Optical amplification and photodegradation in films of spiro-quaterphenyl and its derivatives

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ABSTRACT

Fluorescence spectra and optical constants in planar waveguides of spiro-quaterphenyl and two of its derivatives are investigated. Threshold of amplified spontaneous emission (ASE) and optical gain are determined. The thickness dependence of ASE spectral position, ASE threshold, and optical gain are investigated as well. Additionally, photodegradation in air and in vacuum for spiro-quaterphenyl and methoxy-spiro-quaterphenyl is compared. Films with various thicknesses (30–220 nm) have been deposited by vacuum vapor deposition. A measurement setup based on the variable stripe length method was used to determine the threshold and the optical gain using ASE. A threshold of $22 \pm 5.7 \, \mu J/cm^2$, $51 \pm 2.1 \, \mu J/cm^2$ and $70 \pm 10 \, \mu J/cm^2$ was measured for spiro-quaterphenyl, methoxy-spiro-quaterphenyl and phenoxy-spiro-quaterphenyl respectively. At pump energy fluence of $3000 \, \mu J/cm^2$, maximum gain of $107.5 \pm 7 \, cm^{-1}$, $104 \pm 6 \, cm^{-1}$ and $184 \pm 1.2 \, cm^{-1}$ was achieved for spiro-quaterphenyl, methoxy-spiro-quaterphenyl and phenoxy-spiro-quaterphenyl respectively.

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1. Introduction

First laser action from organic materials has been reported in the 1960s [1,2]. Using organic materials as active media in lasers features various advantages such as broad range of wavelength coverage from UV to IR by chemical modification of the organic material [3,4]. Among organic materials that provide laser action, organic semiconductors have high potential as an active medium for solid state lasers. They provide high photoluminescence quantum yield in solid state form without the need of a host material as compared to the laser dyes [5]. Therefore, thin laser devices with low cost fabrication techniques such as spin casting, thermal evaporation and ink-jet printing can be achieved using organic semiconductors [6].

One of the organic semiconductors, which provides good emission in the blue [7] and near UV [8] spectral region, is the class of oligophenyls. Further advantages of oligophenyls are large Stokes shifts, high fluorescence quantum yields and high morphological

stability of the amorphous form [7]. Furthermore, the maximum of the emission spectrum can be tuned by increasing the number of phenyl rings in the molecule [7]. This is making them ideal candidates for organic solid state lasers. However, the solubility of the oligophenyls especially in polar non-toxic solvents is low which limits their application when spin coating is applied [8]. By introducing a spiro linkage between two oligophenyl molecules, the solubility of the new molecule (spiro-oligophenyl) is enhanced. In the spiro-oligophenyl molecule, the parent molecules are arranged perpendicularly. Thus the interaction between them is minimized and the solubility is better compared to oligophenyl molecules [9,10]. Furthermore, the structure is rigid which increases the glass transition temperature (T_g) of the molecule and hence the stability of amorphous films is increased. This means, the recrystallization of the molecules is suppressed [7,9].

Laser action from 2,2′,7,7′-tetrakis(biphenyl-4-yl)-9,9′-spirobifluoren (*also called spiro-sexiphenyl*) and 2,2′,7,7′-tetraphenyl-9,9′-spirobifluorene (*spiro-quaterphenyl*) spin coated films has been demonstrated by Johansson et al. in 1998 by showing the presence of ASE [11]. Also, detailed characterization of thermally evaporated spiro-sexiphenyl films including the thickness dependence of the ASE threshold has been presented [12,13]. In our work, the dependence of the ASE threshold, optical gain and photodegradation on the film thickness is investigated. Adding functional groups such as the methoxy group or the phenoxy group to the spiro molecule influences the conjugated

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system π-electron which allows spectral tuning of ASE and gain profiles. Furthermore, its thermal properties such as glass transition temperature (T_g), melting temperature (T_m) and decomposition temperature (T_d) are varied. For basics on T_g, T_m and T_d of spiro molecules, see for example Refs. [7,12]. The influence of the substituted groups on the optical and amplification properties of spiro-quaterphenyl derivatives (2,2′,7,7′-tetra(4-methoxyphenyl)-9,9′-spirobifluorene (*methoxy-spiro-quaterphenyl*) and 2,2′,7,7′-tetra(4-phenoxyphenyl)-9,9′-spirobifluorene (*phenoxy-spiro-quaterphenyl*)) is investigated in this paper. The chemical structure and thermal properties of spiro-quaterphenyl and its derivatives are given in Table 1.

2. Experimental details

2.1. Sample deposition and optical characterization

Organic films were deposited using a vacuum evaporation system which provides good quality of deposited films. The design film thicknesses were 40 nm, 80 nm, 120 nm, 160 nm and 200 nm in order to cover various guiding properties of the organic films. The film thicknesses and the optical constants were determined by a variable angle spectroscopic ellipsometer (VASE ellipsometer). The real thicknesses of deposited films from spiro-quaterphenyl are 32 nm, 78 nm, 126 nm, 156 nm, and 195 nm. The real thicknesses of deposited films from methoxy-spiro-quaterphenyl are 35 nm, 70 nm, 105 nm, 165 nm, and 195 nm while only one thickness was deposited for phenoxy-spiro-quaterphenyl (89 nm). The fluorescence spectra were measured using a Hitachi f-4500 fluorescence spectrophotometer.

2.2. Measurement of ASE threshold and optical gain

The measurement technique is based on the variable stripe length method (VSL) which has been demonstrated by Shaklee et al. in 1971 [14]. The sample is illuminated by a narrow stripe of the laser beam in that way, that the pump stripe starts directly at the edge of the sample. In this case, the spontaneously emitted photons at the end of the stripe are amplified by stimulated emission while moving towards the edge of the sample. When the stripe length is elongated, narrowing of the spectrum and exponential increase of the intensity is observed. The collected emission in this case is called amplified spontaneous emission (ASE) [15,16]. The relation between the edge emission (I) and the stripe length (x) is written as [17]

$$I(x, \lambda) = \frac{AI_p}{g(\lambda)} \left(e^{g(\lambda)x} - 1 \right), \tag{1}$$

where g is the net modal gain which is used to fit the data and AI_p corresponds to the part of spontaneous emission that is proportional to the pump energy. The net modal gain g is different from material gain g_m as revealed in [18]

$$g = \Gamma g_m - \alpha, \tag{2}$$

where Γ is the confinement factor and α is the propagation loss coefficient. In contrast to material gain, modal gain is at least smaller by the ratio of full mode volume divided by the mode volume overlapping with the active region of a planar waveguide. Thus, the wording "modal gain" indicates the gain of a mode guided in vertical direction in a planar waveguide.

However, the above given equation (Eq. (1)) is only valid for all stripe lengths less than the saturation length of the material [19]. Beyond the saturation length, the relation between the ASE intensity and the stripe length is not exponential anymore. By measuring the ASE intensity at two fixed stripe lengths of L and $2L$, the optical gain is determined from [20,21]

$$g = \frac{1}{L} \ln \left(\frac{I_{2L}}{I_L} - 1 \right). \tag{3}$$

Using Eq. (3) for the determination of the optical gain spectrum is a simple technique since only two measurements are needed.

The narrowing of the spectrum and exponential increase of the intensity do not only occur when the stripe length is elongated, but also when the pump energy is increased while the stripe length is kept constant. However, the change of the emitted intensity is small and linear and the change of FWHM of the spectrum is small below a certain value of the pump energy (ASE threshold). The value of ASE threshold can be determined either from the relation between the ASE intensity and pump energy [17] or from the relation between the FWHM and pump energy [13,22]. In order to determine the ASE threshold from the relation between the FWHM of the spectra and pump energy (P), the data are plotted and fitted according to Eq. (4) [13,22]

$$\text{FWHM}(P) = \frac{A_1 - A_2}{1 + (P/P_0)^s} + A_2, \tag{4}$$

where P is the pulse energy, A_1 and A_2 are the FWHM in the high and low pulse energy limits respectively. The pulse energy P_0 is the value at FWHM equals $(A_1 + A_2)/2$ and s represents the steepness of the function.

In order to achieve the amplification of the emitted photons, optical waveguiding has to be supported. A planar waveguide is the easiest way to realize guiding of the waves, where the active material with refractive index of n_f is placed between two layers of lower refractive indices (substrate with refractive index of n_s and air with refractive index of n_a). For an asymmetric planar waveguide, only few modes are allowed to propagate depending on the film thickness. Under a certain minimum thickness (cutoff

Table 1
Chemical structure and thermal properties of spiro-quaterphenyl and its derivatives.

Name	Chemical structure	Chemical formula	Molecular weight (g/mol)	T_g (°C)	T_m (°C)	T_d (°C)
Spiro-quaterphenyl		$C_{49}H_{32}$	620.42	168	292	460
Phenoxy-spiro-quaterphenyl		$C_{73}H_{48}O_4$	988.24	116	243	525
Methoxy-spiro-quaterphenyl		$C_{53}H_{40}O_4$	740.29	152	254	451