



Organic distributed feedback laser to monitor solvent extraction upon thermal annealing in solution-processed polymer films



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ABSTRACT

Solution-processed polymer films are used in multiple technological applications. The presence of residual solvent in the film, as a consequence of the preparation method, affects the material properties, so films are typically subjected to post-deposition thermal annealing treatments aiming at its elimination. Monitoring the amount of solvent eliminated as a function of the annealing parameters is important to design a proper treatment to ensure complete solvent elimination, crucial to obtain reproducible and stable material properties and therefore, device performance. Here we demonstrate, for the first time to our knowledge, the use of an organic distributed feedback (DFB) laser to monitor with high precision the amount of solvent extracted from a spin-coated polymer film as a function of the thermal annealing time. The polymer film of interest, polystyrene in the present work, is doped with a small amount of a laser dye as to constitute the active layer of the laser device and deposited over a reusable DFB resonator. It is shown that solvent elimination translates into shifts in the DFB laser wavelength, as a consequence of changes in film thickness and refractive index. The proposed method is expected to be applicable to other types of annealing treatments, polymer-solvent combinations or film deposition methods, thus constituting a valuable tool to accurately control the quality and reproducibility of solution-processed polymer thin films.

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1. Introduction

Polymer thin films, prepared by solution-based methods such as spin-coating, casting, printing, etc. are used in numerous technological applications. Most of the solvent from the polymer solution evaporates during the deposition process, but a part of it remains in the film, which would affect important properties, such as chain mobility, film homogeneity [1] charge carrier transport [2] or substrate adhesion [3]. Therefore, films are typically subjected, right after deposition, to thermal annealing treatments at a temperature above its glass transition temperature, T_g , aiming at its elimination. Determining a proper treatment to ensure the complete solvent elimination and consequently device reproducibility and stability has been investigated by several authors [1,4–6]. The solvent content in thin spin-coated polymer films subjected to thermal treatments has been quantified using techniques such as gas chro-

matography [4] and neutron reflectometry [5]. The dependency on film thickness of the treatment and the amount of remaining solvent are still a matter of controversy, probably because of differences in the many factors that affect the polymer morphology. For example, the polymer concentration, the type of solvent, the parameters used in the spin coating process, the thermal annealing time and temperature and the adhesion to the substrate surface.

Organic lasers with the active materials in the form of thin waveguide films have received much attention in the last decades due to the advantages of easy processability, chemical versatility, wavelength tunability and low-cost [7,8]. Numerous applications in the fields of spectroscopy, optical communications and sensing have already been demonstrated, most of them using surface-emitting second-order organic distributed feedback (DFB) lasers [7–9]. The optical feedback in a DFB laser is achieved generally by a relief grating, in most cases patterned over a conventional inorganic substrate by lithographic and etching techniques, over which the active material is coated as a thin film capable of guiding the light along its plane (see Fig. 1). The DFB emission wavelength (λ_{DFB}) appears close to the wavelength at which the cavity res-

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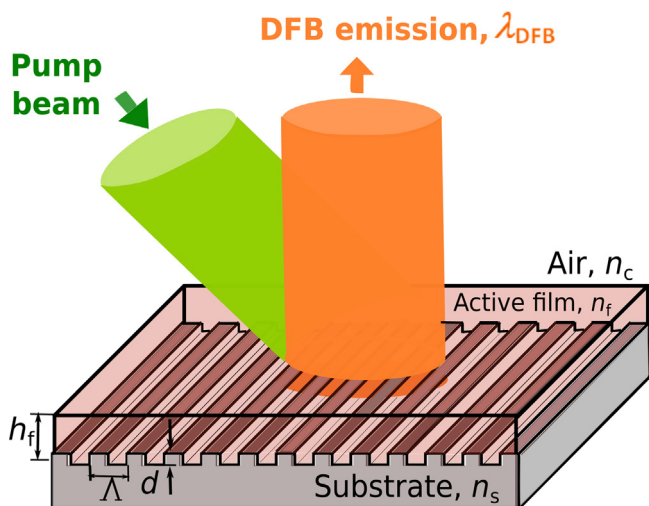


Fig. 1. Schematic representation of the organic DFB laser structure, including the excitation and collection geometry used for laser operation. Parameters n_c , n_f , and n_s are the refractive index of the cover layer (air), organic active film and substrate, respectively; h_f is the active film thickness; Λ and d ($d \ll h_f$) are the period and modulation amplitude of the grating, respectively; λ_{DFB} is the wavelength of the emitted laser beam.

onates (λ_{Bragg}), which is determined by the grating period (Λ), the diffraction order (m) and the effective refractive index (n_{eff}), according to the expression:

$$\lambda_{\text{Bragg}} = (2n_{\text{eff}}\Lambda)/m \quad (1)$$

The n_{eff} parameter depends on the active film thickness (h_f) and on the refractive index of active film, substrate and cover layer (n_f , n_s and n_c , respectively). The principle of operation of previously reported DFB-based bulk refractive index sensors consists on analysing changes in λ_{DFB} upon the deposition over the device of liquid superstrates with different n_c values [10,11]. In comparison to other refractive index sensors, organic DFB lasers are very attractive because of their high sensitivity and resolution, simple fabrication and integration with other devices, wavelength tuning capability and small size. When the DFB laser wants to be used as a biosensor, specificity to a particular analyte is achieved by functionalizing the active film surface as to enable analyte surface binding [12].

In the present work, we report the use of an organic DFB sensor operating differently than the ones just described. Here the DFB laser aims to monitor the extraction of the residual solvent content in polymer films. For that purpose the polymer film of interest is doped with a small amount of an organic laser dye and is deposited over a substrate with a DFB grating, so the polymer film constitutes the organic active layer of a laser device. The polymer used in this study has been polystyrene (PS), which has been the one used in many prior studies aiming to determine the residual solvent content on thermally annealed polymer films. The reported device operates by detecting changes in λ_{DFB} upon n_{eff} variations (see Eq. (1)), due to a modification of the active film parameters (h_f and n_f) as a consequence of the solvent extraction upon the thermal treatments. This is in contrast to previously reported DFB laser sensors in which n_{eff} changed because of variations on the superstrate refractive index, while h_f and n_f remained constant. As for the laser dye, we have used a perylenediimide (PDI) derivative, particularly *N,N'*-bis(1-hexylheptyl)-perylene-3,4:9,10-bis-(dicarboximide) (PDI-C6) dispersed in PS. PDI-doped PS films have demonstrated a very good performance as active media of organic DFB lasers (low excitation threshold and high photostability) [13,14].

The proposed technique has two important characteristics which might be advantageous with respect to other methods to determine refractive index and film thickness. Firstly, it is a simple method for monitoring variations occurring fundamentally in the bulk of the film. Secondly, the wavelength shift determined with the proposed DFB laser sensor is a direct measurement of the effective index, governed by a simple Bragg equation. In this respect, the most classical tool to study surfaces and thin films is ellipsometry, which might have a high sensitivity to detect changes in refractive index, particularly when these occur on the sample surface [15,16]. However, an ellipsometer is in general a relatively complicated instrument. Besides, it is an indirect technique and information is obtained after analysing data by means of optical models.

2. Materials and methods

2.1. Materials

All chemicals were reagent-grade, purchased from commercial sources and used as received. The PDI-C6 dye (molecular weight, $M_w = 755$, purity higher than 99.5%) was supplied by Phiton. PS and toluene were purchased from Sigma-Aldrich. The PS T_g , measured by differential scanning calorimetry (DSC) with a TA Instruments apparatus, is 65 °C. The PS M_w was determined by a Size Exclusion/Gel permeation Chromatograph (SEC/GPC) apparatus, using three columns: Styragel HR6, Styragel HR4 and Styragel HR2. Tetrahydrofuran (THF) was used as eluent at 35 °C. Results have shown that PS consists of a bimodal distribution of two polymers, PS1 and PS2, with M_w values of 72500 and 1300, respectively. By considering the dependence of the PS T_g on molecular weight reported by Blanchard et al. [17], and the studies on PS mixtures, according to the Gordon-Taylor equation, performed by Erischen et al. [18], the relative composition of the PS used in the present work is estimated as 20 wt.% of PS1 and 80 wt.% of PS2 (details in the supporting information section).

2.2. DFB device preparation and characterization

Active layers with $n_f \sim 1.59$ (at $\lambda = 580$ nm) and $h_f \sim 1000$ nm were deposited by spin-coating a toluene solution containing PS, as inert polymer, and 0.5 wt.% of the PDI-C6 laser dye, over a reusable DFB resonator engraved over SiO_2 layers grown on silica plates (more details below). Such low dye concentration was chosen as to avoid perturbations on solvent evaporation, but high enough to have a low laser threshold (1.5 $\mu\text{J}/\text{pulse}$ over an area of 1.0 mm^2) [13]. Additional samples without resonators were prepared by spin-coating PS without PDI-C6 over different substrates as required. Particularly, over transparent fused silica plates (2.5 \times 2.5) cm^2 for accurate measurements of thickness and refractive index, or over glass coverslips (2.2 \times 2.2) cm^2 for accurate measurements of solvent mass. All samples prepared over fused silica without DFB gratings or over SiO_2 with DFB gratings, constitute waveguides because they comply with the two conditions needed for that purpose. Firstly, n_f is larger than n_s and n_c , whose values are 1.46 and 1, respectively. Note that n_s is the same for both, fused silica and SiO_2 ; Secondly, h_f is well above the minimum thickness (the so-called cut-off thickness, $h_{\text{cut-off}}$) needed for the propagation of at least one waveguide mode (the transverse electric fundamental mode, TE_0), which for these structures is 150 nm [19]. In fact, these films support, in addition to the TE_0 mode, also the first order mode, TE_1 , whose $h_{\text{cut-off}}$ value is 600 nm [19].

Right after films were coated, they were subjected to a thermal annealing in an oven in ambient atmosphere for times, t , from 10 min to 24 h. The baking temperature, 90 °C, was chosen as to be

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