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Thermal-nanoimprint lithography for perylenediimide-based distributed feedback laser fabrication

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ABSTRACT

In the present work thermal-nanoimprint lithography of various commercial thermoplastic resists as matrixes for perylenediimides (PDIs) has been studied. This fabrication method reduces the number of fabrication steps, and therefore, the cost of the obtained distributed feedback (DFB) lasers. The optical properties of these devices are analyzed, aiming to optimize their performance.

1. Introduction

In the past years organic solid-state lasers (OSLs) have been widely studied mainly because organic materials offer various advantages, such as easy processability in the form of thin films, chemical versatility, wavelength tunability and low cost [1,2]. The discovery of stimulated emission in semiconducting polymer films [3,4] opened the possibility of using electrical excitation to pump the lasers and increased the interest in OSLs.

Distributed feedback (DFB) lasers are among the most studied OSL structures [1,2]. DFBs present several advantages, such as easy deposition of the organic film, low threshold and no need of mirrors. In a DFB laser, the refractive index and/or the gain vary periodically along the structure due to the inclusion of a grating in the substrate or in the active film. Light is "Bragg-scattered" in the grating, thus providing feedback along the waveguide, as well as the mechanism to extract the laser light out of the device [1,2]. In a one-dimensional (1D) DFB laser, the wavelength that satisfies the Bragg condition (λ_{Bragg}) given by

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

where m is the order of diffraction, n_{eff} the effective refractive index of the waveguide, and Λ the grating period, constitutes the resonant wavelength in the cavity, which will then be diffracted in the grating in different directions. For second-order DFBs ($m = 2$ in Eq. (1)) light is coupled out in a direction perpendicular to the waveguide film, by first-order diffraction.

Different techniques have been used to fabricate DFB structures. In some of them, relief gratings have been prepared over the substrate by holographic lithography [5,6], electron beam lithography (EBL) [7,8], laser interference lithography [8] or nanoimprint lithography (NIL) [9–11], and then the active film was deposited on top of them by spin-casting [5], spin-coating [6,7,9–11] or horizontal-dipping coating [8]. In other works direct patterning of the DFB structure on the active medium by UV laser interference ablation [12], two photon polymerization [13], or NIL [7,14–16] processes have been performed. Among all these fabrication methods, NIL is one of the most promising technologies due to its high throughput, low-cost and high fidelity pattern transfer [17,18]. NIL techniques have already shown numerous applications in biology, electronics, photonics and magnetic devices [18–21]. Among NIL processes, thermal-NIL (T-NIL), room temperature-NIL (RT-NIL), ultraviolet-NIL (UV-NIL) and combined nanoimprint and photolithography (CNP) can be mentioned. T-NIL is the simplest and most standard one used to imprint conventional thermoplastic materials, which are characterized for having a glass transition temperature (T_g), i.e. a temperature at which a transition

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in the amorphous regions between the glassy and rubbery state occurs. In order to process these materials by T-NIL, they need to be pressed and heated up to 70–90 °C above the T_g, so typical imprinting temperatures are in the range between 100 and 300 °C. The application of such high temperatures for imprinting thermoplastics doped with active molecules, often lead to the degradation of the latter ones, which constitutes an important limitation of the method. A possible way to solve that problem is the use of RT-NIL, which has been successfully used to directly pattern conventional thermoplastics as well as low-molar mass organic molecules or conjugated polymers [1,18]. However, since the pressure that must be applied is at least one order of magnitude higher than the one used in a conventional T-NIL, and the pattern cavities in the mold cannot be completely filled during the RT process when thermoplastic materials are used, the achievable imprinting depths are generally lower (typically less than 150 nm) and the quality of the transfer is generally poorer [18]. This fabrication method has been employed to obtain DFB devices [22–24], but due to these problems their performance is often limited, i.e. high laser thresholds, no precise control in the emission wavelength given certain fabrication parameters, poor photostability, etc. In the case of UV-NIL, this technique allows high fidelity pattern transfer and moderate aspect-ratio (A.R.) at low temperatures. However, it is more sophisticated, and consequently more costly than conventional T-NIL, since it needs high quality transparent stamps, usually made of quartz, for curing polymers by UV-flood exposure. Finally, with regards to CNP, it uses a photochemically curing resist as polymer matrix for T-NIL. It allows obtaining the grating at moderate temperatures, by combining UV-flood exposure, annealing and mold release at the same temperature. CNP has been used to produce high performing 2D DFB structures [25–27].

A wide variety of materials have been used to fabricate the active layers of organic DFB lasers [1,2,28,29]. Among them, our research groups have focused in the last years on polystyrene (PS) films doped with perylenediimide derivatives (PDIs) [9,30–36]. The advantage of using polyimides as lasers dyes is that they are photochemically and thermally stable. In particular, those containing perylene units possess high thermal stabilities because of the condensed aromatic perylene rings [37], and the decomposition temperature of PDIs depends on the nature of the substituents attached to the imide N positions [38,39]. In some of our previous works [31–33], the effect of modifying the chemical structure of the PDIs in their spectral, electrochemical and amplified spontaneous emission (ASE) properties when diluted in liquid solutions, as well as in PS films, at various concentrations, was studied. PDIs symmetrically substituted at the imide nitrogen position, such as *N,N′*-di(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic diimide (PDI-C6) and *N,N'*-di(2,6-diisopropylphenyl)perylene-3,4:9,10-tetracarboxylic diimide (PDI-O) (see chemical structures in Fig. 1) showed the best ASE results. So, efficient DFB lasers based on PS films doped with these dyes and with gratings imprinted on the substrate [9,34,36] or directly on the active film [30], were fabricated. Moreover, the influence of the excitation area on the thresholds of DFBs has also been studied [40].

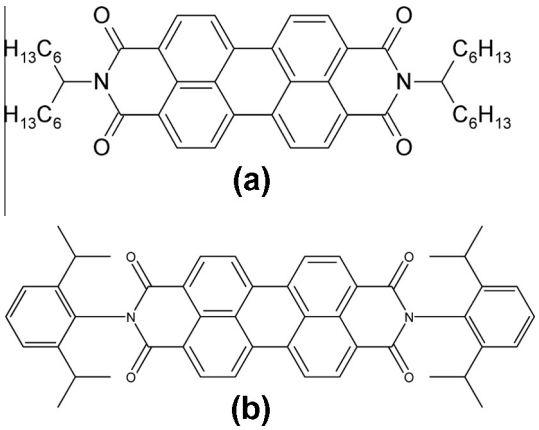

Fig. 1. Chemical structures of PDI-C6 (a) and PDI-O (b).

In this work we have prepared 1D second-order DFB lasers based on polymers doped with PDI-C6 and PDI-O, as laser dyes, fabricated by direct T-NIL of the active film, aiming to optimize the polymers used to disperse the PDIs. For that, thermoplastic polymers, such as mr-I7030E or mr-I8030E have been employed as matrix. The use of direct imprinting of the active films reduces the number of fabrication steps, simplifying the overall process to prepare the DFB lasers and consequently their cost. Results are compared to those previously reported, based on PDI-doped PS films [30].

2. Experimental

2.1. Materials

Several materials were used during the development of the work. Depending on their use they can be classified in:

2.1.1. Matrix to disperse the laser dye

Two commercial thermoplastic polymers for NIL were used as matrix: mr-I7030E and mr-I8030E from Micro Resist Technology GmbH. These resists are methacrylate-based polymers containing aromatic compounds in order to improve the plasma etch resistance and the flow behavior [41]. Their T_g values are 60 and 115 °C, respectively. Polymer concentration in the mr-I7030E solution is 10% (±2%) and 9.8% (±2%) in the mr-I8030E one.

2.1.2. Dyes

Two PDI derivatives have been used: PDI-C6 (M_w = 755 g/mol) and PDI-O (M_w = 711 g/mol). They were purchased from Lambda-Chem and Phiton, respectively, and their purity was higher than 99.5%. The thermal stability of PDI-C6 and PDI-O was analyzed by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) 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 T-NIL process. Results showed that the degradation of PDI-C6 and PDI-O started at a temperature of 345 and 389 °C, respectively. These values are above the temperatures used in the NIL process for mr-I7030E (130 °C) and mr-I8030E (165 °C), indicating that the PDI derivatives are thermally stable under the conditions used to fabricate the gratings.

2.2. Stamp

A 4-inch diameter silicon negative master, i.e., a stamp with the grating area surrounded by elevated area, was fabricated by EBL and posterior RIE processes by Kelvin Nanotechnology Ltd. The grating area of the stamp was 2.5 × 2.5 mm, the periodicity 368 nm, with equal line and space, the depth 260 nm and the A.R. around 1.4. The stamp was subsequently treated with a tridecafluoro-(1,1,2,2)-tetra-hydrooctyl-trichlorosilane antiadhesive coating deposited from the vapor phase in a dessicator connected to the vacuum pump (300 mbar, RT, 40 min).

2.3. Nanofabrication processes

The DFB devices were fabricated by the following steps: first of all, the thermoplastic matrix was mixed with the dye overnight at