Highly photostable organic distributed feedback laser emitting at 573 nm

Victor Navarro-Fuster,¹ Eva M. Calzado,¹ Pedro G. Boj,¹ José A. Quintana,¹ José M. Villalvilla,¹ María A. Díaz-García,^{1,a)} Vera Trabadelo,^{2,b)} Aritz Juarros,² Aritz Retolaza,² and Santos Merino²

¹Dpto. de Física Aplicada, Dpto. de Óptica, Anatomía y Farmacología, Dpto. de Física, Ingeniería de Sistemas y Teoría de la Señal and Instituto Universitario de Materiales de Alicante (IUMA), Universidad de Alicante, Alicante 03080, Spain

²Department of Micro and Nanotechnology, Tekniker, Eibar 20600, Spain

(Received 13 August 2010; accepted 3 October 2010; published online 26 October 2010)

An efficient, low-cost, and highly photostable second-order distributed feedback (DFB) laser, fabricated by thermal nanoimprint lithography and based on a polymer active film containing a perylenediimide derivative, is reported. It shows a photostability half-life of 3.1×10^5 pump pulses (>8 h), when pumped at the same spot of the film. This value is the highest reported to date for organic DFB lasers measured under ambient conditions. The device emits at 573 nm, matching the second low-loss transmission window of poly(methylmethacrylate) (460–590 nm), thus offering potential for applications in data communications based on polymer optical fibers. © 2010 American Institute of Physics. [doi:10.1063/1.3506500]

In the past years a great effort has been devoted to the investigation of organic solid-state lasers (OSLs).^{1,2} Organic materials offer various advantages, such as easy processability, chemical versatility, wavelength tunability, and low cost. Most works published in this field have focused on semiconducting materials and mainly with the aim of reducing the thresholds, in view of achieving lasing under electrical pump.^{1,2} Low-threshold lasers pumped with cheap inorganic diode lasers^{3,4} and even with light emitting diodes⁵ have been reported, thus allowing to build compact and cheap sources. In spite of the large advance in threshold reduction, just a few works have focused on the photostability of the devices, although it is a relevant parameter from a practical point of view. There are many reports on the photostability properties of laser materials in the form of monoliths^{6,7} and thin films.^{8,9} However, with just a few exceptions,^{10–13} information about the device lifetime can be rarely found in works dealing with microcavity or distributed feedback (DFB) organic lasers.

We previously reported that polystyrene (PS) films doped with perylenediimide derivatives (PDIs) have a great potential for the fabrication of lasers.^{8,9} PDIs substituted at the imide nitrogen positions have shown very photostable amplified spontaneous emission (ASE) by optical pump, at low thresholds, when doped at low concentrations (0.5–1 wt %) into PS. Later on, other authors have investigated the role of the matrix in optimizing the photostability properties of the commercially available PDI derivative known as perylene red.⁷ The good laser performance of PDIs, together with their potential for applications based on polymer optical fibers,⁸ prompted us to fabricate lasers by introducing a resonant laser cavity.

DFB lasers are among the most studied OSL structures.^{1,2} As compared to other types of resonators, DFBs

present several advantages, such as easy deposition of the organic film, low thresholds, and no need of mirrors. In a DFB laser a periodic modulation of the 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.”^{1,2} Among the various methods generally used for grating engraving, nanoimprint lithography (NIL) is one of the most promising technologies due to its high throughput, low-cost, and high fidelity pattern transfer. NIL has already demonstrated its capacity to fabricate organic photonic devices, including DFB lasers.^{1,2}

In this work, efficient, low-cost, and highly photostable (under ambient conditions) lasers, based on active PDI-doped PS films, have been fabricated by NIL. The device performance has been optimized by adjusting the PDI content in the active film as well as the grating depth.

DFB gratings were engraved on SiO₂ films grown by thermal oxidation of silicon wafers by using NIL and subsequent etching, as described in detail elsewhere.¹⁴ Various grating depths (d) of 340 nm, 220 nm, and 105 nm have been obtained with etching times of 10 min, 6 min, and 3 min, respectively. The gratings were characterized by field emission scanning electron microscopy (ZEISS Ultra Plus) and atomic force microscopy (NT-MDT Solver PRO). In all cases, high fidelity pattern transfer was achieved. DFB laser fabrication was completed by spin-coating PS films doped with the PDI derivative N,N'-di-(1-hexylheptyl) perylene-3,4:9,10-tetracarboxylic diimide (PDI-C6, Fig. 1) on top of the SiO₂ gratings. For the spin-coating process, the percentage of PS with respect to the solvent was adjusted in order to obtain film thickness of around 580 nm. Such films would support one waveguide mode with a maximum confinement within the gain region, as calculated from waveguide theory¹⁵ (the refractive index for the film and the substrate at $\lambda=573$ nm are 1.592 and 1.457, respectively). Films with various PDI-C6 contents (between 0.08 and 2.4 wt %) with respect to PS were prepared.

The emission properties of the DFB lasers were investigated under excitation with a frequency-doubled Nd:YAG (YAG-yttrium aluminum garnet) laser (10 ns, 10 Hz) operat-

^{a)} Author to whom correspondence should be addressed. Electronic mail: maria.diaz@ua.es.

^{b)} Present address: EMPA-Swiss Federal Laboratories for Materials Science and Technology, Advanced Materials Processing, CH-3602 Thun, Switzerland.

FIG. 1. (Color online) DFB spectrum of a device based on a 0.5 wt % PDI-C6-doped film and a grating depth $d=105$ nm (thick full line); PL (thin full line) and ASE (dashed line) spectra of the film in a region without grating. Top: chemical structure of PDI-C6. Inset: DFB spectrum with expanded x -axis to display the spectral shape.

ing at 532 nm, which lies close to the maximum absorbance of PDI-C6.^{8,9} The pump beam was focused on the samples in a spot (1.20 mm diameter), at a $\sim 20^\circ$ angle with respect to the normal to the film. The emitted light was collected perpendicularly to the surface with a MAYA2000 fiber spectrometer adjusted to reach a resolution of 0.04 nm and placed at 1 cm from the sample. All experiments were conducted under ambient conditions. In order to properly evaluate the effect of the grating, films were also characterized in regions without grating, by using the same experimental setup. This way comparisons of thresholds or doses required to damage the materials can be done regardless on the units used to express the pump intensity.^{8,16}

Figure 1 shows the DFB spectrum (above threshold) of a device based on a 0.5 wt % PDI-C6-doped film and $d=105$ nm. Similar spectra, in terms of shape, linewidth, and emission wavelength, were obtained for films with other PDI-C6 contents or grating depths. As observed, it consists of two peaks (572.4 and 572.6 nm) separated by 0.2 nm. The observation of two peaks at both sides of the Bragg wavelength suggests that index coupling, rather than gain coupling, is the dominating mechanism for the gain process.^{1,16} The effect of the grating in the spectral response is evidenced when comparing with the spectrum obtained from a region without grating (see Fig. 1). Without DFB resonator, gain is also observed above a certain pump energy, in this case due to ASE, as discussed in previous works.^{8,9} The obtained ASE linewidth (around 5 nm) is larger than that measured for the DFB peaks (0.15 nm). Concerning the emission wavelength, ASE takes place at 579 nm, close to the vibrational PL peak, while DFB emission occurs at a wavelength determined by the grating period, the effective index of the film and the order of diffraction (in this case $m=2$) through the Bragg equation.^{1,16} With respect to the threshold, the presence of the grating leads to a decrease up to around 40 times, with respect to the ASE threshold of the film without grating (see Fig. 2). Since the ASE intensity curve does not show a well defined change in slope, the numerical value of the ASE threshold (76 $\mu\text{J/pulse}$) was obtained as the energy at which the emission linewidth (defined as the full width at half of the maximum) decays to half of its maximum value. This

FIG. 2. (Color online) Output intensity vs pump energy for DFB lasers based on 0.5 wt % PDI-C6-doped PS films and various grating depths (see legend), compared to the ASE output intensity for the film in a region without grating.

significant reduction in the threshold achieved by the presence of the grating is remarkably larger than that reported in other works,^{16,17} thus indicating the effectiveness of our resonators. Figure 2 also shows that the decrease in the grating depth leads to a better DFB performance. The best results, i.e., higher slope efficiency and lower threshold (1.8 $\mu\text{J/pulse}$) were obtained for the device with lowest d (105 nm). This can be explained in terms of the device losses, which would be higher in the deeper gratings, due to a poorer confinement of the waveguide mode. Concerning the dependence of the DFB threshold on the PDI-C6 content of the films, it was similar to that of the ASE behavior previously measured in PDI-doped waveguide films. For a given d , the lowest thresholds were obtained for concentrations between 0.3 and 0.8 wt %. For larger concentrations the threshold increases rapidly due to the formation of aggregated species.⁹

The most remarkable property of the DFB devices fabricated in this work is their large operational lifetime under ambient conditions. This has been studied by recording the total DFB intensity as a function of time, at a constant pump energy above the threshold at the same spot of the film. Results for the device with $d=105$ nm and a PDI-C6 content of 0.5 wt % are shown in Fig. 3. The device lifetime, defined as the photostability half-life ($\tau_{1/2}$), i.e., the time or the number of pump pulses at which the emitted laser intensity decays to half of its maximum value, has been represented as a function of the excitation energy in the inset of the figure. As observed, $\tau_{1/2}$ increases rapidly when the pump energy is decreased. At 4 $\mu\text{J/pulse}$ (2.2 times above the DFB threshold, 35 kW/cm^2), $\tau_{1/2}=3.1 \times 10^5$ pump pulses (516 min). This value is two orders of magnitude larger than that obtained for the film without grating ($\tau_{1/2}=4.8 \times 10^3$ pump pulses, i.e., 8 min), when excited at 250 $\mu\text{J/pulse}$ (around three times above the ASE threshold, 2.2×10^3 kW/cm^2). However, note that this ASE $\tau_{1/2}$ value is slightly higher than that obtained for the DFB device ($\tau_{1/2}=3.0 \times 10^3$ pump pulses, i.e., 5 min; see Fig. 3 inset) when excited at the same energy. The reasons to explain this relatively small difference are not clear at the moment. One possibility would be that the grating feedback increases the effective amount of energy

FIG. 3. (Color online) Normalized laser intensity vs irradiation time (bottom axis) and vs the number of pump pulses (10 ns, 10 Hz; top axis) for a DFB device based on a 0.5 wt % PDI-C6-doped PS film and grating depth $d = 105$ nm at various pump energies above the DFB threshold (see legend). Inset: half-life vs excitation energy (error in half-life is 10%).

received by the material in the DFB device. Nevertheless, the main point is that these DFB devices do not need to be pumped at such high energies, since their thresholds are much lower. We have also investigated the possibility of recoverability of the photodegraded samples, or self-healing, as reported for other materials.⁶ Experiments at different excitation intensities and resting periods were performed. Unfortunately, a recovery of the intensity was not observed in any case. Given that self-healing phenomena are highly dependent on the matrix,⁶ future work will focus in replacing PS by other matrices.

The comparison of our device to others published in the literature^{10–13} shows that its lifetime is the highest ever reported under ambient conditions, although precise comparisons are often not straightforward due to the different experimental conditions used to excite the devices. Particularly, the operational lifetime of our laser is clearly superior to those of other DFB devices operated in ambient conditions just above threshold [5×10^3 pump pulses exciting with 35 ps pulses at 10 Hz (Ref. 12) and 5.7×10^4 pump pulses exciting with 10 ns pulses at 10 Hz (Ref. 13)]. Kozlov *et al.*¹⁰ measured a lifetime of 8×10^5 pump pulses (4.5 h) in a microcavity laser but the film was encapsulated. On the other hand, nonencapsulated films deposited in waveguide configuration, showed lifetimes below 10^3 pulses. Finally, Heliotis *et al.*¹¹ fabricated a two-dimensional DFB laser with an operational lifetime of 2×10^7 pump pulses, when pumping seven times above threshold (at 10 Hz and 10 ns pulses) but experiments were conducted in vacuum. Here, a comparison of our results with other published in the literature, from a material's point of view, is not provided since ASE data

(without resonant cavity), obtained under similar experimental conditions, need to be used in order to properly accomplish that task.^{8,16} In fact, a comparison of the performance of PDI-based materials with that of other organic laser materials was already made in previous works.^{7,8}

In conclusion, we have fabricated by NIL an efficient, low-cost, and highly photostable (under ambient conditions) second-order organic DFB laser, based on a PDI-doped active film. The device emits at 573 nm, thus offering potential for applications based on polymer optical fibers. Its performance has been optimized by adjusting the PDI content in the active film and the grating depth d , the lowest threshold ($1.8 \mu\text{J/pulse}$) and highest slope efficiency being obtained for the device containing 0.5 wt % of PDI and $d = 105$ nm. This laser shows a photostability half-life of 3.1×10^5 pump pulses, i.e., >8 h, when pumped at a repetition rate of 10 Hz, in the same spot of the sample. This lifetime is the highest reported to date for organic DFB lasers measured under ambient conditions.

We thank support from the Spanish Government (MEC) and the European Community (FEDER) through Grant No. MAT2008-06648-C02.

- ¹I. D. W. Samuel and G. A. Turnbull, *Chem. Rev. (Washington, D.C.)* **107**, 1272 (2007).
- ²J. Clark and G. Lanzani, *Nat. Photonics* **4**, 438 (2010).
- ³A. E. Vasdekis, G. Tsiminis, J.-C. Ribierre, L. O'Faolain, T. F. Krauss, G. A. Turnbull, and I. D. W. Samuel, *Opt. Express* **14**, 9211 (2006).
- ⁴T. Riedl, T. Rabe, H.-H. Johannes, W. Kowalsky, J. Wang, T. Weimann, P. Hinze, B. Nehls, T. Farrell, and U. Scherf, *Appl. Phys. Lett.* **88**, 241116 (2006).
- ⁵Y. Yang, G. A. Turnbull, and I. D. W. Samuel, *Appl. Phys. Lett.* **92**, 163306 (2008).
- ⁶N. B. Embaye, S. K. Ramini, and M. G. Kuzyk, *J. Chem. Phys.* **129**, 0545041 (2008).
- ⁷I. García-Moreno, A. Costela, M. Pintado-Sierra, V. Martín, and R. Sastre, *Opt. Express* **17**, 12777 (2009).
- ⁸E. M. Calzado, J. M. Villalvilla, P. G. Boj, J. A. Quintana, R. Gómez, J. L. Segura, and M. A. Díaz-García, *J. Phys. Chem. C* **111**, 13595 (2007).
- ⁹E. M. Calzado, J. M. Villalvilla, P. G. Boj, J. A. Quintana, R. Gómez, J. L. Segura, and M. A. Díaz-García, *Appl. Opt.* **46**, 3836 (2007).
- ¹⁰V. G. Kozlov, V. Bulovic, P. E. Burrows, M. Baldo, V. B. Khalifin, G. Parthasarathy, S. R. Forrest, Y. You, and M. E. Thompson, *J. Appl. Phys.* **84**, 4096 (1998).
- ¹¹G. Heliotis, R. Xia, D. D. C. Bradley, G. A. Turnbull, I. D. W. Samuel, P. Andrew, and W. L. Barnes, *J. Appl. Phys.* **96**, 6959 (2004).
- ¹²H. Watanabe, H. So, Y. Oki, S. Akine, and T. Omatu, *Jpn. J. Appl. Phys.* **49**, 072105 (2010).
- ¹³Y. Oki, T. Yoshiura, Y. Chisaki, and M. Maeda, *Appl. Opt.* **41**, 5030 (2002).
- ¹⁴V. 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, *Microelectron. Eng.* **87**, 1428 (2010).
- ¹⁵E. M. Calzado, M. A. Díaz-García, J. M. Villalvilla, P. G. Boj, and J. A. Quintana, *J. Appl. Phys.* **97**, 0931031 (2005).
- ¹⁶E. M. Calzado, J. M. Villalvilla, P. G. Boj, J. A. Quintana, P. A. Postigo, and M. A. Díaz-García, *Appl. Opt.* **49**, 463 (2010).
- ¹⁷E. B. Namdas, M. Tong, P. Ledochowitsch, S. R. Mednick, J. D. Yuen, D. Moses, and A. J. Heeger, *Adv. Mater.* **21**, 799 (2009).