Selective mode excitation in dye-doped DNA polyvinyl alcohol thin film

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A solid-state laser based on a dye-doped deoxyribonucleic acid (DNA) matrix is described. A thin solid film of DNA has been fabricated by treating with polyvinyl alcohol (PVA) and used as a host for the laser dye Rhodamine 6G. The edge emitted spectrum clearly indicated the existence of laser modes and amplified spontaneous emission. Lasing was obtained by pumping with a frequency-doubled Nd:YAG laser at 532 nm. For a pump energy of 10 mJ/pulse, an intense line with FWHM ≈0.2 nm was observed at 566 nm due to selective mode excitation. © 2009 Optical Society of America

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1. Introduction

The continued development of photonics technology is crucially dependent on the availability of suitable optical materials. Biomaterials are emerging as an important class of materials for a variety of photonic applications [1,2]. From the rich world of organic materials, biomaterials are of particular interest as they often have unusual properties that are not easily replicated in conventional organic or inorganic materials in the laboratory. Furthermore, natural biomaterials are a renewable resource and are inherently biodegradable [2]. The most important and famous biomaterial known to man is deoxyribonucleic acid (DNA), the polymeric molecule that carries the genetic code in all living organisms. It is clear that the unique structure of DNA results in many optical and electronic properties that are extremely interesting for photonic applications [1].

The importance of organic solid-state lasers using variety of host and lumophore combinations were discussed in various reviews [3–7]. Organic materials, in particular, offer advantages such as ease of processing, which permits the fabrication of devices in virtually any shape and potentially at a very low cost. The combination of the tunability and high efficiency of laser dyes with the high power density that can be easily achieved in waveguide structures make devices based on dye-doped organic material waveguides and fibers very promising [3,4]. There have been numerous investigations on laser emission from polymer planar microcavities [5,6] and polymer microring lasers, as well [7]. Recently, a tandem organic light-emitting diode structure, excited electrically in the pulsed domain and confined within a double interferometric configuration, was observed to emit a low-divergence beam with a near-Gaussian spatial distribution. The emission originates from the laser dye Coumarin 545 T used as dopant [8].

There have been numerous investigations on lumophore-doped DNA and laser emission from solid-state thin film of DNA as well. For example, Kawabe *et al.* [9] reported a synthesis and film formation method of complexes composed of DNA, lipid, and Rhodamine 6G and observed amplified spontaneous emission (ASE) from relatively highly doped DNA films under pulsed-laser excitation. DNA–cetyltrimethylammonium (CTMA) thin-films doped with the luminescent dye sulphorhodamine (SRh)

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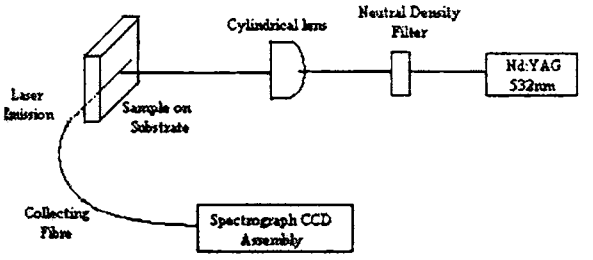

Fig. 1. Schematic diagram of experimental setup.

have been reported to exhibit photoluminescence intensity more than an order of magnitude higher than that of SRh in poly(methyl methacrylate), which is a popular polymer host [10]. Other lumophores have also been reported to luminescence very efficiently in DNA thin films [11,12].

We have been working on various photonic-based applications of dye-doped biomaterials [13,14]. It has been found that dye fluorescence can be used to study the kinetics of bacterial colony [13]. Here we report the observation of multimode laser emission from a transversely pumped polyvinyl alcohol (PVA)–DNA blended film doped with Rhodamine 6G. PVA has excellent film forming, emulsifying, and adhesive properties. Since DNA and PVA are water soluble, it is very easy to make thin film of a DNA–PVA mixture by allowing it to get dry. In the DNA–PVA system we incorporated Rhodamine 6G dye, which is frequently investigated to characterize solid-state dye lasers in

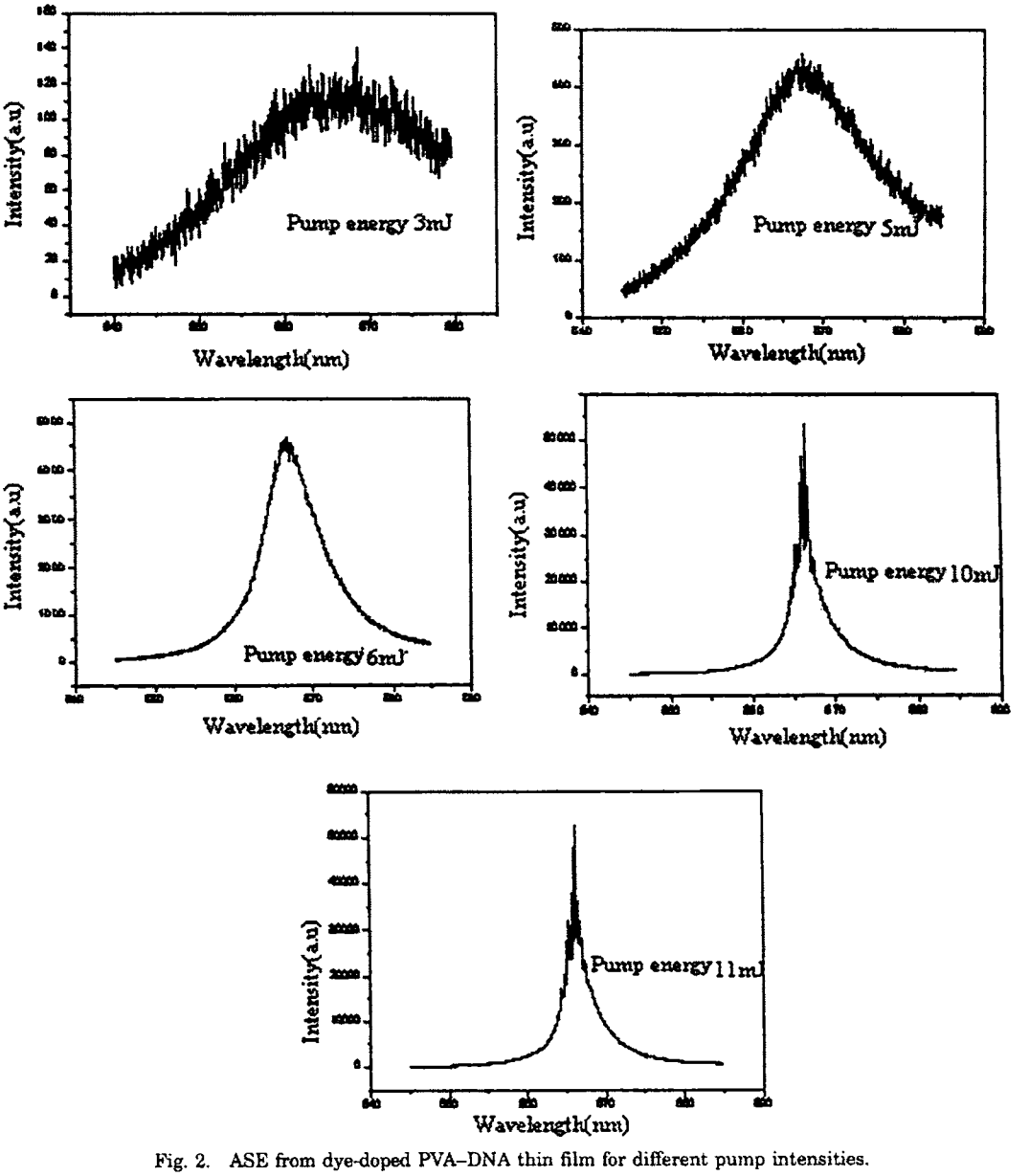

Fig. 2. ASE from dye-doped PVA–DNA thin film for different pump intensities.

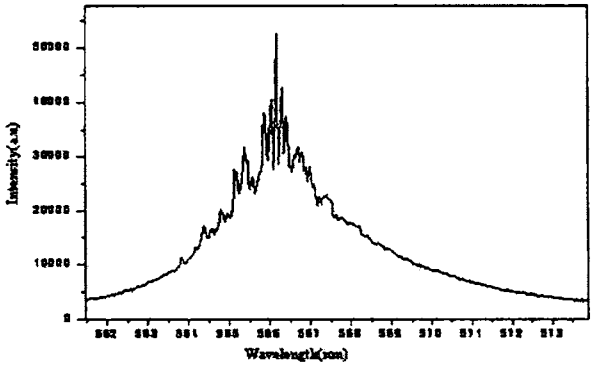

Fig. 3. Laser modes with a spacing of 0.2 nm from a dye-doped DNA–PVA thin film.

a variety of solid hosts, on account of its high fluorescence quantum yield, low intersystem crossing rate, and low excited state absorption at both pump and lasing wavelengths [15].

2. Experimental Methods

A PVA solution of 8 wt% concentration was prepared by dissolving a certain amount of PVA into distilled water at 80 °C under continuous stirring for 3 h. A 1.5 wt% DNA solution was prepared in water by dissolving DNA in distilled water in which Rhodamine 6G dye at a concentration of 2×10^{-3} M was added. The PVA and DNA solutions were then mixed for 4 h. After mixing the solutions, the film waveguides were fabricated on glass substrates by the dip coating technique. These films show best optical transparency in the visible spectral range. Film thickness can be varied either by changing the viscosity of the solution or by increasing the number of coating layers. We have used a film of thickness 530 μm for the study.

Figure 1 shows a schematic diagram of the experimental setup. The samples were transversely pumped using 10 ns pulses from a frequency-doubled Nd:YAG laser (532 nm, 10 Hz). A set of calibrated neutral-density filters was used for varying the pump energy. The laser beam was focused onto a stripe shape on the samples from a normal incident angle using a cylindrical lens. The size of the strip was typically 1 mm × 4 mm. The fluorescence emission from the sample was collected from the edge by a fiber and directed to a spectrograph coupled with a cooled CCD array. The distance between the collecting fiber and the waveguide edge was 1 cm. We kept one end of the excitation strip at the edge of the waveguide. The intensity of fluorescence emission measured as a function of pump pulse energy. This helped us to determine the threshold energies and confirm the spectral narrowing of the emission spectra as the excitation intensity was enhanced.

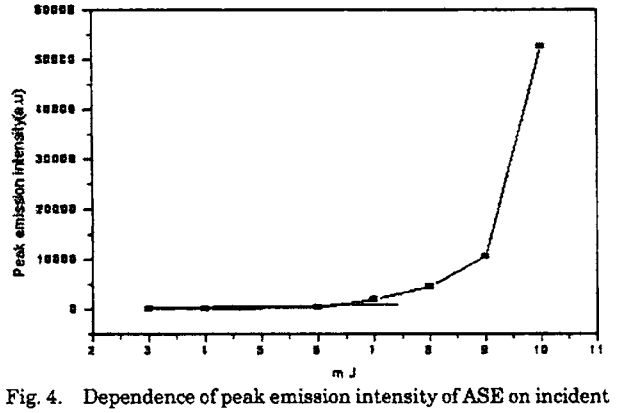

Fig. 4. Dependence of peak emission intensity of ASE on incident pump energy.

3. Results and Discussion

To study the nature of emission from the dye-doped DNA–PVA blended film, the emission spectra are recorded for various pump intensities starting from 3 mJ/pulse. Figure 2 shows the emission spectra recorded for different values of pump energy. At lower pump intensities, fluorescence spectra are broad with a spectral width of 25 nm. Amplification of the light emission and spectral narrowing are observed when the pump intensity is gradually increased. To understand the nature of amplified spontaneous emission (ASE) in detail, the dependence of peak emission intensity on incident pump intensity is studied (Fig. 4). As is evident from the plot, threshold pump energy of around 6 mJ/pulse is observed for the occurrence of ASE. Similar observations were made by previous workers also [9–12]. However, in contrast to the reports available in the literature, we observed mode structure at higher pump power (Fig. 3). It is observed that at higher pump power one mode selectively gets excited to high intensity with a narrow width of about 0.2 nm.

Laser emission requires an external feedback. In the present structure, there are no external mirrors

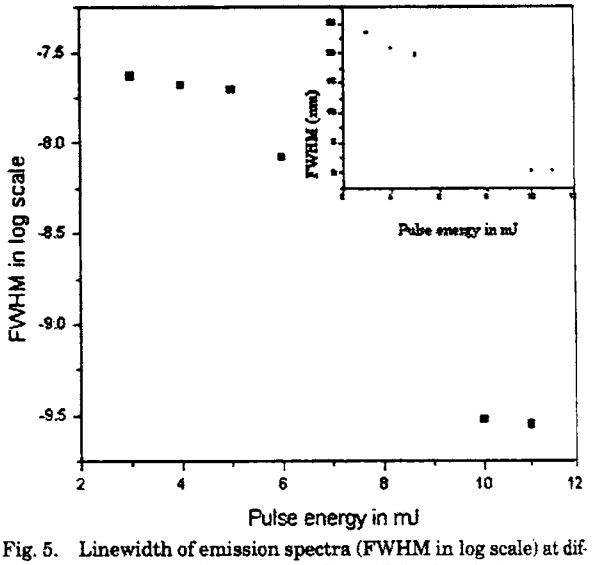

Fig. 5. Linewidth of emission spectra (FWHM in log scale) at different pump energy levels. Inset: linewidth of emission spectra (FWHM in normal scale) at different pump energy levels.

to provide the feedback. Lasing studies are performed in the film along with the substrate. With this arrangement the film acts as an asymmetric waveguide with air and glass on both sides of the film. The Fabry–Perot-like behavior of an asymmetric thin-film waveguide was explained to be quite similar to that of thin-film microcavities [5,16]. It is interesting to note that the spacing of sharp peaks in Fig. 3 matches with the mode spacing calculation. Considering the sample geometry and pumping scheme, the modes of this cavity are analogous to the transverse modes of a Fabry–Perot type cavity. Thin-film structure can be modeled as a serially connected Fabry–Perot etalon. In this case, stimulated emission occurs in the direction along the stripe [17]. Both the stimulated emission along with the propagation in the guiding gain medium and the feedback at the lateral faces induces high gain for laser action. The system can also be thought of as a distributed feedback (DFB) device. The mode spacing at λ can be calculated using an equation for mode spacing in a Fabry–Perot cavity, namely,

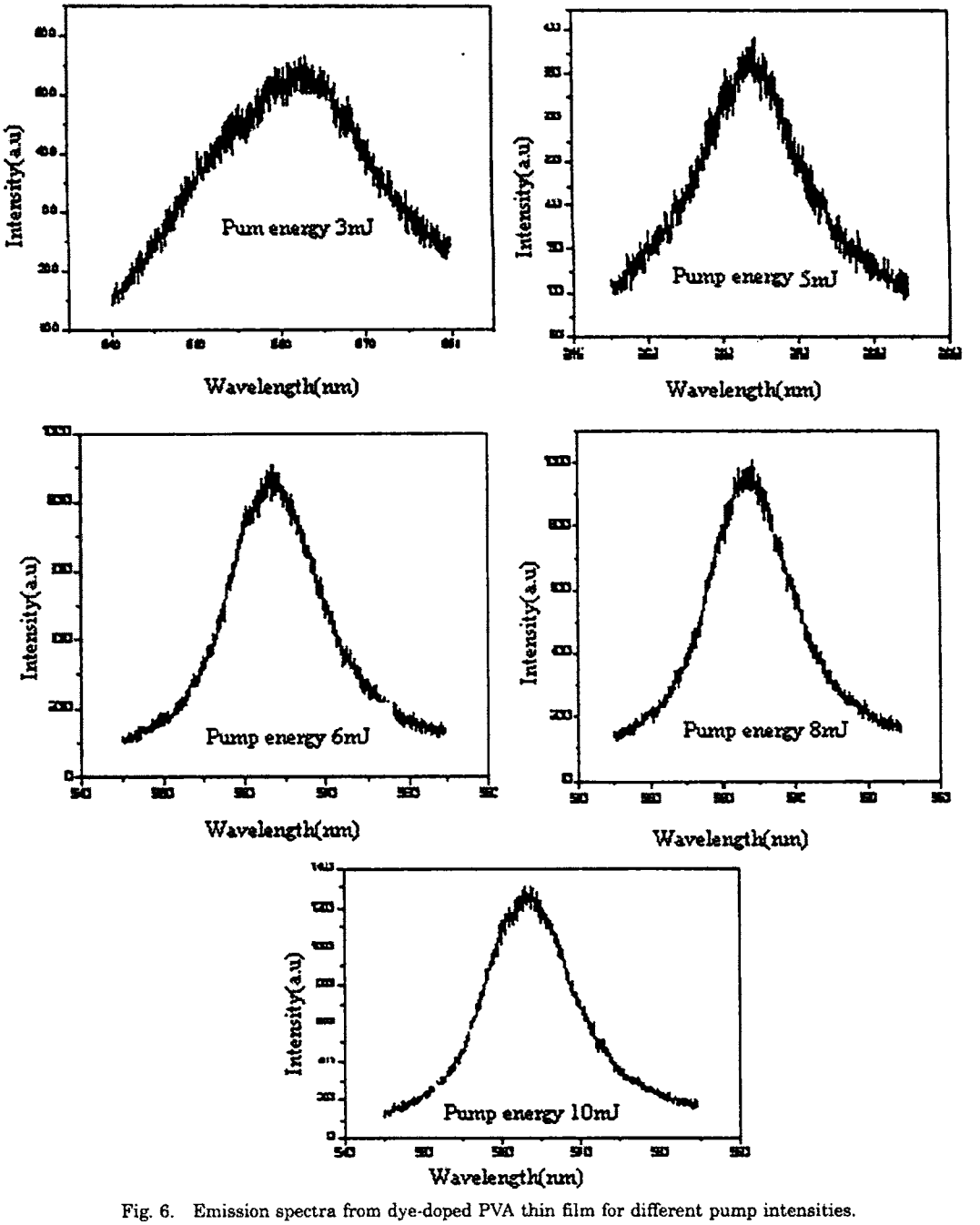

Fig. 6. Emission spectra from dye-doped PVA thin film for different pump intensities.

$$\Delta\lambda = \frac{\lambda^2}{2nL}, \quad (1)$$

where λ is the wavelength of the strongest emission line, n is the refractive index, and L is the length of the resonator cavity. In the present case, the length of the Fabry–Perot cavity corresponds to the thickness of the polymer film with the values for λ, n, and thickness as 566 nm, 1.5, and 530 μm, respectively. We get the mode spacing as 0.201 nm, which is the same as the observed value 0.2 nm.

The spectral width of the emission (FWHM) is summarized in Fig. 5 as a function of pump energy. It is clear from the figure that the linewidth converges to 0.2 nm in the strong pumping region. This value is also found to be very small when compared with other dye-doped DNA matrices [9–12].

To study the effect of DNA as a host material for thin-film lasers, we performed the same experiment on dye-doped PVA film under the same experimental conditions. Although the film showed strong fluorescence under the same pumping condition, mode structure is absent (Fig. 6), even though there is a tendency to reduce linewidth in the fluorescence emission spectra. By comparing Figs. 2 and 6, it is clear that DNA plays an important role in laser emission. Many fluorescent dyes can readily be intercalated into helices of DNA. These dye molecules can be situated inside the double helix structure or at some grooves beside the main chains. Because of the intercalation or groove binding of dyes in the DNA strand, molecules get isolated from each other, thereby reducing the fluorescence quenching caused by aggregation [1,3]. The ASE not only depends on the type of host material, but on the quality and morphology of the films. In our case, morphology of the PVA film may be modified by adding DNA, which may favor the ASE.

4. Conclusion

A DNA–PVA matrix has been found to be an excellent host material for the laser dye Rhodamine 6G. We have observed multimode laser emission from transversely-pumped dye-doped DNA–PVA blended film. Reflections from the lateral faces of the film provided optical feedback. This, together with the guidance through the gain medium, gave rise to intense narrow emission lines. For pump energy of 10 mJ/pulse, an intense line with a FWHM was observed at 0.2 nm due to energy transfer from other modes. This value is found to be very small when compared with other dye-doped DNA matrices.

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