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# Study lasing properties of Rhodamine 4c dye in the pores of anodized aluminum

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**Abstract.** In this paper we study the spectral and luminescent properties of the Rhodamine 4C in porous anodic alumina matrix. It was the excitation of anodic aluminum oxide films doped with Rhodamine 4C molecules second harmonic of a Nd: YAG laser with a power of 0.8 mW/cm$^2$ on the background of the spectrum of spontaneous fluorescence appears band of stimulated emission with a peak of wavelength in 620 nm.

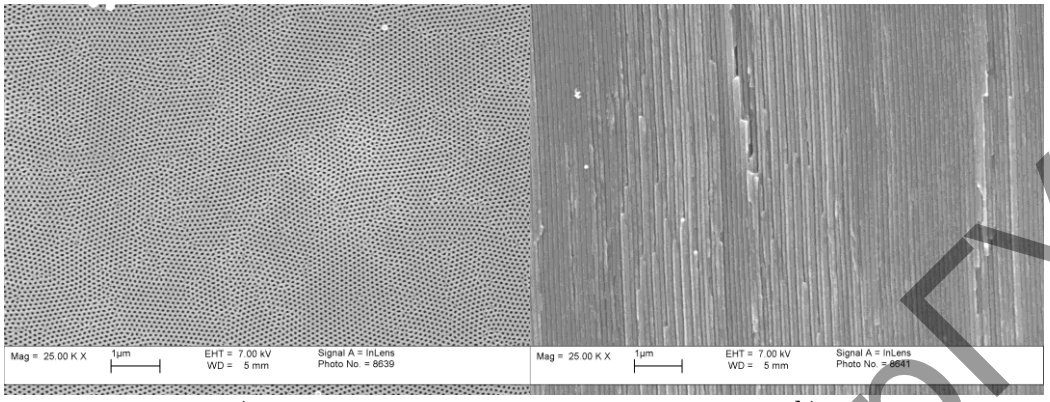
## 1. Introduction

Currently, active research in obtaining of lasing nanostructured materials doped with the laser dye [1-4] are performed. Dye molecules are deposited on the surface of the nanoparticles [5,6], or embedded in the nanoporous structure [7,8]. Cylindrical microcavities in such structures can maintain high quality mode due to the effect of total internal reflection of electromagnetic waves from the cavity walls [9]. Intensity of radiation processes are enhanced due to the effective concentration of the electromagnetic field inside the microcavity [10]. In the case of filling of microcavities with the laser dye, such system can be used as active medium for tunable laser. In this aspect, one of the promising materials, which can be used as the active medium is a porous anodic aluminum oxide doped with a laser dye. Structure of anodic aluminum oxide films is a system of ordered close-packed pores. The pores are perpendicular to the film surface, and the diameter and spacing can be varied by changing of the anodization conditions [11].

## 2. Experimental

This paper presents the results of a research of transformation of the spontaneous fluorescence to stimulated emission of Rhodamine 4C molecules embedded in porous anodic aluminum. Anodizing of aluminum was carried out in a two-electrode electrochemical cell using a DC power source MPS-7081. Auxiliary electrode was a platinum plate and polished aluminum foil was used as the working electrode. The electrolyte was obtained on the basis of deionized water that was purified with AquaMax 360 Basic system. The resistivity of the water was 18.2 M Ohms /cm.

The aluminum oxide matrixes are separated from unreacted aluminum by selectively dissolving of the latter in solution of $CuCl_2$ in HCl. The surface morphology and cross-cleaved samples, obtained with scanning electron microscope Leo Supra 50VP are presented on figure 1 The measurements were performed at an accelerating voltage of 7 kV in the high vacuum. The pores of ~ 50 nm diameter and the distance between the pores of about 105 nm are observed on the film surface (Figure 1a). On cross-cleaved sample parallel lines channels located perpendicular to the surface are observed (Figure 1b).




a) b)

**Fugure 1.** SEM images of porous anodic aluminum oxide film obtained by a two step anodizing: a) the surface of the oxide film after removal of the barrier layer, b) a cross-section.

Sorption of Rhodamine 4C molecules into the pores was carried out by keeping the porous aluminum in solution of dye with concentration C = 0.1 mMol within 3 hours, followed by drying the film in an oven at 100 °C for 1 hour. Measurement of absorption and fluorescence spectra of Rhodamine 4C in a film was carried on a spectrophotometer CM2203 (Solar).

**3. Results and discussion**

Figure 2 shows the absorption and fluorescence spectra of molecules of Rhodamine 4C embedded in a porous alumina. It can be seen that the absorption band of the dye in the matrix has a maximum at a wavelength of $\lambda_{max}$ = 550 nm. Photoexcitation of the dye fluorescence was carried at a wavelength equal to $\lambda$ = 530 nm. The fluorescence spectrum has a maximum at a wavelength of $\lambda$ = 578 nm. The quantum yield of fluorescence ($\Phi_{fl}$) Rhodamine 4C in the pores of the alumina was determined by using an absolute Reflectometric sphere AvaSphere-50-REFL (Avantes BV). The accuracy of determining the fluorescence quantum yield is not more than 5%.

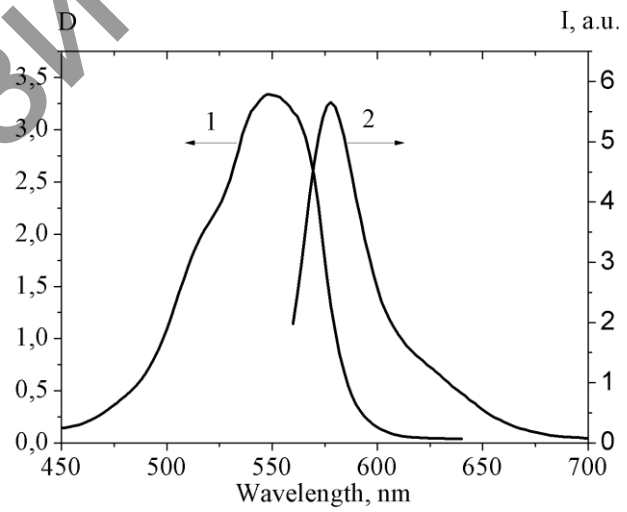
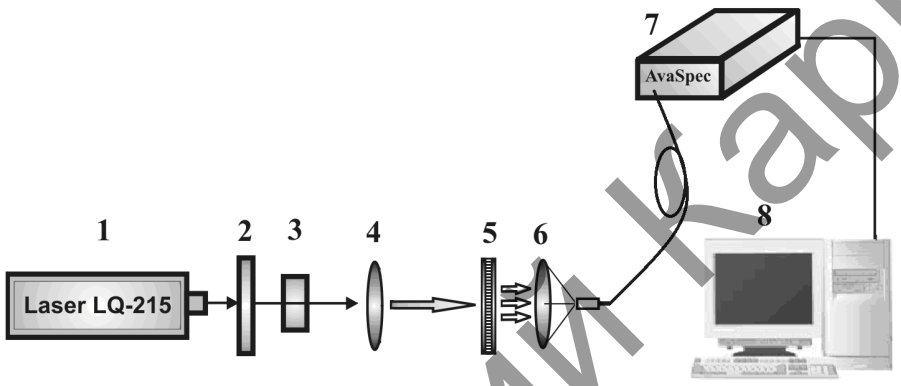



**Figure 2.** The absorption (1) and fluorescence (2) spectra of Rhodamine 4C in the porous of alumina.

Quantum yield of Rhodamine 4C fluorescence in pore alumina, defined by de Mello method for calculating of absolute quantum yield of mixed systems [12], was equal to $\Phi_{fl}$ = 0.3.

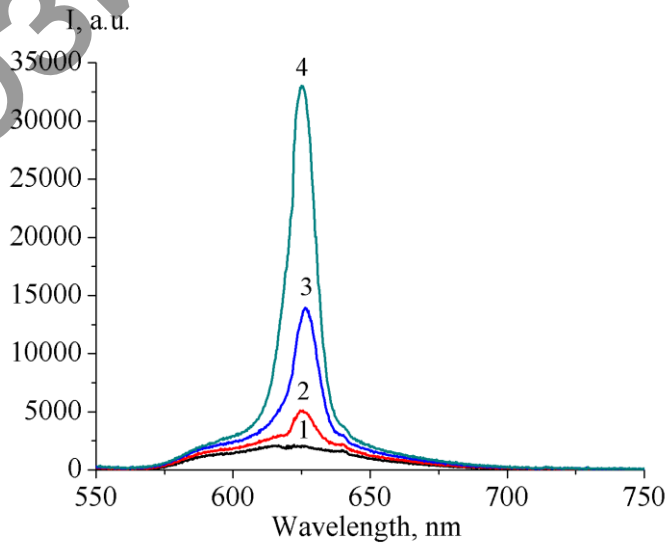
The measurement of the stimulated emission spectra of films was carried out on the special facility, its scheme is shown in Figure 3. The spectra were measured in the excitation of the samples by the second harmonic of Nd: YAG laser (1) (SOLAR LQ 215, $\lambda_{gen}$ = 532 nm, $E_{pulse}$ =90mJ, $\tau_{duration}$ = 10 ns) in the longitudinal version. The pumping radiation, after passing a diaphragm (3) with a lens (4) then focused on the surface of the film (5) in form of strip with area about 0.1 $cm^2$. Pump power density was varied using neutral density filter (2) and was 0.01-1 MW / $cm^2$. Stimulated emission using a converging lens (6) focused on the input fiber of spectrometer AvaSpec-2048. Stimulated emission spectra were measured on spectrometer AvaSpec-2048 (7), connected to a computer (8). The relative error in the determination of the spectra was 3%.




1– laser LQ 215; 2– neutral density filters; 3– diaphragm; 4, 6– converging lens; 5– test sample; 7– spectrometer AvaSpec-2048; 8– computer

**Figure 3.** The scheme of facility for investigation the properties of thin films stimulated emission.

Stimulated emission of the dye molecules in the anodic aluminum oxide film was obtained in the long-wavelength band of the fluorescence spectrum (Figure 4). With the power density of the pump source till 0.04 mW/$cm^2$ the only stationary fluorescence of dye was observed in the pores as seen in Figure 4, curve 1.




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/$cm^2$

**Figure 4.** The emission spectra of Rhodamine 4C molecules in anodic alumina at different pump power density.

When the power source of the pump reached 0.2 MW/cm$^2$ a narrow band of stimulated emission with a wavelength peak 625 nm appeared on the background of the fluorescence spectrum (curve 2). A further increase in the power density of the pump source increased the intensity and narrowing of the stimulated emission band (Figure 4, curves 3-4). When the density of the pump power was 0.8 mW/cm$^2$ the component of stimulated emission prevailed over spontaneous emission component (curve 4), however, completely eliminate the spontaneous emission component was not possible. The appearance of stimulated emission when using low quality resonator containing two glass plates due to the fact that the walls of cylindrical pores of the matrix acts as microresonators in addition to the Fresnel reflection from two glass plates in studied system.

Due to the effect of total internal reflection of electromagnetic waves from the walls of the pores the high energy density of the electromagnetic field concentrated in the microcavity, that greatly strengthens the emission intensity of the dye molecules in the pores.

Dependence of the half-width of the emission band ($\Delta\lambda_{1/2}$) and the luminescence intensity of the film versus the pump power density of stimulated emission spectra were obtained (Figure 5 a, b).

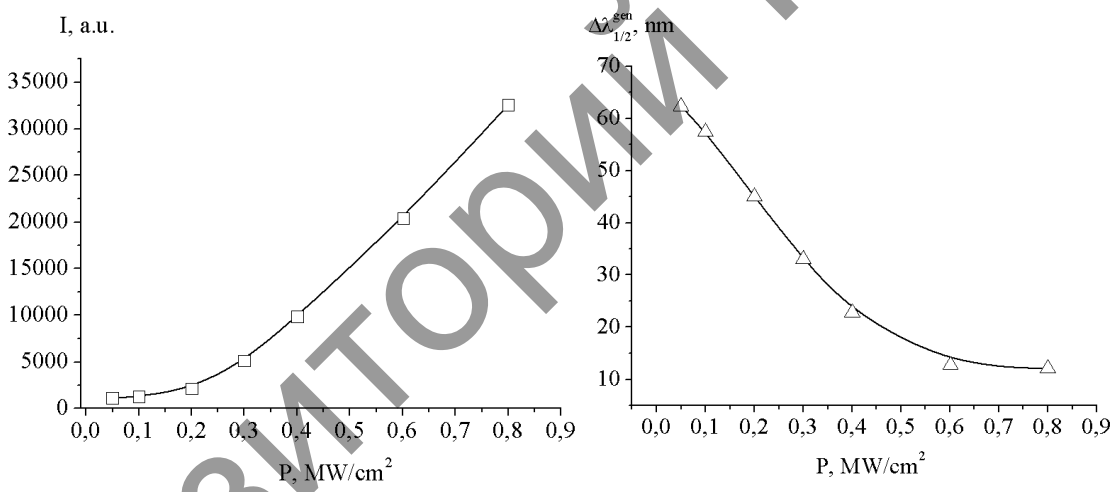



**Figure 5.** Dependence of the stimulated emission intensity (a) and its half-width (b) via the pump power density.

When changing the pump power density from 0.1 to 0.8 MW/cm$^2$ the intensity at the maximum of emission spectrum is increased by almost of 35 times, and $\Delta\lambda_{1/2}$ decreases of 6.5 times. The narrowing of the emission band with increasing of excitation intensity indicates about the prevalence of stimulated emission over the spontaneous emission, and reveals that the system pass into generation mode. Further increase in the power density of the pumping source leads to a narrowing of the band of generation and increase of its intensity. Threshold of stimulated emission was determined on a tangent in Figure 5 (a) and equal to 0.2 MW/cm$^2$.

These results demonstrate the potential use of the porous alumina for developing of active elements of quantum electronics.

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