

Distributed feedback lasers based on dichromated poly(vinyl alcohol) reusable surface-relief gratings

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Abstract: A simple, low-cost and versatile holographic method to produce reusable surface-relief gratings on dichromated poly(vinyl alcohol) (DCPVA) films, with periods $\Lambda \geq 270$ nm and modulation depths up to 300 nm, is reported. DCPVA presents processing advantages with respect to other photoresists, such as dichromated gelatine, i.e. higher light sensitivity, simpler fabrication process and better batch to batch reproducibility. The successful use of these DCPVA relief gratings as distributed feedback (DFB) laser resonators is demonstrated. Second-order DFB devices emitting in the wavelength range 577–614 nm have been easily prepared by coating a dye-doped polymer film on top of the resonators.

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 21. The "GSolver" software is available from Grating Solver Development Co. at www.gsolver.com.
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1. Introduction

Holographic lithography (HL), also known as interferometric lithography, constitutes a facile, inexpensive and large area nanolithography technique, which is receiving great attention in the area of nanophotonics [1]. Recent advances in various fields, such as metamaterials, negative-index materials, nonlinear optics, plasmonics, photonic crystals or organic distributed feedback (DFB) lasers [2,3], have implied the use of HL to pattern nanostructures on a size-scale comparable to or less than a wavelength. HL offers various advantages with respect to other nanolithographic techniques, such as electron-beam lithography (EBL) or nanoimprint lithography (NIL). EBL produces patterns of high quality, but the method is expensive and limited to small areas (generally below 1 mm²). NIL is very attractive for its potential for mass production, but it requires the use of a costly stamp master. HL is a convenient low-cost method, particularly when flexibility in changing parameters (dimensionality, periodicity and modulation depth) is needed. In addition, it allows producing small size structures over a large area (up to a few squared centimeters).

In the context of DFB lasers with active materials in the form of organic waveguide films, the most common geometry consists in a surface-relief grating engraved on top of a conventional substrate, such as glass or SiO₂, over which the organic active film is deposited [2–5]. Typically, gratings are recorded over an appropriate resist with EBL, NIL or HL, and then transferred to the substrate by ion-beam etching. Some efforts have focused on simplifying the grating fabrication process, for example by avoiding the ion-beam etching step. This can be done by engraving the grating directly on the active film (supported over a flat substrate) [2,3,6] or by using the resist with the grating directly as the substrate which supports the active film. This latter approach has been followed in the context of DFBs fabricated by HL, often using as photosensitive materials azo-containing polymers, which exploit the photo-isomerization properties of the azo-compounds [7–9], and in a few cases conventional photoresists [10]. Recently we reported DFB lasers consisting of organic active films deposited over relief gratings recorded on layers of the negative photoresist dichromated gelatine (DCG) [11]. Despite their relatively good laser performance, fabrication of relief gratings with DCG presents various difficulties in handling and processing, as well as a rather poor batch to batch reproducibility, both due to its complex and not well defined chemical composition [12,13]. To overcome such difficulties, we considered using dichromated polyvinyl alcohol (DCPVA), as an alternative photoresist to DCG. The PVA material is simpler and its composition well defined, so a better batch to batch reproducibility is expected. In addition, the whole processing can be carried out at room temperature (RT), in contrast to DCG that requires different temperatures in certain process steps, i.e. ~40°C for film deposition and 15°C for desensitization. Although DCPVA has been often used in holography to record real time volume holograms [14,15], as far as we know, it has not been previously used to produce surface-relief gratings.

A wide variety of organic materials has been employed to fabricate the active laser layers of organic DFBs [2,3]. Among them, our research group has focused on perylenediimide (PDI) derivatives dispersed in polystyrene (PS) films, which have shown excellent photostabilities and relatively low thresholds in lasers of different geometry and prepared by

different methods [5,6,11,16,17]. In the case of devices based on DCG resonators, the use of PS as matrix lead to some complications, since its refractive index ($n = 1.59$) is close to that of DCG ($n = 1.55$) [11]. So a laborious adjustment of several parameters was needed in order to improve the confinement of the fundamental waveguide mode and to avoid laser emission in high-order modes, being both aspects important to achieve a good device performance. Given that n of DCPVA is 1.53, only slightly inferior than n of DCG, similar difficulties would be expected in devices based on dye-doped PS and DCPVA. A possible strategy to avoid such limitations would be to use a matrix polymer with a higher n [18].

In the present work, we have fabricated reusable surface-relief gratings on DCPVA by HL with periods $\Lambda \geq 270$ nm and modulation depths (d) up to 300 nm. The potential of these gratings to be used as resonators for second-order DFB lasers has been explored. Devices emitting in the wavelength range 577-614 nm have been prepared by depositing dye-doped polymer films on top. Grating fabrication and laser performance parameters are compared to those of DCG.

2. Experimental techniques

The new method to make surface-relief gratings on DCPVA consists of the following steps: (1) Photoresist deposition: Filtering and spin-coating of DCPVA over 2.5×2.5 cm² SiO₂ plates take place at RT. The sensitizer (ammonium dichromate) concentration with respect to the polymer is kept constant (35%). Film thickness (measured with an interferometer coupled to an optical microscope) between 200 nm and 1.2 μ m were obtained by varying the PVA concentration in the water solution between 7% and 15%; (2) Grating recording: One dimensional (1D) gratings are recorded with an Argon laser emitting at the wavelength $\lambda = 364$ nm, which is close to the wavelength of maximum absorbance of ammonium dichromate, i.e. $\lambda_{\text{max}} = 372$ nm [19]. The pattern recorded is obtained by the interference of the direct beam (5 cm diameter) and the reflected beam in a mirror attached with a 90° angle to the sample holder (a scheme of the setup can be found in [4]). The light intensity pattern was uniform over the whole sample area. Inter-beam angles (θ) of 84.8° y 58.9° were used to obtain Λ values [$\Lambda = \lambda/2\text{sen}(\theta/2)$] of 270 and 370 nm, respectively; Desensitization: Samples are soaked in a mixture 1:5 of water and isopropyl alcohol for 60 s, rinsed in isopropyl alcohol for 20 s, and finally centrifuged at 500 rpm for rapid drying; (4) Development: Unexposed PVA is removed in an oxygen electron cyclotron resonance stream. Different d values are obtained by varying the development time. Some of the gratings were characterized by field emission scanning electron microscopy (FE-SEM, ZEISS Ultra Plus) and atomic force microscopy (AFM, NT-MDT Solver PRO). Active films were spin coated from toluene solutions over the gratings recorded on DCPVA layers. Two types of materials were used: (1) Poly(vinyl carbazole) (PVK), doped with the laser dye 4-Dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran (DCM); and (2) PS doped with the PDI derivative *N,N'*-di-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxydiimide (PDI-C6). Films over DCPVA layers without gratings were also prepared for film thickness and amplified spontaneous emission (ASE) characterization. Dye concentrations were 0.5 wt%, for PDI-C6 in PS, and 3 wt%, for DCM in PVK, since they have shown to provide the lowest thresholds [17]. Chemicals were supplied by Sigma-Aldrich. We used PVK (secondary standard, $M_w = 81,800$) with $n = 1.68$, which was purified before use by dissolving in toluene followed by precipitation in ethanol.

DFB and ASE characterization was performed under excitation with a pulsed Nd:YAG (YAG-yttrium aluminum garnet) laser (10 ns, 10 Hz) operating at 532 nm [11,16]. The pump beam over the sample (elliptical with a minor axis of 1.1 mm) was incident at $\sim 20^\circ$ with respect to the normal to the film plane. The small deviation from normal incidence aimed to facilitate light collection, by means of a 0.13 nm resolution fiber spectrometer, in a direction perpendicular to the sample surface.

3. Results and discussion

3.1 Grating fabrication and characterization

Diffraction efficiency (η), defined as the ratio of first-order diffracted to incident ($\lambda = 364$ nm) light intensity, and modulation depth (d) of DCPVA gratings with $\Lambda = 270$ nm, as a function of average exposure and development time, respectively, are shown in Fig. 1. Results corresponding to gratings obtained by using DCG and the process described in detail in [11], using the same photoresist and sensitizer concentrations as for DCPVA, are also included.

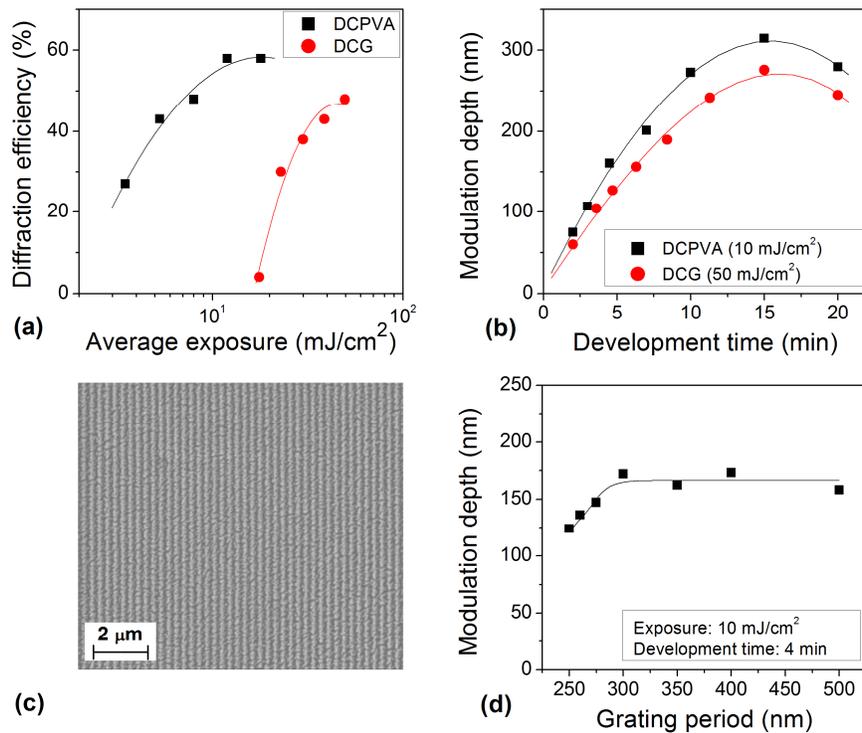


Fig. 1. (a) Diffraction efficiency versus average exposure and (b) modulation depth, d , versus development time, for DCPVA and DCG gratings with period $\Lambda = 270$ nm. Solid lines are guides to the eye; (c) SEM photograph of a DCPVA grating with $d \sim 100$ nm; (d) d versus Λ for DCPVA.

Firstly, the development time was fixed to 10 min and the average exposure was varied [Fig. 1(a)]. Results show that η increases with average exposure up to a maximum of 60% and 50% for DCPVA and DCG, respectively. In addition, light sensitivity of DCPVA is between 5 and 10 times higher than that of DCG. Note that high η values are possible because these relief gratings behave as “thick” gratings due to the large d and small Λ [20]. Secondly, an average exposure for obtaining a high selectivity between exposed and non-exposed regions was fixed, 10 and 50 mJ/cm² for DCPVA and DCG, respectively, and the development time was varied to obtain gratings with different d [Fig. 1(b)]. The Gsolver program was used to calculate d from η [21]. Depths were also measured with AFM, but values were appreciably lower than the calculated ones due to the effect of the tip radius on scans. It can be seen that for DCPVA gratings the maximum achievable d is around 300 nm, slightly larger than that for DCG gratings. Development times over 15 min lead to a decrease in d because the whole resist from unexposed regions is removed.

Grating uniformity over the whole sample area was confirmed by performing SEM scans in different sections of the same sample. A SEM image of a DCPVA grating developed for 3

min, so $d \sim 100$ nm, is shown in Fig. 1(c). Its texture is grainy and the grating lines irregular, similarly to those obtained with DCG consisting of randomly distributed fibers of diameters around 50 nm [11]. These fibers, formed during the grating fabrication process (for any Λ), establish the resolution limit of the material. It was observed [see Fig. 1(d)] that for $\Lambda < 270$ nm, a few times above the size of the fibers, d diminishes since gratings become poorer. On the other hand, for $\Lambda \geq 270$ nm the grating structure is clear and the period well defined, indicating that in those cases DCPVA is a useful material to record gratings with depths up to 300 nm. It is also remarkable that DCPVA is a water-soluble photoresist, insoluble in most organic solvents (e.g. toluene). Therefore, whenever the deposition of the organic active layers on top to fabricate devices such as DFB lasers is done from solutions based in organic solvents, which is the most common case, the DCPVA resonators remain unaltered. This also implies that these can be reused multiple times in different devices, after dissolving the active film (also with an organic solvent).

3.2 Fabrication and characterization of DFB lasers

The applicability of DCPVA gratings as DFB laser resonators was tested by preparing a set of devices emitting at different wavelengths (λ_{DFB}). The DCPVA film thickness (before recording) was 1100 nm. The grating period was 370 nm, so DFB feedback along the waveguide occurs via second-order diffraction and laser light is coupled out perpendicularly by first-order diffraction [16]. Modulation depths were in the range 75-100 nm, which required development times of only 2-3 min. Device fabrication was completed by depositing active layers of PVK/DCM or PS/PDI-C6 on top of the DCPVA resonators. The thickness of the active film (h) was adjusted to obtain emission at a wavelength close to the maximum of the gain spectrum (i.e. the wavelength at which the active material deposited over a substrate without grating shows ASE, λ_{ASE}). The emission spectra of these lasers (labeled as **1-3** and **4-5**, for PVK/DCM and PS/PDI-C6, respectively) are displayed in Fig. 2(a).

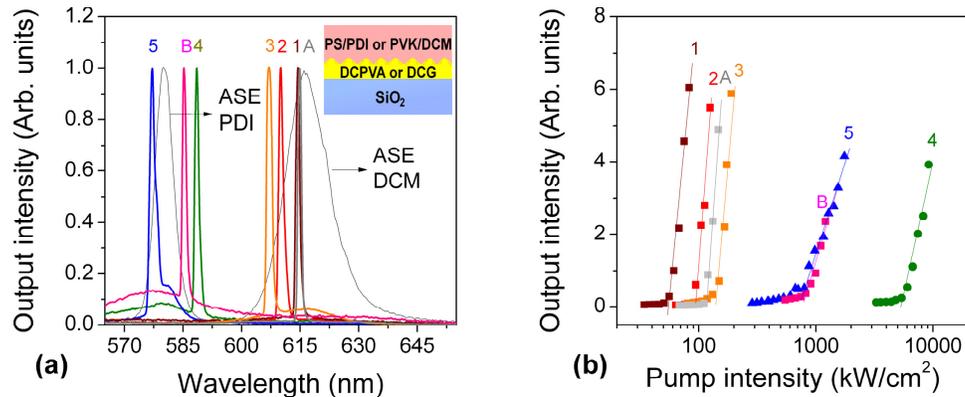


Fig. 2. (a) Emission spectra (labeled thick lines) of DFB lasers (scheme of the device in inset) based on DCPVA resonators with $\Lambda = 370$ nm (**1-3** and **4-5** for active films of DCM-doped PVK and PDI-doped PS, respectively) and on DCG resonators with same active material (**A**) and (**B**); Data for (**B**) were taken from [11]; ASE spectra of similar active films deposited over photoresist layers without gratings are displayed (thin solid lines); (b) Output intensity at λ_{DFB} versus pump intensity for DFB lasers **1-5** and (**A**), (**B**). Solid lines are guides to the eye.

The interest of preparing devices based on the PVK matrix was to improve the waveguide properties, with respect to PS, thanks to its higher n . In this case, the DCM laser dye was selected because we observed quenching of the PL emission of PDI-C6 when dispersed in PVK. Data for PS/PDI-C6-based lasers are also shown in order to compare to previous results with DCG resonators [11] as well as to assess the benefits of increasing the polymer matrix index. Spectra for devices based on DCG resonators (labeled with **A** and **B** for PVK/DCM

and PS/PDI, respectively) are also shown in Fig. 2(a). Graphs of output versus pump intensity for all the lasers are shown in Fig. 2(b). These are useful to determine the laser threshold (pump intensity at which the output intensity increases abruptly) and the relative laser efficiency (from the curve slope above threshold). For each type of active material, lasing occurs in a different spectral region, determined by the dye PL spectrum.

In lasers **1-3** (PVK/DCM and DCPVA), h was varied from 630 to 480 nm, allowing to tune λ_{DFB} by around 7 nm. Calculations such as those performed in [11], but adapted to these devices, have shown that DFB emission is associated to the fundamental transverse electric (TE_0) waveguide mode. Device **1** shows the lowest threshold because its λ_{DFB} is closer to λ_{ASE} , at which gain is maximum. Comparison of DCPVA to DCG can be made by comparing the performance of laser **1** to that of device **A** (with PVK/DCM and DCG), both lasers having similar h and λ_{DFB} . The threshold is somewhat lower for **1**, which can be attributed to the slightly lower n of DCPVA in comparison to DCG. This would be an added advantage of DCPVA, although the differences are not very significant.

With regards to lasers based on PS/PDI-C6 and DCPVA (devices **4** and **5**), their performance is inferior to that of the PVK/DCM lasers just discussed (i.e. higher thresholds are smaller slope efficiencies). For device **4**, whose h is similar to that of lasers **1-3** (i.e. $h = 600$ nm), lasing also occurs at the TE_0 mode, but its threshold is very large. This is mainly because lasing occurs far from λ_{ASE} , but also because waveguide mode confinement is very poor, due to small refractive index difference between film and substrate [11]. Mode confinement can be improved by increasing h , so we prepared a laser with $h = 1000$ nm (device **5**), whose λ_{DFB} is closer to λ_{ASE} , so its threshold is lower. However, DFB emission corresponds to the TE_1 mode, preventing to obtain the lowest possible thresholds. This illustrates the difficulty of achieving DFB emission at the TE_0 mode and good mode confinement at the same time, when using PS as matrix [11]. As shown above, these limitations can be overcome by using a matrix polymer with higher n , such as PVK. The performance of device **5** can be compared to that of the previously reported DCG-based laser (device **B**) [11], whose laser emission is also associated with the TE_1 mode. Laser **B** emits at a longer λ_{DFB} because film thickness is slightly higher ($h = 1100$ nm), but the separation from λ_{ASE} is around the same as for device **5**, explaining the similar threshold value obtained. These results indicate that also with the PS/PDI-C6 active material, DCPVA and DCG show similar results in relation to their functionality as DFB resonators.

4. Summary and conclusions

DCPVA is a useful photosensitive material to fabricate, by means of HL, low-cost, simple, versatile and multiple-use surface-relief gratings, with periods $\Lambda \geq 270$ nm and modulation depths up to 300 nm. DCPVA presents advantages with respect to DCG from the point of view of the grating fabrication procedure: light sensitivity is between 5 and 10 times higher, processing can be carried out at RT and a better reproducibility is obtained. The applicability of DCPVA gratings as DFB laser resonators has been demonstrated by fabricating second-order DFB lasers with two types of active materials. The use of a high index polymer matrix such as PVK, to host the laser dye, has allowed improving the waveguide properties of the devices (i.e. emission at the TE_0 mode at low threshold). From the point of view of the functionality as DFB resonators, no significant differences have been found between DCPVA and DCG. Overall, this work proposes a method to fabricate relief gratings on DCPVA, which might be useful for a variety of nanophotonic applications, in addition to DFB lasers.

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