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The Laser Active Element Based on Dye on Porous Alumina

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Abstract

Luminescent properties of Rhodamine 6G in porous alumina matrix have been investigated. From the SEM images the pore diameter is determined to be ~ 50 nm and the distance between the pores to be about 250 nm. Specific surface area of nanoporous alumina films measured by gas adsorption (BET method) was 6 m^2/g. Absorption and fluorescence spectra of Rhodamine 6G embedded in pores of anodic alumina oxide were measured. Decreasing of absorbance of monomers was observed upon increasing of Rhodamine 6G concentrations. At the same time appearing of new maximum at the short-wavelength part as a result of formation of dimer of dye was registered. Increasing of concentration of dye molecules in the pores leads to quenching of fluorescence of Rhodamine 6G. The lasing characteristics were examined upon excitation of the samples by second harmonic Nd: YAG laser λ_{gen} = 532 nm, E_{imp} = 90 mJ, τ = 10 ns in the longitudinal form. The dye generation spectra in nanoporous alumina under different power densities of the pump source were measured. It is established that when the pumping source power is 0.4 MW/cm^2 on the background spectrum of laser - induced fluorescence the narrow strip of the laser emission with a peak wavelength of 572 nm appears. Further increase in the power density of the pumping source leads to a narrowing of the band of generation and an increase in its intensity. The obtained results demonstrate the potential of using nanoporous alumina for creating the active elements of quantum electronics.

Introduction

Currently one of the most important problems in laser physics is the development of highly efficient laser media. Increase of effectiveness of using of dye lasers could be associated with the creation of new solid-state active elements on the basis of nanostructured materials. As a solid active medium for dye lasers the polymeric matrices, the matrices based on sodium borosilicate porous glass [1] and the sol-gel glasses are widely used [2, 3].

One of the long-term materials, which can be used as the active medium for lasers containing dyes, is nanoporous alumina oxide. Nanoporous alumina oxide films are widely used as a matrix for preparation of various nanostructures by template method [4-6]. Nanoporous aluminum oxide has many advantages: chemical, thermal stability, transparency in the visible region of the spectrum, excellent adsorptive properties due to a large volume of pores having a branched surface [7, 8]. Starting materials for such matrices are available and their manufacturing processes allow obtaining elements of low cost compared with other laser elements. The unique pore structure parameter (diameter, length and distance between neighboring pores) which may be varied during the synthesis allows using a film of porous alumina as a manufacture of various devices and nanomaterials [9].

Aluminum oxide based optical materials are interested because of luminescent ability both matrix and composite materials on its basis. Nanoporous alumina is known to be characterized by photoluminescence in the blue region of the spectrum, the properties of which are largely dependent on the composition of the electrolyte used in the anodizing. Photoluminescent properties of porous alumina membranes which were prepared by anodic oxidation with oxalic or sulfuric acids were studied in [10]. A blue band of fluorescence in the wavelengths region of 400-600 nm with intensive maximum at 460 nm was observed. This band is the result of single-ionized oxygen vacancy (F^+-centers) of nanoporous alumina in membranes. Fluorescence intensity of the porous film of alumina oxide increases at the annealing at high temperature. Fluorescence intensi-

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ty of nanoporous alumina prepared with oxalic acid was considerably higher than intensity of nanoporous alumina prepared with sulfuric acid.

Optically active materials based on porous alumina oxide were prepared at doping of the matix with non-organic and organic components. Intensive emission of ZnO nanoparticles [11], titanium dioxide with erbium and terbium was observed in nanoporous alumina matrix [12]. An array of nanowires CdS, obtained by electrodeposition, manifested in the form of three UV bands and one yellow-green fluorescence band [13].

Fluorescent properties of dyes embedded in the pores of alumina oxide was studied in [14,15]. Authors associate increasing of fluorescence intensity of Rhodamine 6G in the matrix of alumina oxide in comparing with porous glasses with energy transfer to luminophores molecules from oxygen vacancy.

One of the main disadvantages of the existing laser active element based on colored polymeric materials is their lack of thermal stability due to the low thermal conductivity of the polymer. For example, the thermal conductivity of the widely used polymethylmethacrylate is 0.19 W/m/K [16]. It has been shown [17] that the anodic alumina membranes are promising material for high-tech devices that operate at high temperatures. The porous anodic aluminum oxide structure undergoes no substantial change and remains stable over a wide temperature range up to 1000 °C. Heat conductivity factor of aluminum oxide films is equal to 1.6 W/m/K. It opens the possibility of using porous alumina to create solid-state active elements of tunable dye lasers. Using the matrix of the porous alumina will contribute to the rapid dissipation of heat which occurs upon absorption of light by the process of internal conversion in the dye molecules.

In the present work for the first time the laser operation in a thin film of nanoporous aluminum oxide doped with Rhodamine 6G dye was obtained. Choice of Rhodamine 6G due to the fact that the dye is widely used in laser technology as the active medium and has high value of lifetime of excited state, high fluorescence yield and photostability [1].

Experimental

Synthesis of alumina was carried out on "mild" anodizing conditions including two-stage synthesis at low values of the voltage (U = 40 V) in a solution of 0.3 M oxalic acid [18].

For electrochemical synthesis of nanoporous alumina as a starting material the aluminum plates (purity is 99.99%) with a thickness of 0.5 mm and dimensions of 3.5×3.5 cm have been used. To increase the size of crystallites of aluminum, to remove microstresses in the sample and subsequent to achieve a better ordering of received pore the alumina substrate was annealed in a muffle furnace at atmosphere for 10 hours at T = 500 °C. To remove surface defects of aluminum the electrochemical polishing was conducted in pulse mode in solution of CrO_3 and H_3PO_4. Thereafter their surfaces were washed in distilled water and dried in air.

Synthesis of nanoporous alumina was carried out in a two-electrode electrochemical cell using the constant-current source MPS-7081. Auxiliary electrode was a platinum plate and the working electrode was polished aluminum plate. The electrolyte was prepared on the basis of dual water filtration and water purifiers for deionization AquaMax 360 Basic. Water resistivity was 18.2 MOhms/cm. The resulting matrix of alumina was separated from the substrate by selective dissolution of the aluminum plate in a solution of $CuCl_2$ in HCl.

The sorption of the dye Rhodamine 6G molecules in the pores was carried out by exposing the alumina films in ethanol solution with an initial concentration of the phosphor C = 10^{-3} mol/l for 5 hours followed by drying the film in an oven at a temperature of 100 °C for 1 hour.

$$C = \frac{N_A * C^{||} * V}{M * S}(1 - A_2 / A_1)$$

Amount of adsorbed molecules of the phosphor is determined by the absorbance change of the solution before and after sorption by the equation:
where, V – volume of solution, C'' – the concentration of the dye in solution, A_1 and A_2 – absorbances of the solution before and after sorption S – specific surface of the porous alumina.

Specific surface area of the film was determined by BET method (Brunauer, Emmet, Teller) according to nitrogen adsorption at measuring complex «Sorbi MS».

Measurement of absorption and fluorescence spectra of Rhodamine 6G in the film was carried out on a spectrophotometer SM2203 (Solar). Measurement of the fluorescence decay kinetics of Rhodamine 6G were measured by using a pulsed spectrofluorimeter with picosecond resolution and recording mode time-correlated photon counting. Excitation of fluorescence of the sample was performed by using a semiconductor laser with a wavelength of generation λ_{gen} = 488 nm and a pulse duration of τ = 40 ps.

Measurement of the spectral characteristics of the laser films was conducted at the facility; the block diagram is shown in Fig. 1. Lasing characteristics were studied at the second harmonic excitation of samples by Nd: YAG laser (1) (SOLAR LQ 215,

λ_{gen} = 532 nm, E_{imp} = 90 mJ, τ = 10 ns) in the longitudinal version. Cavity was formed by two glass plates between which the film is placed (6). The pumping radiation passing a diaphragm (2) by means of cylindrical lenses (4, 5), is focused on the rear side of the film in the strip with the area of 0.07 cm^2.

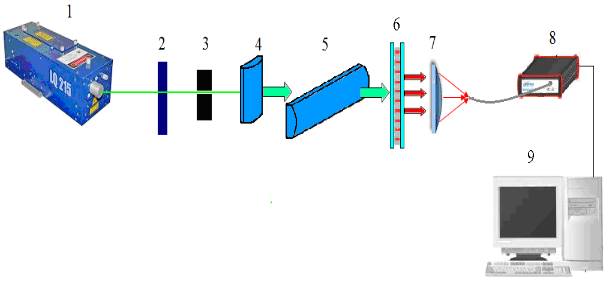


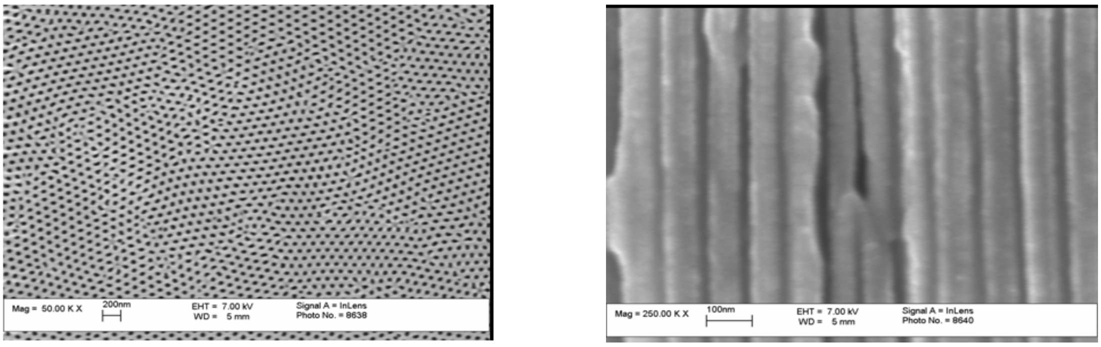
Fig. 1. Diagram of apparatus for the study of the lasing characteristics of thin films: 1 – laser LQ 215; 2 – neutral density filters; 3 – aperture; 4, 5 – cylindrical lens; 6 – the sample, 7 – converging lens; 8 – spectrometer AvaSpec-2048; 9 – computer.

Pump power density was varied with the help of neutral density filter (2) and was 0.01-1 MW/cm^2.

Stimulated emission with the help of converging lens (7) focused on the input of optical fiber spectrometer AvaSpec-2048. The lasing spectra were measured on spectrometer AvaSpec-2048 (8) connected to the computer (9). Relative error in the determination of the spectral characteristics was 3%.

Results and Discussion

The surface morphology and cross - cleaved samples obtained in a scanning electron microscope are shown in Fig. 2. Measurements were carried out at an accelerating voltage of 7 kV, a working distance of 7 mm in high vacuum. From the obtained image (Fig. 2a) at the upper side of the film the pore diameter equal ~ 50 nm and the distance between the pores of about 250 nm are observed. On cross - cleaved sample (Fig. 2b) the parallel straight channels arranged perpendicularly to the surface are visible. Specific surface area of obtained alumina membranes is 6 m^2/g.



a b

Fig. 2. The SEM images of the surface and cross cleavage nanoporous alumina obtained in oxalic acid solution: a – top side, b – the transverse cleavage without remote barrier layer.

Figure 3 shows the absorption and fluorescence spectra of Rhodamine 6G molecules in the pores of alumina oxide. As could be seen the absorption band of monomers of the dye in the matrix has a maximum at a wavelength λ = 524 nm. Photoexcitation of the dye fluorescence was carried out in the absorption band of the luminophor at a wavelength equal to λ = 500 nm. The fluorescence spectrum has a peak at λ = 572 nm.

Increasing of the concentration of Rhodamine 6G leads to decreasing of absorbance of monomers band. At the same time appearing of new maximum at the short-wavelength part of spectrum (curve 2) as a result of formation of dimer of dye was registered. Absorption of dimers leads to broadening of the absorption spectrum. The half-width of absorption band of monomers is equal to $\Delta\lambda^{abs}_{1/2} = 42\,nm$. Absorption band of dye broadens to the value of $\Delta\lambda^{abs}_{1/2} = 54\,nm$ with the growth of dye concentration. Increasing in concentration of dye molecules in the pores leads to quenching of fluorescence of Rhodamine 6G (curve 4). Obtained data is typical for concentrated liquid and solid solutions of Rhodamine 6G and conforms to results of other works [19, 20].

Thus, observed changes of the absorption and fluorescence spectra evidence that in molecular aggregation occurs in nanoporous alumina upon increasing of the number of adsorbed molecules in the pores of alumina oxide.

The dependence of fluorescence intensity of the phosphor on the amount of dye molecules adsorbed within the pores of the alumina was shown in Fig. 4.

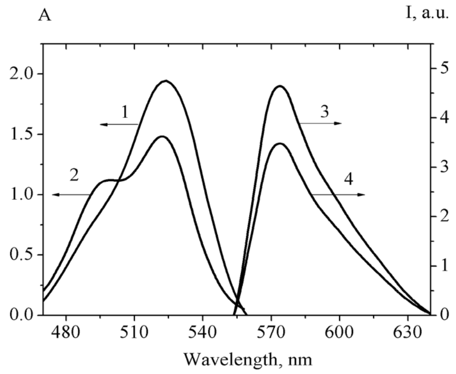


Fig. 3. The absorption and fluorescence spectra of Rhodamine 6G in the matrix of nanoporous alumina.

The figure shows that the fluorescence intensity of the dye (λ = 572 nm) with increasing concentration in the pores increases to a certain critical value, after reaching a critical concentration the fluorescence intensity decreases. The optimal time of the dye adsorption under which the fluorescence intensity has a maximum value was 5 hours. At this time, the amount of molecules adsorbed into the pores of the aluminum oxide was $0.36*10^{14}$ mol/m^2. Decrease in fluorescence intensity over a critical concentration is associated with the development of the process of aggregation of the dye molecules [19].

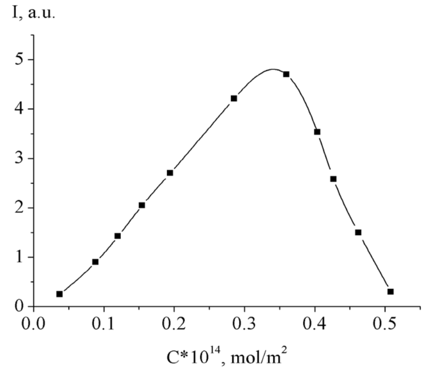


Fig. 4. Intensity dependency (λ_{reg} = 572 nm) of fluorescence dye on the concentration of adsorbed molecules.

The quantum yield of dye fluorescence molecules (F_{fl}) in the pores of alumina was determined by a relative method [21]. As reference was used an ethanol solution of Rhodamine 6G (F_f = 0.94 [22]). In the pores of alumina fluorescence quantum yield of Rhodamine 6G was F_f = 0.78, which is more than the quantum yield of luminescence of the dye in the matrix of methylmethacrylate (F_f = 0.53 [23]) and epoxypolymer (F_f = 0.67 [24]).

Stimulated emission of the dye molecules in the film of anodized aluminum is obtained at the maximum of the fluorescence band (Fig. 5). As seen in Fig. 5, at the power density of the pump source equal to 0.2 MW/cm^2 we see only the spectrum of the laser-induced fluorescence of the dye (curves 1, 2). To achieve the power of the pump source about 0.4 MW/cm^2 on the background of laser induced fluorescence spectrum the narrow band with a maximum at 572 nm wavelength (curve 3) appears, which refers to the band of the laser emission. Further increase in the power density of the pumping source leads to a narrowing of the excitation of the fluorescence spectrum and lasing band development. Reaching the pump power density 0.8 MW/cm^2 the component of stimulated emission prevails over spontaneous emission (curve 4), but to eliminate spontaneous emission component in the spectrum of stimulated emission completely is not possible. Table 1 shows the lasing characteristics of Rhodamine 6G in nanoporous alumina.

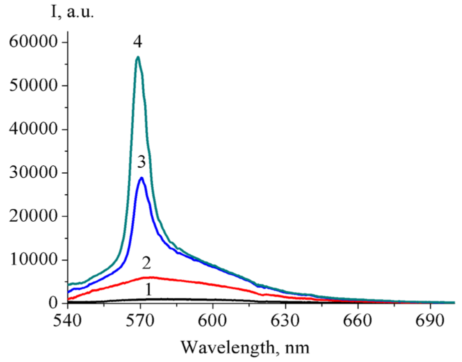


Fig. 5. The fluorescence decay kinetics of Rhodamine 6G molecules in nanoporous alumina (1) and in ethanol solution (2).

Table 1

Lasing characteristics of Rhodamine 6G in nanoporous alumina

The density of the pumping power, MW/cm^2	The lasing threshold, MW/cm^2	λ_{gen}, nm	$\Delta\lambda_{1/2}$, nm	I_{max}, a.u. (λ_{reg}=572 nm)
0.04	0.35	-	64	1042
0.2		-	56	5971
0.4		571	14	28885
0.8		571	9	56860

From the emission spectra, obtained in the course of the experiment, the dependences of intensity of fluorescence of the film were plotted as the function of the pump power density (Fig. 6a,b) and thresholds values of pumping of film were determined. Narrowing of the emission band with increasing excitation intensity indicates the predominance of stimulated emission over spontaneous emission, i.e. the system transfers to generation mode (Fig. 6a). Lasing threshold values were determined by an abrupt change in the growth rate of the emission intensity of the film. Lasing threshold at excitation λ_{gen} = 532 nm is an average about 0.35 MW/cm^2 (Fig. 6b).

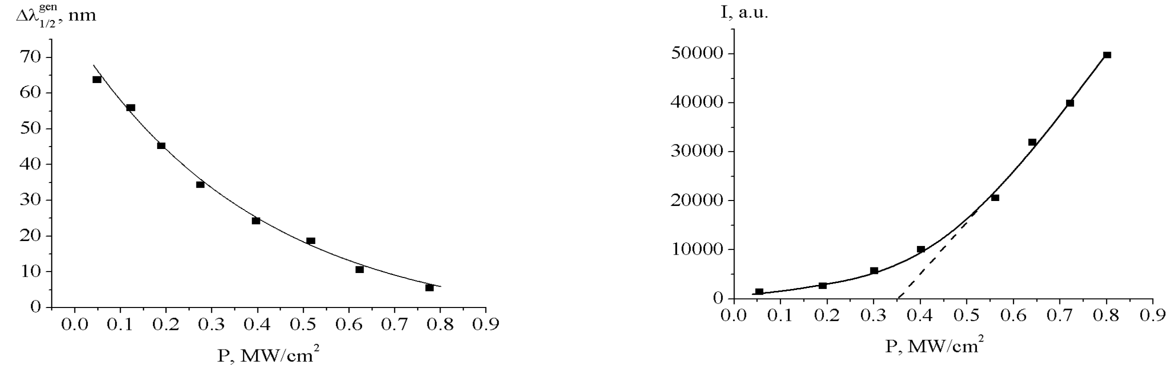


Fig. 6. The lasing spectra of Rhodamine 6G molecules in nanoporous alumina at different pump power densities: 1– P = 0.04 MW/cm^2; 2 – P = 0..2 MW/cm^2; 3 – P = 0.4 MW/ cm^2; 4 – P = 0.8 MW/cm^2.

Conclusion

Thus, in this work the luminescent properties of anodized aluminum oxide films with high-ordered structure, doped with Rhodamine 6G dye molecules were investigated. The fluorescence quantum yield of the dye in the matrix of the alumina is 0.78. Generation of stimulated emission of Rhodamine 6G molecules in the film of anodized aluminum oxide was obtained. It's determined that under excitation of the samples with the pump source power density of 0.1 MW/cm^2 the spectrum of laser- induced fluorescence of the dye is only observed. To achieve the power of the pump source about 0.35 MW/cm^2 on the background of laser induced fluorescence spectrum the narrow band laser oscillation with a peak wavelength of 572 nm appears. Threshold of the dye generation in the film is equal to 0.35 MW/cm^2.

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