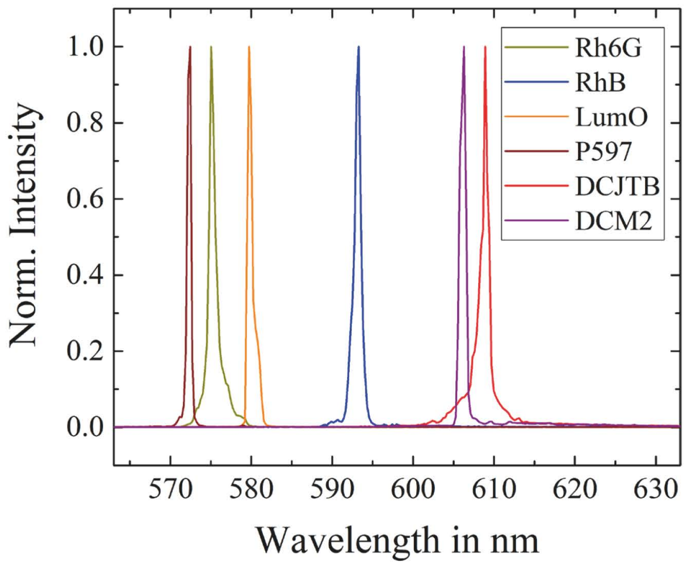
Pen Yiao Ang

Organic Dye-Doped PMMA Thin-Film Laser



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Journal

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- S. Spelthann, S. Unland, J. Thiem, F. Jakobs, J., Kielhorn, P. Y. Ang, H.-H. Johannes, D. Kracht, J. Neumann, A. Ruehl, W. Kowalsky, D. Ristau. "Towards Highly Efficient Polymer Fiber Laser Sources for Integrated Photonic Sensors." *Sensors* 20.15 (2020): 4086.

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- P. Y. Ang, J. Kielhorn, F. Jakobs, W. Kowalsky, H.-H. Johannes. "Lumogen-doped polymer fibers", *Drittes Deutsches POF-Symposium 2020*, Tewiss Verlag, 2020, ISBN: 978-3-95900-442-8

Conferences

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Abstract

Organic dye laser stands a chance to become the next generation of the light source. It is very interesting because organic dyes can cover a wide range of the spectrum of visible light. To realise organic solid-state laser, several organic dyes can be doped in a polymer matrix. One of the examples of low-priced polymer is poly(methyl methacrylate) (PMMA). However, the study of PMMA as a polymer matrix for organic dyes as a thin-film laser was not extensive. This thesis focused on the feasibility of organic dye-doped PMMA as a thin-film laser.

Six different sample structures were suggested to determine the best sample model with the best lasing properties. First, the structure consisted of a merely dye-doped thin-film. In the second design, a grating structure was built directly on top of the gain medium. Third, the dye-doped thin-film was covered with a layer of photoresist, EpoClad. In the fourth design, the grating structure was established on top of the gain medium and enclosed by the EpoClad layer at the same time. Next, the dye-doped thin-film was sandwiched between the substrate and the EpoClad layer in the fifth design, in which the grating structure was produced on top of the EpoClad layer. In the sixth design, the dye-doped PMMA was spin-coated on top of an EpoClad layer with a grating structure. Lasing properties like narrowing of Full Width at Half Maximum (FWHM) and a clear lasing threshold were focused. In this experiment, Rhodamine 6G was selected as the dye-dopant for PMMA thin-film because it was commonly used for fiber lasers. It was discovered that the fifth design presented the best performance with the smallest FWHM, the highest polarisation extinction ratio (PER) and the highest output energy. To ensure good lasing performance, the thickness of the EpoClad layer and the Rhodamine 6G doped PMMA layer was manipulated. The best sample structure had an EpoClad layer thickness of 661 nm and a PMMA layer thickness of 1200 nm. With the sample model, further experiments proceeded.

On top of the detection of a small FWHM and a clear lasing threshold, changes of the gain medium and the resonator should be proceeded to assure the laser state. At first, the Rhodamine 6G concentration in PMMA was varied to check its influence. When the dye concentration was too low (100 ppm), no lasing properties were determined. The best result was measured by the sample doped with 400 ppm Rhodamine 6G concentration. Therefore, the dye concentration was fixed at 400 ppm for further experiments. Second, changes in the grating period of the grating structure on the sample would influence the lasing properties because the grating structure functioned as the resonator. Lasing properties were observed when the grating period was in the range from 370 nm to 390 nm. With the variation of grating periods, a 25 nm of wavelength shift was measured.

Moreover, the workability of PMMA with other organic dyes was also investigated. It was noticed that there were in total six organic dyes, which could function well with PMMA as an organic dye laser. They were Rhodamine 6G (Rh6G), Rhodamine B (RhB), Lumogen Orange (LumO), Pyrromethene 597 (P597), 4-(Dicyanomethylene) -2-tert-butyl-6- (1,1,7,7-tetramethyljulolidin-4-yl-vinyl)- 4H-pyran (DCJTB) and 4-(Dicyanomethylene)-2-methyl-6-julolidyl-9-enyl-4H- pyran (DCM2). By using these dyes, the laser peak

wavelength was found at the range from 572 nm to 609 nm. Among these dyes, Pyrromethene 597 doped sample showed the best result with a peak wavelength of 572.45 nm, a FWHM of 0.57 nm, a lasing threshold of 0.253 µJ, a PER of >30 dB, and an output energy of 18 nJ. The P597 doped sample was modified to detect sugar solution. When the sugar concentration increased from 0wt % to 40wt %, a 4 nm of wavelength shift was detected.

It can be concluded that an organic dye-doped PMMA thin-film can work as an organic dye laser. The best sample design was found, in which the dye-doped PMMA thin-film was sandwiched in between the substrate and the EpoClad layer, where the grating structure was built on top of the EpoClad layer. A narrow FWHM (<1 nm) and an obvious lasing threshold were observed. The lasing properties were affected by the modification of the gain medium and the resonator. Six various organic dyes could be doped in PMMA to function as an organic dye-doped PMMA thin-film laser. The sample stood the potential to detect e.g. sugar concentration. Further experiments should be carried on for more applications.

Contents

1 Introduction

The role of organic materials is essential in our daily life. In former times, the only possibility to achieve light was to ignite woods or oil, which are organic materials. Nowadays, organic semiconductors have gained extensive attraction due to their large-area and low-cost fabrication. Besides, the optoelectronic properties of organic semiconductors can be easily tuned by their convenient molecular design, which increases their potential to be applied in various kinds of electronics products.

Organic semiconductors are been an important material for numerous devices such as organic light-emitting diodes (OLEDs) [1–3], organic solar cells (OSCs) [4, 5], organic thin-film transistors [6, 7] and organic solid-state lasers (OSSLs) [8, 9]. Since there is high interest in the industry and technology field, a variety of organic semiconductors have been researched. Especially, OLEDs are been strongly promoted into commercial applications as the display of smartphones and televisions. OSSLs have the possibility to be another organic light emitter. Yet, it is still a young and challenging research topic. OSSLs provide another new horizon for simple, low-cost, time-saving, versatile, and environmentally-friendly fabrication of new and desirable laser structures. There is numerous literature about OSSLs. Diverse application fields have been found, such as lab-on-chip spectroscopy [10], absorption and transmission spectroscopy [11, 12], data/optical communication [13], refractive index sensor [14], vapour pressure detector [15] and etc.

The first-ever OSSL was discovered in 1967 when Rh6G doped in poly(methyl methacrylate) (PMMA) was found to be an organic gain medium [16]. Afterwards, much effort was done into this topic. One of the organic semiconductor lasers (OSLs) was reported, in which the materials were anthracene in doped and non-doped single crystals [17]. The first thin-film OLED was proposed by Tang and Van Slyke in 1987 [18]. This significant achievement of OLEDs contributes to a better understanding of the structural design and functions of organic materials. Subsequently, this leads to the significant development of OSLs. In 1996, Friend and Heeger introduced an OSL based on conjugated polymers by using poly(p-phenylenevinylene) (PPV) and PPV derivatives as gain medium [19, 20]. Later, Samuel's group introduced a polymer laser pumped by LED, in which a fluorene copolymer was used as the gain media [21]. In 2009, a deep-blue laser with a very low lasing threshold and high slope efficiency using monodisperse starburst macromolecular semiconductor as emitter was proposed [22]. A few years later, Gather et al. discovered the first observation of lasing behaviour in a living system with green fluorescent protein [23]. Recently, Adachi et al. demonstrated a quasi continuous-wave OSL based on near-infrared thermally activated delayed fluorescent emitters and the possibility of an electrically pumped organic laser [24–26]. Figure 1.1 shows the development milestones of organic gain media.

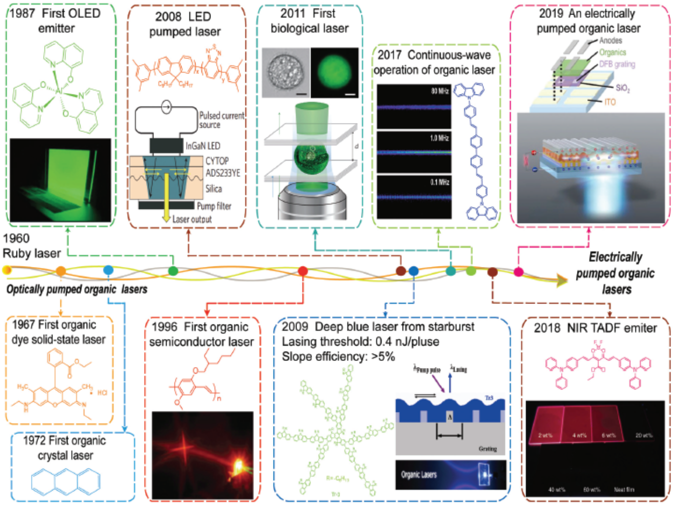

Figure 1.1: Timeline of development of organic main media.

To function as organic gain media, organic dyes have been dissolved in liquid solvents for the lasing purpose for decades [27]. However, this kind of operation can induce unnecessary evaporation of the solvents. To solve this problem, organic dyes can be doped in non-conjugated polymers, such as polystyrene (PS) and PMMA, which are suitable for OSSLs. This resulted laser is defined as organic dye lasers, which is quite similar to OSLs. According to Samuel el al., there are properties to make a division for organic semiconductors: (i) easy thin-film fabrication, (ii) high photoluminescence quantum yield (PLQY), and (iii) potential of charge transport [28]. There is abundant literature about organic dye lasers. It is observed that there are several sample designs for the dye-doped PS samples [14, 29–32]. On the other hand, the dye-doped PMMA samples were mostly based on only thin-film structure [33, 34].

In this work, the feasibility of organic dye-doped PMMA laser was studied. There were in total six different sample designs proposed to find out the sample model with the best performance. Next, the layer thickness of the gain medium and the resonator of the best sample model was manipulated to assure the outcome. Lasing properties like narrowing of Full Width at Half Maximum (FWHM) and lasing threshold were monitored. Besides, alternations of gain medium and resonator were performed to observe the effect on the lasing properties, in which the concentration of dye and the grating period were manipulated. Moreover, the workability of different organic dyes with PMMA was also determined. It was shown that organic dye-doped PMMA could function as a laser, which had an application potential.

2 General theory

In this chapter, one will get an overview of the general basics. At first, a short description of light propagation is elucidated here. Then, it is followed by a brief explanation of optical waveguides, which are an example of the medium for light propagation. Besides, general information about organic semiconductors is shown, as the material used in this research is mainly made up of organic material. Moreover, two important characteristics of organic materials are briefly described, which are the photoluminescence quantum yield and the fluorescence lifetime. Furthermore, a compact description of quenching is presented to understand the processes, which can reduce the intensity of fluorescence.

Every single section provides elementary theories, which provide adequate physics information for the readers to understand this work better. Detailed explanations can be found on the indicated references.

2.1 Light Propagation

Electromagnetic radiation can be defined as a form of energy. In this form of energy, all the waves of the electromagnetic field such as gamma rays, X-rays, ultraviolet radiation, visible light, infrared, radio waves, etc are included. According to Figure 2.1, visible light is only a very small portion of the total electromagnetic radiation. Based on the DIN 5031-7, visible light starts from 380 nm to 780 nm [35]. Radiation energy can be induced by the propagation of electromagnetic radiation, which can be calculated using the equation below:

$$E_{\mathrm{radia}} = h\upsilon = \frac{hc}{\lambda} = \frac{hc}{2\pi}k \tag{2.1}$$

whereas E_{radia} is the radiation energy, h is the Planck constant, υ is the frequency, c is the velocity of light in a vacuum, λ is the wavelength and k is the wavenumber.