ISSN 1063-7850, Technical Physics Letters, 2013, Vol. 39, No. 4, pp. 341–343. © Pleiades Publishing, Ltd., 2013.
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Spherical Microresonators with Luminescent a-Si : C : H Coating

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Received November 29, 2012

Abstract—Microresonators (MRs) comprising spherical particles of amorphous silicon dioxide with diameters of 2.0 and 3.5 μm coated with a 60-nm-thickness luminescent coat of amorphous hydrogenated silicon carbide (a-Si : C : H) were produced. Enhancement and modification of the continuous wide photoluminescence spectrum of the a-Si : C : H in the visible–near-infrared region at room temperature into a line spectrum displaying intense narrow bands with positions coinciding with the whispering-gallery modes of spherical MRs were demonstrated.

DOI: 10.1134/S1063785013040068

An amorphous hydrogenated silicon carbide (a-Si : C : H) has a large width of the band gap [1–3] and luminesces at room temperature [2, 4]. Plasma-enhanced chemical vapor deposition (PECVD) is one of the main methods of synthesis of a-Si : C : H films. The optical properties and position of the maximum of the photoluminescence (PL) line of the material in the spectral range of 600–900 nm are controlled by the change of the methane to silane concentration ratio in the gas mixture [4–7]. Thin a-Si : C : H films hold promise for the development of light-emitting diodes [8] and solar cells [9, 10].

Application of this material for the development of light-emitting devices on the basis of microresonators (MRs) is of interest for the purpose of increasing intensity and narrowing the a-Si : C : H spectral band. Planar Fabry–Perot MRs based on the α-Si : C : H layers were obtained in [11–13], which exhibited enhanced photo- and electroluminescence of the a-Si : C : H in the active mode of MRs in the visible spectral region. Efficient modulation and enhancement of PL can be achieved with the help of MRs with whispering gallery modes (WGMs). These modes propagate within a narrow surface layer of an MR and are subjected to total internal reflection on the boundary of an axially symmetrical dielectric body [14, 15]. MRs with WGMs are characterized by a high Q factor and low effective mode localization volume. Unlike for the planar Fabry–Perot MR with active layer, enhancement in which is reached at resonance wavelength and in the range of wavelengths corresponding to the edges of the stop zone, a narrowband line spectrum that consists of multiple intense narrow lines in a wide spectral range, the position of which correspond to the whispering gallery modes, can be obtained for WGM MRs. WGM MRs are sensitive with respect to the detection of molecules and biological objects located on the surface [16, 17]. Currently, WGM MRs are considered to be a platform for the development of sensitive optical biosensors.

WGM MRs are prepared in this work comprising an amorphous silicon dioxide (a-SiO_2) spherical particle coated with the a-Si : C : H layer using the PECVD method. The dependence of the characteristics of the obtained PL line spectrum on the size of the spherical particle was demonstrated. The parameters of the a-Si : C : H synthesis were selected in a way to obtain an intensive PL of the a-Si : C : H in the visible–near-infrared range of the spectrum (600–800 nm), which is transparent to biological tissues.

Monodisperse spherical particles of the a-SiO_2 with diameters of 2.0 and 3.5 μm were synthesized in two steps. First, SiO_2 particles with a diameter of 700 ± 25 nm were prepared with the method of tetraethoxysilane (TEOS) hydrolysis in a mixture of alcohol, water, and ammonia [18]. The parameters of the synthesis process were molar ratio TEOS : NH_3 : H_2O : C_2H_5OH 1 : 15 : 50 : 72, temperature 30°C, and volume of the mixture 1 L. The obtained particles were annealed in air for 2 h at 500°C followed by redispersion in deionized water (10 MΩ) with the help of ultrasound.

The so-called "successive growth" procedure was conducted at the second step [18]. For this purpose, 5 g of TEOS was added every 10 min to 1 L of NH_3 : H_2O : C_2H_5OH (30 : 50 :72) mixture containing 1 g of

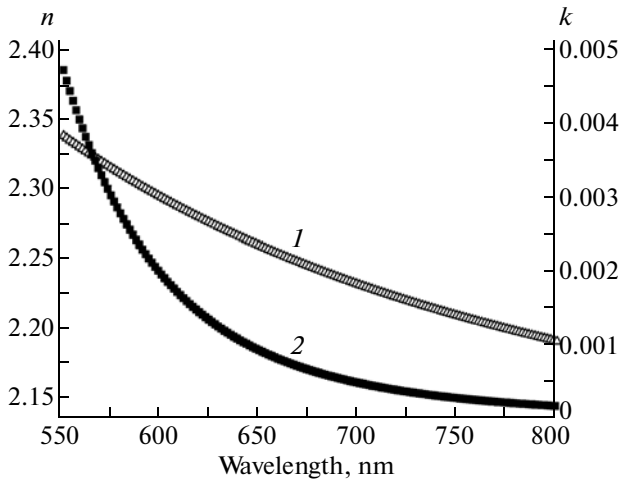

Fig. 1. Spectral dependences of the real n (*1*) and imaginary k (*2*) part of the refractive index of the a-Si : C : H film.

700 nm a-SiO_2 particles. Hydrolysis products were concentrated in the vicinity of the submicron particle surface that coated them with a layer of hydrated a-SiO_2 and, hence, providing their further growth. Ammonia concentration was doubles in the reaction mixture in comparison with the previous step in order, first, to reduce the duration of the TEOS hydrolysis process to 10 min and, second, to prevent the emergence of new nucleation centers. a-SiO_2 particles with diameters of 2.0 ± 0.1 and 3.5 ± 0.15 μm were obtained after the addition of 15 and 85 portions of TEOS, respectively. Next, the particles were annealed again at 500°C and dispersed in water.

The spherical a-SiO_2 particles were applied to a 20×30-mm silica and quartz wafer with the method of aerosol sputtering of the water suspension [19]. The weight concentration of the particles in suspension was 0.01–0.1%. The suspension was subjected to ultrasound treatment immediately before application to disperse the sediment particles and to provide their even distribution in the volume. Next, the particles were coated with a a-Si : C : H layer with the PECVD method. The parameters of the technological process were methane content in the methane–silane mixture of ~50%, working pressure 0.1–0.2 Torr, frequency of high-frequency radiation 17 MHz, high-frequency power 0.03–0.1 W/cm^2, temperature of wafer 200–250°C, and net flow of the gas mixture 5–10 sccm. Reference a-Si : C : H films were deposited on the quartz and silicon wafer in a single PECVD process. Reference films were used to control the thickness of the a-Si : C : H films (coatings) in the PECVD process with the method of in situ interferometry and investigate their optical properties with the ellipsometry method. The optical properties and thicknesses of the a-Si : C : H films and a-Si : C : H coatings in MR were assumed to be similar.

Excitation and recording of the PL spectra were conducted at room temperature in the geometry of the back scattering using a micro Renishaw InVia Raman spectrometer equipped with 50× and 100× microobjectives (Leica) and a multichannel detector cooled to −70°C that allows recording of spectra with a spectral resolution of ~3 cm^{-1}. Linearly polarized 514.5-nm argon laser radiation focused on the sample as a spot with ~1-μm diameter was used for excitation. Radiation was focused on the edge of a single spherical particle and a maximum recorded intensity of the WGM lines in the PL spectrum was reached using a fine tuning of the height with a 1 μm step. The power of the exciting radiation on the sample in the process was minimized to ~5 μW to avoid an irreversible change of the sample due to the thermal effect of the exciting radiation.

The optical parameters and thickness of the reference a-Si : C : H films on the quartz wafer were determined with ellipsometry method. Measurements of the spectra of ellipsometric angles were performed with an M-2000 instrument (J.A. Woollam Co., Inc.) at three incidence angles $\varphi = 59°$, 67°, and 75°. The following model was used for calculation: external medium–homogeneous isotropic film–semi-infinite quartz wafer. Determination of a dispersion of real part of the refraction index n, imaginary part of the refraction index k, and thickness d of the a-Si : C : H film was performed on the basis of the solution of the reverse ellipsometry problem with fitting of the ellipsometric angles calculated according to the model to the experimental dependencies of ellipsometric angles on the wavelength. It was taken into account in the process that optical parameters n and k can change in the ranges 1.5–3.5 and 0–1, respectively. The ranges of the n and k changes correspond to the values for the a-Si : C : H films obtained at different methane concentrations in the gas mixture [20]. The range of the thickness change was selected on the basis of data obtained from measurements of the thickness with in situ interferometry. The spectral dependencies of the real and imaginary parts of the refractive index of the a-Si : C : H coating obtained with the ellipsometry method are presented in Fig. 1. The value of the absorption coefficient of the film at a wavelength of 700 nm did not exceed 100 cm^{-1}; the thickness of the a-Si : C : H film was 60 nm.

The PL spectrum of the a-Si : C : H film on the silicon wafer presented in Fig. 2 (curve *3*) has an intensity maximum at the wavelength of 720 nm, which is in the transparency region of biological tissues. The PL spectra of MR on the basis of spherical particles with diameters of 2 and 3.5 μm coated with 60 nm a-Si : C : H layer are presented in Fig. 2 (curves *1* and *2*). Intense lines that are characteristic of WGMs are observed on the background of the structureless band. The WGM modulation depth determined as a ratio of intensity of the WGM peak amplitude to the

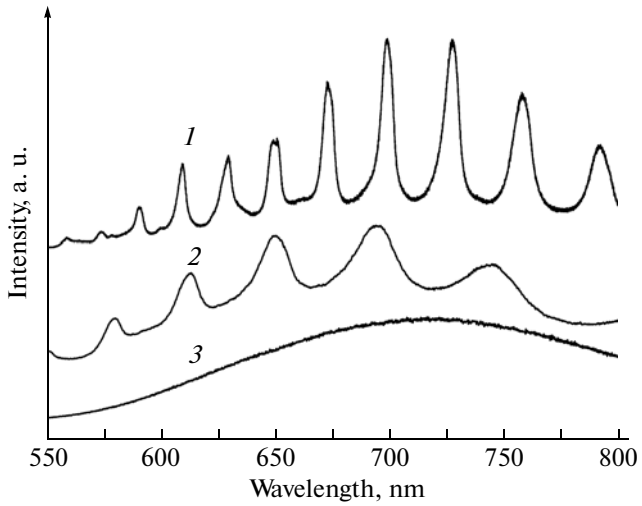

Fig. 2. Photoluminescence spectra of microresonators consisting of spherical a-SiO_2 particles with diameters of (*1*) 3.5 and (*2*) 2 μm coated with the 60-nm a-Si : C : H coating and (*3*) a-Si : C : H film on the silicon wafer. Spectra are shifted vertically for convenience.

background signal of the PL is 3.6 and 0.7 for the MR with diameter 3.5 and 2 μm, respectively. The ratio of spectral (intermode) distances between the nearest lines of the 3.5 and 2 μm size WGM MR is 0.6, which corresponds approximately to the reciprocal ratio of their diameter ~0.58. The Q value related to the quality factor of MR was determined according to the equation $Q = \lambda/\Delta\lambda$, where λ is the position of the WGM line and $\Delta\lambda$ is the line width at half height. The $Q \sim 120$ was demonstrated for the 3.5 μm MR.

In conclusion, MR on the basis of a-SiO_2 spherical particles coated with photoluminescent a-Si : C : H film deposited with the PECVD method were prepared in this work. The emission range of the coating is in the transparency region of biological tissues. A set of intense narrow PL spectral lines in the visible–near-infrared region of the spectrum were obtained through effective interaction of the a-Si : C : H radiation with WGMs of the spherical resonator.

Acknowledgments. This work was supported by the Presidium of the Russian Academy of Sciences, Fundamental Research Program no. 24, and in part by the Ministry of Education and Science of the Russian Federation (project no. GK 11.519.11.3026).

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Translated by L. Brovko