Efficient organic distributed feedback lasers with imprinted active films

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Abstract: We report on the fabrication of efficient organic distributed feedback (DFB) lasers with thermally-nanoimprinted active films, emitting between 565 and 580 nm. The use of thermal-NIL has allowed, as opposed to room temperature or solvent-assisted techniques, high grating quality and excellent modulation depth. The 155°C heat exposure of the NIL process, does not significantly affect the thermal and optical properties of the active material (polystyrene films doped with a perylenediimide derivative). These devices combine a simple and low-cost preparation method with good laser characteristics, i.e. thresholds of 1 μJ/pulse, single-mode emission with linewidths below 0.2 nm and photostability half-lives of ~ 10^5 pump pulses under ambient conditions. In comparison to more standard DFBs with gratings on the substrate, their fabrication is much easier, while they show a similar laser performance.

OCIS codes: (140.2050) Dye lasers; (140.3490) Lasers, distributed-feedback; (250.2080) Polymer active devices; (220.4241) Nanostructure fabrication.

References and links
1. I. D. W. Samuel and G. A. Turnbull, “Organic semiconductor lasers,” Chem. Rev. 107(4), 1272–1295 (2007).
2. F. Hide, M. A. Díaz-García, B. J. Schwartz, M. R. Andersson, Q. Pei, and A. J. Heeger, “Semiconducting polymers: a new class of solid-state laser materials,” Science 273(5283), 1833–1836 (1996).
3. N. Tessler, G. J. Denton, and R. H. Friend, “Lasing from conjugated-polymer microcavities,” Nature 382(6593), 695–697 (1996).
4. J. Clark and G. Lanzani, “Organic photonics for communications,” Nat. Photonics 4(7), 438–446 (2010).
5. A. E. Vasdekis, G. Tsiminis, J. C. Ribierre, L. O’ Faolain, T. F. Krauss, G. A. Turnbull, and I. D. W. Samuel, “Diode pumped distributed Bragg reflector lasers based on a dye-to-polymer energy transfer blend,” Opt. Express 14(20), 9211–9216 (2006).
6. Y. Yang, G. A. Turnbull, and I. D. W. Samuel, “Hybrid optoelectronics: a polymer laser pumped by a nitride light-emitting diode,” Appl. Phys. Lett. 92, 163306 (2008).
7. M. Lu, S. S. Choi, C. J. Wagner, J. G. Eden, and B. T. Cunningham, “Label free biosensor incorporating a replica-molded, vertically emitting distributed feedback laser,” Appl. Phys. Lett. 92, 261502 (2008).
8. M. B. Christiansen, J. M. Lopacinska, M. H. Jakobsen, N. A. Mortensen, M. Dufv, and A. Kristensen, “Polymer photonic crystal dye lasers as optofluidic cell sensors,” Opt. Express 17(4), 2722–2730 (2009).
9. L. J. Guo, “Nanoimprint lithography: methods and material requirements,” Adv. Mater. (Deerfield Beach Fl.) 19(4), 495–513 (2007).
10. M. B. Christiansen, T. Buß, C. L. C. Smith, S. R. Petersen, M. M. Jorgensen, and A. Kristensen, “Single mode dye-doped polymer photonic crystal lasers,” J. Micromech. Microeng. 20(11), 115025 (2010).
11. M. M. Jørgensen, S. R. Petersen, M. B. Christiansen, T. Buß, C. L. C. Smith, and A. Kristensen, “Influence of index contrast in two dimensional photonic crystal lasers,” Appl. Phys. Lett. 96(23), 231115 (2010).
12. A. Costela, I. García-Moreno, and R. Sastre, “Polymeric solid-state dye lasers: recent developments,” Phys. Chem. Chem. Phys. 5(21), 4745–4763 (2003).
versatility, wavelength tunability and low cost. In 1996 the interest in the field was renewed mainly due to the various advantages of organic materials: easy processability, chemical stability, and the potential for low-cost fabrication. Organic solid-state lasers (OSLs) have been a subject of intense research for many years [1].

1. Introduction

Among the various types of resonators used in the field of OSLs, distributed feedback (DFB) structures, are probably the most extensively studied [1,4]. As compared to other types of lasers, DFBs present several advantages, such as easy deposition of the organic film, low thresholds, single mode emission and no need of mirrors. In addition, DFBs have potential for the development of applications in the field of biosensing and chemical sensing, that is presently receiving great attention [7,8]. In a DFB structure a periodic modulation of the refractive index is introduced into the waveguide, which results in the formation of Fabry-Perot cavities. The thickness of the active region is chosen such that the gain line matches one of the resonant modes of the cavity. This results in the emission of a single mode with very low threshold.

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13. Y. Yang, M. Wang, G. Qian, Z. Wang, and X. Fan, “Laser properties and photostabilities of laser dyes doped in ORMOSILs,” Opt. Mater. 24(4), 621–624 (2004).
14. E. M. Calzado, J. M. Villalvilla, P. G. Boj, J. A. Quintana, R. Gómez, J. L. Segura, and M. A. Díaz-García, “Amplified spontaneous emission in polymer films doped with a perylenediimide derivative,” Appl. Opt. 46(18), 3836–3842 (2007).
15. Y. Oki, T. Yoshiura, Y. Chisaki, and M. Maeda, “Fabrication of a distributed-feedback dye laser with a grating structure in its plastic waveguide,” Appl. Opt. 41(24), 5030–5035 (2002).
16. H. Watanabe, H. So, Y. Oki, S. Akine, and T. Oomatsu, “Picosecond-pulse-pumped distributed-feedback thick-film waveguide blue laser using fluorescent brightener 135,” Jpn. J. Appl. Phys. 49(7), 072105 (2010).
17. S. Riechel, U. Lemmer, J. Feldmann, S. Berleb, A. G. Mückl, W. Brütting, A. Gombert, and V. Wittwer, “Very compact tunable solid-state laser utilizing a thin-film organic semiconductor,” Opt. Lett. 26(9), 593–595 (2001).
18. V. Navarro-Fuster, E. M. Calzado, P. G. Boj, J. A. Quintana, J. M. Villalvilla, M. A. Díaz-García, V. Trabadelo, A. Juarros, A. Retolaza, and S. Merino, “Highly photostable organic distributed feedback laser emitting at 573 nm,” J. Appl. Phys. 97(17), 171104 (2010).
19. V. Trabadelo, A. Juarros, A. Retolaza, S. Merino, M. G. Ramírez, V. Navarro-Fuster, J. M. Villalvilla, P. G. Boj, J. A. Quintana, and M. A. Díaz-García, “Highly photostable solid-state organic distributed feedback laser fabricated via thermal nanoimprint lithography,” Microelectron. Eng. 87(5-8), 1428–1430 (2010).
20. E. M. Calzado, J. M. Villalvilla, P. G. Boj, J. A. Quintana, R. Gómez, J. L. Segura, and M. A. Díaz-García, “Effect of structural modifications in the spectral and laser properties of perylenediimide derivatives,” J. Phys. Chem. C 111(36), 13595–13605 (2007).
21. J. A. Rogers, M. Meier, A. Dodabalapur, E. J. Laskowski, and M. A. Cappuzzo, “Distributed feedback ridge waveguide lasers fabricated by nanoscale printing and molding on nonplanar substrates,” Appl. Phys. Lett. 74(22), 3257–3259 (1999).
22. M. Salerno, G. Gigli, M. Zavelani-Rossi, S. Perissinotto, and G. Lanzani, “Effects of morphology and optical contrast in organic distributed feedback lasers,” Appl. Phys. Lett. 90(11), 111110 (2007).
23. E. M. Calzado, J. M. Villalvilla, P. G. Boj, J. A. Quintana, and M. A. Díaz-García, “Tunability of amplified spontaneous emission through control of the thickness in organic-based waveguides,” J. Appl. Phys. 97(9), 093103 (2005).
24. E. M. Calzado, J. M. Villalvilla, P. G. Boj, J. A. Quintana, P. A. Postigo, and M. A. Díaz-García, “Blue surface-emitting distributed feedback lasers based on TPD-doped films,” Appl. Opt. 49(3), 463–470 (2010).
25. G. Heliotis, R. Xia, D. O. Bradley, G. A. Turnbull, I. D. W. Samuel, P. Andrew, and W. L. Barnes, “Two-dimensional distributed feedback lasers using a broadband, red polyfluorene gain medium,” J. Appl. Phys. 96(12), 6959–6965 (2004).
26. E. M. Calzado, J. M. Villalvilla, P. G. Boj, J. A. Quintana, and M. A. Díaz-García, “Concentration dependence of amplified spontaneous emission in organic-based waveguides,” Org. Electron. 7(5), 319–329 (2006).
27. V. Navarro-Fuster, E. M. Calzado, M. G. Ramírez, P. G. Boj, J. T. Henssler, A. J. Matzger, V. Hernández, J. T. López, and M. A. Díaz-García, “Effect of ring fusion on the amplified spontaneous emission properties of oligothiophenes,” J. Mater. Chem. 19(36), 6556–6567 (2009).
28. E. B. Namdas, M. Tong, P. Ledochowitsch, S. R. Mednick, J. D. Yuen, D. Moses, and A. J. Heeger, “Low thresholds in polymers lasers on conductive substrates by distributed feedback nanoimprinting: Progress toward electrically pumped plastic lasers,” Adv. Mater. (Deerfield Beach Fla.) 21(7), 799–802 (2009).
29. M. Ichikawa, Y. Tanaka, N. Suganuma, T. Koyama, and Y. Taniguchi, “Low-threshold photopumped distributed feedback plastic laser made by replica molding,” Jpn. J. Appl. Phys. 42(Part 1, No. 9A), 5590–5593 (2003).
refractive index by a surface grating (on the substrate or on the active medium) is made in order to obtain light reflected by “Bragg-scattering” [1,4]. Among the various methods generally used for grating engraving [1], nanoimprint lithography (NIL), with its increasing number of process variations, such as thermal-NIL, UV-NIL, combined nanoimprint and photolithography (CNP), etc., is one of the most promising technologies [9]. Due to its high throughput, low-cost and high fidelity pattern transfer, it has great potential to be scaled to volume production. Thermal-NIL is the simplest and most standard NIL technique used to imprint conventional thermoplastics, which provides very high fidelity pattern transfer and excellent aspect ratio [9]. It generally uses a combination of pressure and temperature to imprint the surface structure of a master grating into a softened polymer film. Thermal-NIL has been extensively used to fabricate DFBs with gratings on a substrate [1,9]. However, in general it could not be used to directly imprint active films, since very often the active materials degraded due to the high temperatures used in the process (typically in the range 100-300 °C). A variation of NIL performed at room temperature (RT-NIL) to avoid degradation of the active material, has been successfully used to pattern conventional thermoplastics as well as low-molar mass organic molecules or conjugated polymers [1,9]. However, RT-NIL has several drawbacks and limitations. On the one hand, the pressure that must be applied is at least one order of magnitude higher than the one used in a conventional thermal-NIL process, so the mold and the sample might break. On the other hand, when thermoplastic materials are used, the pattern cavities in the mold cannot be completely filled during the RT process. Consequently, the imprinting depths that can be achieved are generally lower (typically less than 150 nm) and the quality of the transfer is generally poorer [9]. As a result, the laser performance of these devices is generally inferior, i.e. high laser thresholds, no precise control in the emission wavelength given certain fabrication parameters, poor photostability, etc. Other approaches to complete an almost RT process have used CNP to produce two-dimensional (2D) DFB structures from UV-curable materials [10,11]. This technology uses a photochemically curing resist as polymer matrix for thermal imprint lithography, allowing imprinting at moderate temperatures combining UV-flood exposure, annealing and mold release at the same temperature. UV-NIL processes allows high fidelity pattern transfer and moderate aspect-ratio at low temperatures, so producing high performing DFB lasers. However, the technique is more sophisticated, and consequently more costly, than conventional thermal-NIL, since it needs high quality transparent stamps usually made of quartz and curing polymers by UV-flood exposure.

In spite of the large advance in developing low-cost techniques to fabricate OSLs with a high performance (low threshold, large efficiency, narrow and single-mode emission), just a few works have focused on the photostability of the devices, although it is a relevant parameter from the point of view of applications. There are numerous reports on the photostability of the laser emission properties of organic materials in the form of monoliths placed in external laser cavities [12,13] and on the amplified spontaneous emission (ASE) of active organic waveguide films [14]. However, concerning devices based on films, i.e. microcavity or DFB lasers, just a few of the numerous articles published, provide photostability data [1,15–17] and in some of them, laser characterization was performed in vacuum or in inert atmosphere. Within this context, we recently reported low-threshold and highly photostable (under ambient conditions) DFB lasers, based on polystyrene (PS) films doped with perylenediimide (PDI) derivatives as active laser materials [18]. The DFB gratings were fabricated by thermal-NIL on a resist and then transferred to the substrate (SiO₂) [19]. The selection of the active material was based on previous investigations performed in our group on the ASE properties, under optical pump, of PS films doped with PDIs [14,20]. In addition, these materials offer potential for applications based on polymer optical fibers, since they emit at wavelengths within the second low-loss transmission window of poly(methylmethacrylate) (460-590 nm). Through those studies we found that among various PDI derivatives, those substituted at the imide nitrogen positions, had the best performance [20]. They showed efficient and photostable ASE, at low thresholds, when doped at low concentrations (0.5 - 1 wt.%) into PS.
Since DFB devices with high quality gratings (such as those achieved with NIL) based on PDIs have great potential for applications [18], we thought about possible ways to further improve their performance. A very attractive strategy consists in engraving the DFB gratings directly on the active material, instead of on the substrate, in order to simplify the fabrication process and therefore reduce the cost of the devices. Since no transfer of the grating to the substrate by etching methods is needed, the process would be reduced to only one step. In addition, DFBs with imprinted active films allow a better control of the overall structure. Note that when the active films are deposited over corrugated substrates to fabricate devices with gratings on the substrate, it is not possible to control the way the material fills the grooves and it is difficult to predict the final thickness of the film. Moreover, the corrugation of the substrate might be transferred to the surface in contact with air. All these difficulties do not appear in the case of DFBs with imprinted active films. Therefore, given the clear processing advantages of these latter devices, it is important to know whether their laser performance is at least similar to that of the more standard devices with gratings engraved on the substrate. At this respect, it is somewhat surprising that despite the large amount of work performed with DFB lasers, at present it is not clear whether having the grating on the active film is better in terms of performance than having it on the substrate. Some authors reported that no difference in threshold was found when comparing devices with these two geometries [21]. On the other hand, Salerno et al. [22] concluded that DFB lasers with gratings imprinted on the active film showed lower thresholds. It should be noted that in those studies several aspects were not addressed, such as the effect of the thermal treatments due to the NIL process on the optical properties, the effect of film thickness on the emission wavelength, which is a very important parameter influencing the threshold, and the photostability properties.

In this work, we report on the fabrication and characterization, under optical pump, of organic DFB lasers based on PS films doped with a PDI derivative as active material. High quality DFB gratings with high aspect-ratio have been engraved by thermal-NIL directly on the active films in a single step process, with no need of etching methods to transfer them to the substrate. The effect of the high-temperature treatment (155 °C for 900 s) used in the NIL process on the thermal stability and on the optical properties of the active films has been investigated, in order to ensure that grating fabrication does not negatively affect the laser performance. The emission wavelength of the devices was tuned by film thickness variation. The performance, in terms of threshold, linewidth, emission wavelength and photostability is compared to that of devices based on the same active material but with gratings on the substrate [18].

2. Experimental techniques

PS films doped with 0.5 wt.% of the PDI derivative PDI-C6 (see chemical structure in Fig. 1(a)) were spin-coated on thermally oxidized 4” silicon wafers. This PDI concentration provides the lowest ASE thresholds in films without gratings, in accordance with results obtained with another PDI derivative with similar chemical structure (substituted at the N positions) [14]. Film thickness (determined with a Veeco Dektak8 surface profilometer) was varied between 300 to 900 nm, by adjusting the percentage of PS with respect to the solvent (toluene).

One-dimensional DFB gratings were engraved on the PDI-C6-doped PS films by using thermal-NIL. A 4” diameter silicon master with a grating area of (2 x 2) mm², period \( \Lambda = 368 \) nm and equal line and space, fabricated by e-beam lithography (Kelvin Nanotechnology Ltd.), was used as stamp. This was treated with a fluorosilane-based antiadhesive coating deposited from the vapour phase, in order to avoid adhesion of the polymer to the stamp during the imprinting process and to facilitate demolding. The embossing was carried out in a Jenoptik HEX03 press under vacuum at 155 °C and the applied force (15 kN), that corresponds to a pressure of 1.85 MPa, was held for 900 s. Vacuum was used to prevent bubble formation. The demolding temperature was 50 °C. The gratings were characterized by field emission scanning electron microscopy (ZEISS Ultra Plus) and atomic force microscopy (NT-MDT Solver PRO).
Fig. 1. (a) Chemical structure of PDI-C6; (b) Schematic of the DFB device ($\Lambda = 368$ nm, $d = 260$ nm, $h = 320-890$ nm), (c) SEM image and (d) AFM profile of the grating engraved on the active film.

The thermal stability of PS (Sigma Aldrich, $M_w = 35000$ g/mol) and PDI-C6 (LambdaChem, $M_w = 755$ g/mol) were analyzed by differential thermal analysis (DTA) and differential scanning calorimetry (DSC) in a TGA/SDTA851e/LF/1600 Mettler Toledo apparatus, in order to ensure that they do not degrade under the high temperature conditions of the thermal-NIL process.

The emission properties of the DFB devices were investigated under ambient conditions by optical excitation with a frequency-doubled Nd:YAG (YAG-yttrium aluminum garnet) laser (10 ns, 10 Hz) operating at 532 nm, which is close to the maximum absorbance of PDI-C6 [20]. The energy of the pulses was controlled using neutral density filters. The pump laser beam was expanded, collimated and only the central part was selected in order to ensure uniform intensity. The pump beam was incident upon the samples at $\sim 20^\circ$ with respect to the normal to the sample plane in a spot of 1.2 mm diameter. The emitted light was collected normal to the surface with an Ocean Optics USB2000-UV-VIS fiber spectrometer (resolution 1.3 nm) placed at 1 cm from the sample. For a detailed inspection of the laser spectral shape, a MAYA2000 spectrometer with higher resolution (0.13 nm), was used. The effect of the thermal-NIL process on the emission properties of the active films was studied by characterizing, also in this setup, the ASE properties in film regions without gratings, before and after the thermal-NIL. In order to evaluate the effect of performing these thermal treatments in vacuum, as well as the effect of the temperature on the photostability of the materials, the ASE properties were also studied in independent samples without gratings that were subjected to thermal treatments in air. Photostability studies were performed by studying the time evolution of the ASE and the DFB laser emission intensity under constant excitation above threshold, on the same spot of the sample and in ambient conditions.

3. Results and discussion

3.1 Device fabrication by thermal-NIL: effect on the thermal stability and the optical properties of the active films

Devices with active films of thickness $h$, measured from the lowest part of the grating to the substrate (see scheme of the device in Fig. 1(b)), ranging from 320 to 890 nm were obtained.
The gratings over the active films had the same period of the master ($\Lambda = 368$ nm) and a depth $d = 260$ nm. In all cases, high fidelity pattern transfer was achieved (see Figs. 1(c) and 1(d)).

DTA and DSC experiments performed in powder samples of PS and PDI-C6 have shown that degradation starts at temperatures around 170 °C and 220 °C, respectively. These values are higher than the temperature used in the NIL process (155 °C), indicating that the materials contained in the active films are thermally stable under the conditions used to fabricate the gratings. Concerning the optical properties, we found that not only they do not degrade due to the thermal treatments, but they improve. The effect of temperature on the emission properties of the active films is illustrated in Fig. 2, where the emission intensity from a film in a region without grating, before and after the NIL process, is displayed as a function of excitation intensity. Although in this case no grating is present, gain narrowing is observed due to ASE. The evolution of the emission linewidth (defined as the full width at half of the maximum, FWHM) with the excitation intensity has been plotted in Fig. 2(b) for a numerical determination of the threshold. As observed, the thermal treatment leads to a higher slope efficiency and a lower threshold (in this case around half of the value obtained from the fresh sample). We found a fairly large dispersion in the absolute values of the ASE thresholds measured in different samples (50% and 30% for the non-treated and treated films, respectively). Despite this large dispersion, considering the relative comparison between treated and not-treated film in each case, we could conclude that the thermal treatment led to a decrease in threshold by 2-3 times. This improvement in the ASE performance is mainly due to the increase also observed in the overall PL emission of the films due to the thermal treatments, caused mainly by the evaporation of the residual solvent present in the films after deposition. Similar results were obtained in independent samples (without gratings), subjected to thermal treatments in air, indicating that for these materials using vacuum is not a critical issue to prevent degradation of their optical properties. These samples were also used to investigate the effect of the thermal treatments on the ASE photostability. Experiments were performed under excitation well above their ASE thresholds at the same energy (0.46 mJ/pulse) in all cases. Results have shown that the thermal treatments lead to a decrease in the photostability lifetime by 2-3 times. Interestingly, we observed a correlation between this decrease in photostability and the previously discussed decrease in threshold, assigned to solvent evaporation. It is possible that the residual solvent might aid to dissipate the heat, so when it is eliminated, the lifetime gets reduced. The observed improvement of PL efficiency and ASE threshold due to the 155 °C heat exposure, seems to indicate that the decrease in photostability is not caused by the photodegradation of the active material, but to changes experienced by the matrix, which plays a very important role in these mechanisms. We observed that the degree of improvement achieved in PL efficiency and ASE threshold and the corresponding decrease in photostability half-life, due to the thermal treatments, depended on the time and temperature used. So detailed investigations at this respect are currently in progress and will be reported elsewhere.

Figure 2 also shows data for two DFB devices, i.e. from regions with gratings, based on films of thickness 590 and 800 nm. As expected, they show much lower thresholds and narrower linewidths than the ASE thresholds measured in regions without gratings. Obviously, the emission of the DFB devices correspond to films subjected to thermal treatments, since these are inherent in the fabrication of the DFB gratings. As observed, there is a clear difference in the thresholds of the two DFB devices because they emit at different wavelengths: 574 nm and 579 nm for $h = 590$ nm and $h = 800$ nm respectively. In section 3.3 the dependence of the DFB emission wavelength and threshold on film thickness is described in detail. The device based on a 800 nm thick film is the one with the lowest threshold among the various lasers prepared in this work. On the other hand, the device with $h = 590$ nm has a structure (active film thickness, grating depth and period) similar to that of one of the lasers described in Ref. 18, but with the grating on the substrate. So it will be useful for the comparison of both types of lasers, which will be done later in sections 3.3 and 3.4. The ASE data shown in Fig. 2 from a region without grating correspond to the device with $h = 590$ nm,
although similar results were obtained for the one with $h = 800$ nm. For the range of film thickness used in this work (far away from the cut-off thickness for the propagation of one mode), the ASE thresholds measured in regions without gratings were approximately the same, since ASE appears at the same wavelengths. These results are in accordance with a previous study with other organic material in which the effect of changing film thickness on the ASE properties was investigated [23].

Fig. 2. Output intensity (a) and linewidth (b) versus pump pulse energy for two DFB devices based on active films of thickness $h = 590$ nm (full squares) and $h = 800$ nm (open circles). Data for the former device from a region without grating, performed before (full triangles) and after (open squares) the thermal-NIL process have been included to illustrate the effect of the thermal treatment in the emission properties.

3.2 Spectral shape of the DFB emission

Figure 3(a) shows the laser emission spectrum (above threshold) for a DFB device based on an active film of thickness $h = 323$ nm. The PL and ASE spectra from a region without grating have also been included in the figure. Without DFB resonator, gain due to ASE takes place at 579 nm, close to the vibrational PL peak. In contrast, DFB emission occurs at a wavelength determined by the grating period, the effective index of the film, that depends on film thickness, and the order of diffraction (in this case $m = 2$) through the Bragg equation [1].

In addition, the obtained ASE linewidth (around 5 nm) is larger than that measured for the DFB laser (< 0.2 nm, see the high-resolution spectrum in Fig. 3(b)). The spectrum of the device under low-energy excitation (below threshold), is also displayed in Fig. 3(b). It exhibits a dip in the emission intensity centered at $\lambda_{\text{Bragg}} = 563.6$ nm, due to an inhibition of the propagation of the waveguided light by the grating, which can be envisaged as a photonic stop band for waveguided modes [1]. As observed, DFB lasing occurs at the long-wavelength edge of the Bragg dip (at $\lambda_{\text{DFB}} = 564.6$ nm for this particular device). By assuming that index-coupling modulation is the dominating gain mechanism in these lasers (supported by the observation outside the dip), two laser modes, one slightly below $\lambda_{\text{Bragg}}$ and the other slightly above it should be observed. The inhibition of the lasing mode below $\lambda_{\text{Bragg}}$ could be explained [1,24] by the fact that the cavity losses for this band edge are lower than for the short-wavelength one, so the long-wavelength mode has a lower threshold.
3.3 Effect of film thickness variation on the emission wavelength and threshold: experimental results and modeling

Devices emitting at different wavelengths, ranging from 565 to 580 nm, were fabricated by changing film thickness (see Fig. 4). In all cases, the shape and linewidth of the spectra above threshold were similar to those displayed in Fig. 3. However, the Bragg dip obtained at low pump intensity, such as the one shown in the inset of Fig. 3, could be observed only for the devices with high index contrast (defined as the ratio between the effective index of a waveguide of thickness \( h+d \) and a waveguide of thickness \( h \)), i.e., \( d/h \) ratios larger than approximately 0.52, that would correspond to film thickness \( h \) below 500 nm (note that \( d = 260 \) nm for all devices). For thicker films, coupling constants are weak and therefore the Bragg dips can hardly be observed. Nevertheless, DFB emission takes place in all cases. In fact, the variation of emission wavelength achieved by changing film thickness is mainly due to the change of the effective index \( n_{\text{eff}} \).

In order to understand the behavior in more detail, several models have been developed (lines in Fig. 4). In model 1, denoted as “Model \( h \)”, we neglect the presence of the grating, so...
$n_{\text{eff}}$ is that of a waveguide of thickness $h$. In model 2 (“Model $h+(d/2)$”) the presence of the grating is taken into account by averaging the film thickness assuming that the $n_{\text{eff}}$ is that of a waveguide of thickness $h+(d/2)$. This model was previously used to explain the behavior of polyfluorene-based DFB lasers [25]. Finally, in model 3 (“Model average $n_{\text{eff}}$” or “Model $n_{\text{eff} \text{av}}$”) $n_{\text{eff} \text{av}}$ is obtained by averaging two effective indexes, denoted as $n_{\text{eff},h}$ and $n_{\text{eff},h+d}$, calculated for waveguides of thickness $h$ and $h+d$ respectively from Eq. (1)

$$n_{\text{eff} \text{av}} = \sqrt{\frac{n_{\text{eff},h}^2 + n_{\text{eff},h+d}^2}{2}}$$ (1)

This latter method (the most rigorous one among the models considered) is similar to the MIT photonic bands package (MPB) program (available on-line) used recently by other authors to model the dispersion relations and the emission frequencies of 2D organic photonic crystal lasers [11]. As observed in Fig. 4, the “Model $h$” is not appropriate in any case, even for weak index contrasts. On the other hand, both “Model $n_{\text{eff} \text{av}}$” and “Model $h+(d/2)$” provide similar results and are in good agreement with the experimental results.

DFB thresholds were determined as the excitation pulse energy at which the FWHM decreased to half of its maximum value (see Fig. 2(b)). Results obtained for all the DFB devices prepared have been represented in Fig. 5 as a function of their corresponding emission wavelengths.

![Fig. 5. DFB thresholds as a function of emission wavelength (full squares, left axis) and inverse of the intensity of the PL(0-1) transition (open circles, right axis). Solid lines are guides to the eye.](image)

As observed, the threshold increases drastically when the emission wavelength decreases and it shows a minimum when the wavelength is close to that at which ASE appears when no grating is present. Different parameters might have a role in such behavior: PL efficiency (integrated area), confinement of the waveguide mode (directly related to the losses), PL intensity of the vibrational 0-1 transition (at which ASE takes place) and absorption at the DFB wavelength. In previous works with PS films doped with other active organic molecules, the decrease of the ASE threshold for increasing $n_{\text{eff}}$, achieved by increasing the concentration of active molecule, was correlated with the inverse of the PL efficiency of the material [26,27]. In other studies, in which $n_{\text{eff}}$ was varied by changing the film thickness, while keeping a constant concentration of active molecule [23], the confinement of the waveguide mode seemed to be the dominant parameter to explain the ASE behavior. Note that the absorption, the inverse of PL efficiency and the confinement of the waveguide mode, all decrease when the thickness (and therefore the effective index and emission wavelength) increases and then saturate above a certain value. Although all these parameters might contribute to the large increase in threshold observed at low emission wavelengths, the overall behavior seems to be driven mainly by the PL intensity of vibrational 0-1 transition (PL(0-1)). The type of dependence observed for the DFB threshold is similar to that of the PL(0-1) (see...
Fig. 5), although the former is red-shifted, so its minimum coincides with that of the ASE emission. A red-shift of the ASE emission with respect to the PL peak has been observed in many materials [1,2].

In order to evaluate whether having the grating on the active film or in the substrate has an influence on the threshold, we compare the results obtained in this work with those recently reported by us for DFB devices based on the same active material but with the gratings engraved on the substrate [18]. For a proper comparison, the ASE thresholds of the films in regions without gratings should be the same. As observed in Fig. 2(b), in the present work the ASE threshold measured after the NIL treatment is around 80 μJ/pulse. For the devices with gratings on the substrate [18], whose films did not receive any thermal treatment, a similar value (76 μJ/pulse) was reported, in contrast with the value measured in this work in the fresh sample (130 μJ/pulse, see Fig. 2(b)). This apparent inconsistency is due to the large dispersion in the absolute values of the thresholds measured in different samples, as discussed in section 3.1. Therefore, within experimental uncertainty both values are approximately the same. Another aspect to be considered to ensure a proper comparison of devices with these two geometries is that they should have the same grating depth and period, as well as film thickness, so they emit at approximately the same wavelength. This aspect is crucial given the strong dependence of the threshold on the emission wavelength (Fig. 5). Taking into account these considerations, the device of this work with \( h = 590 \text{ nm} \) (\( d = 260 \text{ nm} \) and \( \Lambda = 368 \text{ nm} \) in all cases) that emits at \( \lambda_{\text{DFB}} = 574 \text{ nm} \) (see Fig. 4) and whose data were displayed in Fig. 2, can be compared to that reported in ref. 18 emitting at \( \lambda_{\text{DFB}} \approx 573 \text{ nm} \), with \( h = 580 \text{ nm} \), \( d = 220 \text{ nm} \) and \( \Lambda = 368 \text{ nm} \). Both devices show similar DFB thresholds (\( 2.3 \pm 0.2 \mu \text{J}/\text{pulse} \)), in contrast with results reported by other authors [22] that claimed that the thresholds of imprinted devices were lower. From our experiments, no significant differences can be found in the threshold of both types of devices. In fact, if the factor that has a major influence on the threshold is the emission wavelength, as observed in Fig. 5, and this one is defined by the \( n_{\text{eff}} \) (determined by \( h \) and \( d \)), this would be in fact the expected result in the frame of our models. For both “Model average \( n_{\text{eff}} \)” and “Model \( h+(d/2) \)”, both types of geometries (for the same \( h \), \( d \) and \( \Lambda \)) are equivalent. It should be noted though, that these models do not consider propagation losses, that could be important for certain active materials (with large scattering or highly absorbing at the laser emission wavelength), highly reflective substrates or under certain geometrical conditions (for example high \( d/h \) ratios) that lead to DFB emission wavelengths far away from the ASE wavelength. In our case, both the active material and the substrate are very transparent and the emission wavelength is close to the ASE wavelength. So waveguide propagation losses seem to be low enough not to be influenced by the location of the grating (at the interface air-active film or at the interface active film-substrate). At least when these conditions apply, our result would possibly be applicable to DFBs based on active materials different than the ones used in this work.

Finally, it would be interesting to compare the thresholds of our devices with others reported in the literature. However, such comparison is not straightforward, since thresholds (given in energy density or power density units) depend on the laser characterization setup and on the size of the excitation beam over the sample, as discussed in more detail in previous works [20,24]. In the literature, most of ASE investigations are performed by exciting with stripes of various mm long and collecting the emitted light from the edge of the film, while second-order DFBs are pumped with circular spots of diameters ~1 mm (or less) and light collection is a direction perpendicular to the sample plane. Therefore, to avoid misunderstandings, here thresholds have been given in energy per pulse units. In addition, to properly assess the effect of the DFB resonator in the laser performance, we have measured in the same setup the ASE properties of the film in a region without grating. The good quality of our resonators is illustrated by the 80 times decrease in the DFB threshold, with respect to the ASE threshold (measured in the same setup) of the film without grating. This significant reduction in threshold is larger than that reported in other works in which data for reference films without gratings were reported [24,28]. Note that although the absolute values of the DFB thresholds obtained here (1 μJ/pulse, 10 kW/cm²) might seem higher than others.
reported in the literature, the experimental conditions under which they were measured were different. For example, the best results reported for soft lithography based devices (0.5 kW/cm²) [29], were obtained with a considerably larger excitation area (a stripe of 1 mm by 5 mm) than the one use in this work (a spot of 1.2 mm diameter).

3.4. Device lifetime under operation in ambient conditions

The operational lifetime of the devices was quantified by measuring the photostability half-life ($\tau_{1/2}$), defined as the time at which the DFB intensity decays to half of its maximum value. The excellent photostability properties of the ASE emission of PDI-doped materials have been previously reported [14,20]. Also recently, as already mentioned, highly photostable DFBs with the gratings on the substrate, based on the same active material as in the present work, have been demonstrated [18]. In that study, a $\tau_{1/2}$ value as long as 3.1 × 10⁵ pump pulses was measured, when excited under ambient conditions at 4 μJ/pulse (2 times above threshold). In the present work, by using the same experimental conditions (excitation source, geometry of excitation and collection, etc...), so direct comparison is feasible, half-lives of 1.1 × 10⁵ pump pulses have been obtained for the devices with the lowest thresholds ($h > 600$ nm) when excited at the same energy (4 μJ/pulse). These differences in lifetime might be due to either the different geometry or either to differences induced by the thermal treatments in the material. In section 3.1, we showed that the ASE photostability lifetimes of films without gratings were reduced by 2-3 times, due to the thermal treatments. Given that the films used in the devices with gratings on the substrate were not subjected to thermal treatments, the reduction in the operational lifetime of the devices reported here seems to be due to the thermal treatments applied in this case, and not to the different geometry. At present, further work is in progress in order to clarify the photodegradation mechanisms, in view of proposing materials and designs with improved photostability, while keeping the fabrication process as simple as possible. In any case, the operational lifetime obtained here for devices imprinted on the active films are still of the same order of magnitude (10⁵ pulses). This value is larger than those reported for other organic DFB lasers under ambient conditions [1,15–17]. Particularly, for DFB devices with imprinted active films, there is little information in the literature. Nevertheless, the most important conclusion is that this value is more than enough of what a device would require to be used for biosensing or chemical sensing applications.

4. Summary and conclusions

We have been able to use thermal-NIL to fabricate high quality and high aspect-ratio DFB devices in a single step, while keeping a very good laser performance: thresholds of 1 μJ/pulse, single-mode emission with linewidths below 0.2 nm and photostability half-lives of ~10⁵ pump pulses under ambient conditions. Laser emission wavelength, tuned between 565 and 580 nm by film thickness variation, was successfully modeled by considering an average effective index or an average thickness of the active film. DFB thresholds, strongly dependent on the emission wavelength, correlate well with the emission intensity of the vibrational PL(0-1) peak. These DFB devices with imprinted active films show a similar laser performance (same threshold and slightly lower photostability half-life) than that of lasers based on the same material but with the gratings on the substrate.

From the point of view of processing, the properties of the active material used in our devices (polystyrene films doped with 0.5 wt% of a perylenediimide derivative) are very unique. It can be directly imprinted at 155 °C with standard thermal-NIL processes without degradation of its thermal properties and producing only slight changes in its optical properties i.e. a decrease in the threshold, as well as in the photostability half-life, by 2-3 times. Using thermal-NIL has allowed to obtain high quality resonators, superior to those obtained with room temperature NIL or solvent-assisted techniques. From a practical point of view, simplifying the fabrication process is a very important aspect, but it should be done without losing its laser performance capability.

In conclusion, in the context of DFB lasers with imprinted active films, devices based on PS doped with PDI derivatives fabricated by thermal-NIL offer great promise due to the
combination of simple fabrication and good laser properties. We have also shown that laser performance of devices based on these materials do not seem to be significantly affected by the location of the grating (at the active film-air interface or at the active film-substrate interface). On the other hand, devices with imprinted active films show clear advantages from the point of view of ease processing and low cost.

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