the deposition angle.

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1. Introduction

Structures consisting of Si nanocrystals embedded in SiO_2 are good objects for optoelectronic and photonic applications due to their intensive emission at room temperature [1-8]. Photoluminescence (PL) observed in such structures in visible and near infrared range is connected with quantum-confinement effect of silicon nanoclusters (nc-Si) in annealed at high temperature SiO_x films. For the fabrication of such films usually few basic techniques are used: plasma-enhanced deposition, ion implantation, laser ablation, magnetron sputtering, evaporation in vacuum and others. All these methods allow to fabricate films with required x. Thermally induced decomposition of the oxide and formation of Si nanoparticles in SiO_x matrix is described by the reaction:

$$y\mathrm{SiO}_x \rightarrow x\mathrm{SiO}_y + (y - x)\mathrm{Si}, \qquad (1)$$

where $y > x$, and SiO_y, probably, consist of SiO_x and SiO_2 [9]. The annealing temperature determines the structure of inclusions: annealing at 500 to 900 °C favors the coalescence of Si atoms into amorphous clusters, at higher temperature nanocrystalline Si particles are formed [2,3].

There are a number of papers devoted to the mechanism of changes in structure of SiO_x films during thermal treatment [10-13]. Thermally stimulated formation of Si nanoparticles results in considerable dispersion of nc-Si sizes that in it's turn, decrease the intensity of PL and increase the half-width of PL band. As for control of size and volume density of Si nanoinclusions it seems to be useful to change the structure of SiO_x layers by the change of conditions of their deposition. There were performed investigations on usage of SiO_x films for orientation of liquid crystals since the 80-th. It was shown [14-15] that thermal evaporation of silicon monoxide on the substrate obliquely oriented to the direction of the stream of the evaporated substance lead to the formation of the porous SiO_x films with columnar structure. Depending on the angle of evaporation and other parameters of technological process the diameter of deposited columns vary from 10 to 30 nm.

Thermostimulated formation of Si nanoinclusions in such films takes place in limited volume of SiO_x columns that can results in smaller dimensions of nc-Si, than in continuous films with the same

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content (x). It was shown in our previous paper [15], that during the annealing in nitrogen such structures are subjected to additional oxidation because of their high porosity. In this paper we carried out investigation of structural transformation and PL spectra of porous SiO_x films annealed in vacuum.

2. Experiment

Samples were prepared by thermal evaporation in vacuum (residual pressure $1\div2\times10^{-3}$ Pa) of silicon monoxide (Cerac Inc., 99.9 % purity). The angle (β) between the vapor stream and the substrate normal was 0°, 60° and 75° for different samples. As the substrate were used polished silicon wafers. The rate of deposition onto normally oriented substrate was 1.5 nm/sec and decreased with increasing β. The time of deposition was chosen to provide the deposition of the same mass on the same area of the samples, independently on substrate orientation. Thickness of the films were monitored in situ by the quartz-crystal-oscillator monitor system (KIT-1) and measured after deposition by microinterferometer MII-4 with accuracy ± 5nm. After deposition the samples were annealed in vacuum (10^{-3} Pa) at 700 °C and 950 °C during 15 minutes to obtain amorphous and crystalline Si inclusions in the oxide matrix. The density (ρ) of investigated samples was determined by the comparing of thickness of film deposited at different angles with films deposited normally. The density of normally deposited film was measured early and is equal to 1.90 g/cm^2 [11].

After annealing the samples were passivated by RF plasma treatment in $H_2 + N_2$ atmosphere. Infrared transmission spectra were measured in range 800-1200 cm^{-1} using spectrometer Specord 80 with silicon substrate as the reference. PL spectra were measured at room temperature using SPM2 monochromator with nitrogen-cooled FEU-62 photomultiplier. The 488 nm line of an Ar^+ laser was used for excitation.

3. Results and discussions

The main characteristics of the samples are given in Table 1.

Table 1. Characteristics of deposited films.

Deposition angle	x As-deposited	y Annealed 700 °C	y Annealed 950 °C	ρ, g/cm^3	Maximum position in IR absorption band, cm^{-1}: As-deposited sample	Annealed sample 700 °C	Annealed sample 950 °C
0°	1.27	1.41	1.91	1.90	1023	1040	1073
60°	1.42	1.53	1.91	1.28	1043	1054	1074
75°	1.51	1.60	1.92	0.88	1052	1063	1076

As it can be seen from Table 1 the density of the films decrease rapidly with increasing of deposition angle that is the evidence of porous structure of such layers (at annealing the density does not change almost). The porosity of samples with the same mass of deposited SiO_x on the same area of substrate was determined as $(d(\beta) - d(0))/d(\beta)$, where $d(\beta)$ – thickness of film deposited at angle β, $d(0)$ – thickness of athwart deposited film. For the investigated films values of porosity 32% and 54% for angles 60° and 75° respectively were obtained. These values were determined relative to film deposited at $\beta = 0°$. However as it were shown in our previous paper even films deposited normally have porosity in the range 8-10% [11]. Therefore whole content of cavities in oblique deposited samples is 43%, and 66% for angles 60° and 75°, respectively.

To estimate the oxide composition in both as- deposited (*x*) and annealed (*y*) samples we used the monotonous dependence [16] of maximum position of main IR absorption band for SiO_x in range 1000-1100 cm^{-1} (which corresponds to the asymmetric stretching vibration of the oxygen atom in its two-fold coordinated bridging bonding site) on oxide composition.

Fig. 1-3 shows IR absorption spectra for as-deposited samples (1) and annealed at 700 (2) and 950 °C (3), respectively. For as-deposited films it can be seen the shift of maximum position depending on angle of deposition from 1023 cm^{-1} (for $\beta = 0°$) to 1052 cm^{-1} (75°). Using the dependencies [16] between *x(y)* and maximum position there was evaluated the composition of oxide phase of investigated samples (columns 2-3 in Table 1). Intensity of the IR band slightly changes after annealing for all samples, it means that the oxidation in vacuum is weak.

The change of composition as-deposited films may be connected with oxidation of evaporated SiO in initial atmosphere. It were shown in previous papers [2,3,11] that composition of normally deposited SiO_x film can be controlled by essential change of deposition rate or initial pressure. (in range $10^{-2} \div 10^{-4}$ Pa) However all our samples were deposited in identical conditions so the change of composition is the result of porosity in structure. Oxidation of films in the process of deposition appreciably accelerates with growth of it's porosity that is determined by the angle of deposition. So by changing of the deposition angle it is possible to change the structure and composition of as-deposited SiO_x layer.

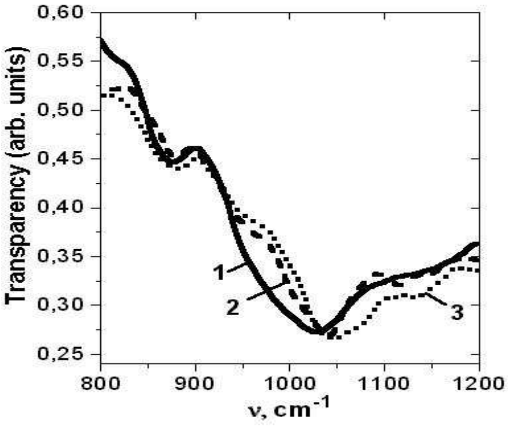

Fig.1. IR absorption spectra of as-deposited. Curves 1,2,3 refers to samples deposited at angles 0°, 60° and 75°, respectively.

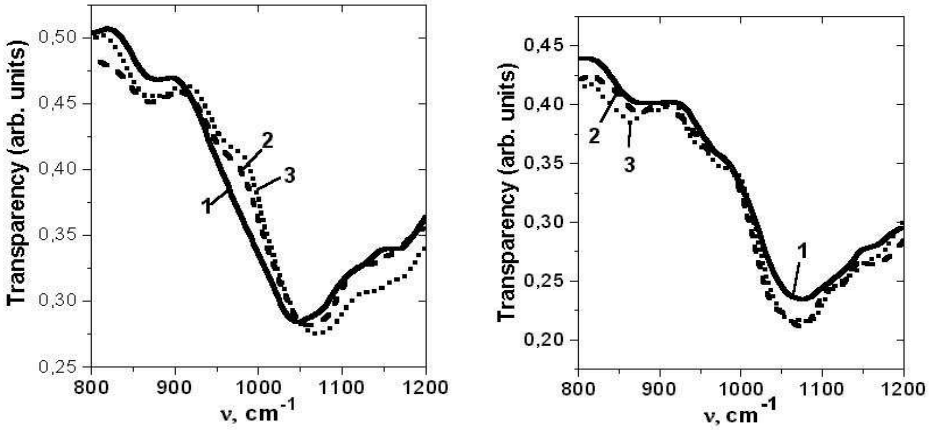

Fig. 2 and 3. IR absorption spectra of annealed at 700 °C (left) and 950 °C (right) samples. Curves 1,2,3 refers to samples deposited at angles 0°, 60° and 75°, respectively.

After annealing IR absorption maximum of all samples shifts to higher wavenumbers. The peak position for samples annealed at 700 °C vary from 1040 to 1063 cm^{-1} for different deposition angles. It means that composition of oxide matrix in annealed at 700 °C films depends on deposition angle.

In samples annealed at 950 °C IR absorption band has maximum about 1074 cm^{-1} for all angles of deposition. Such position refers to the vibration of bridge oxygen in SiO_x matrix for x about 1.91 (Tab. 1). So in these samples the almost full decomposition of SiO_x in silicon and SiO_2 phases takes place. It must be pointed out that the degree of structural transformation depends on the annealing temperature: at higher temperatures the volume fraction of the precipitated Si is larger and the composition of a matrix becomes more similar to SiO_2. Using the known molecular weights and densities of the components formed and taking into account the coefficients in the reaction equation (1), that are x and y from Tab. 1, we can easily find the volume shares v_{Si} of the Si phase formed in annealed samples. After annealing at 700 °C v_{Si} equal to 5.8 %, 3.9 % and 3.0 % of amorphous nanoclusters in the SiO_y matrix for samples deposited at angles 0°, 60° and 75°, respectively, and after annealing at 900 °C v_{Si} equal to 19.4 %, 14.2 % and 11.5 % of Si nanocrystals in the $SiO_{1.91}$ matrix for angles 0°, 60° and 75°, respectively.

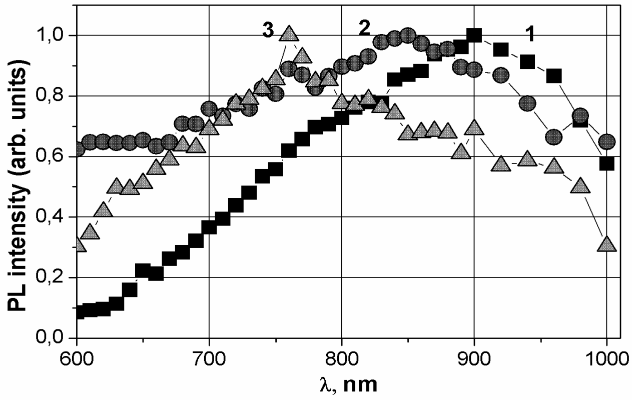

Fig. 4. PL spectra of annealed at 700°C samples. Curves 1,2,3 refers to samples deposited at angles 0°, 60° and 75°, respectively (normalized values).

The as-evaporated SiO_x films show rather weak photoluminescence in the visible range. After the annealing at 700 °C an intense band appears in the PL spectrum of normally deposited sample centered around 900 nm. Samples deposited at 60° and 75° shows PL with peak position near 850 and 750 nm, respectively (Fig. 4).

Fig. 5 shows room-temperature PL spectra obtained for samples annealed at 950 °C. All samples are characterized by a broad PL bands that ranges from 650 nm to beyond 1000 nm. The most long-wavelength band is observed on samples deposited normally – position of maximum equal to 960 nm. With the growth of deposition angle PL peak position moves to short wavelength and for samples deposited at angles 60° and 75° is equal to 920 and 860 nm, respectively.

PL in annealed at high temperatures SiO_x structures is connected with the presence of silicon nanoparticles [1,3-8]. The change of mean sizes of nanocrystals leads to the shift of PL maximum position [3, 6-8]. It means that shift of PL peak position towards short wavelengths with increasing of angle of deposition (Fig. 4 and 5) can be attributed to decrease of average size of Si inclusions that are formed in porous oxide matrix during high temperature annealing. This diminution can be caused by two reasons: change of composition (growth of x) or limited volume of nc-Si formation in oxide columns. Both factors must lead to diminution of nc-Si sizes and short wavelength shift of PL band.

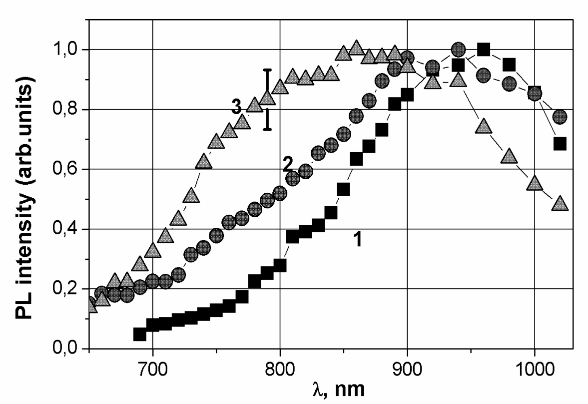

Fig. 5. PL spectra of annealed at 950°C samples. Curves 1,2,3 refers to samples deposited at angles 0°, 60° and 75°, respectively (normalized values).

It can be seen from Fig. 5, that half-width of PL bands in samples annealed at high temperature depends on angle of deposition, it increase from 150 nm for normally deposited sample to 250 nm for films deposited at 75°. When blueshift in deposited samples caused by change of composition the half-width of band does not change [3]. These results suggest that in oblique deposited SiO_x samples the average size of Si nanoparticles decreases, and the dispersion of sizes is increased in comparison with non-porous layers. Columnar structure of oblique deposited porous SiO_x films includes oxide columns of the various sizes. In columns of small diameter (less than 10 nm), at high-temperature annealing, the Si nanoparticles of smaller size are formed, in columns of greater diameter the size of particles is the same as in continuous SiO_x films. With increasing of the deposition angle the porosity of the deposited films is increased and the average diameter of columns decreases. This enables to control by change of the deposition angle the light-emitting characteristics of nc-Si-SiO_x structures.

4. Conclusions

The density of oblique deposited SiO_x films and their composition strongly depend on the deposition angle. For the investigated films values of porosity 43%, and 66% for angles 60° and 75°, respectively, were obtained.

PL emission from the samples annealed at 700 °C is blueshifted as compared with the samples annealed at 1000 °C. For both temperatures with increasing of deposition angle PL peak position moves to short wavelength and half-width of PL bands essentially increase. This means that in obliquely deposited SiO_x samples the average size of Si nanoparticles decreases, and the size dispersion is increased in comparison with non-porous layers. So by changing of the deposition angle it is possible to change the structure, composition and, hence, PL spectra of nc-Si-SiO_x layers.

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