Polymer gratings based on photopolymerization for low-order distributed feedback polymer lasers

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Novel polymer distributed feedback (DFB) gratings are fabricated based on photopolymerization to reduce lasing threshold of polymer lasers. A photopolymer formulation sensitive to 355-nm ultraviolet (UV) light is proposed for the fabrication of polymer gratings and it can be used to form polymer films by spin-coating process. A very low surface-relief depth ranging from 12.5 to about 1.0 nm has been demonstrated with a refractive-index modulation of about 0.012. The experimental results indicate that such polymer gratings have promising potentials for the fabrication of low-order DFB organic semiconductor lasers.

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Polymer luminescent material is a kind of superior gain material with high gain coefficient and low self-absorption coefficient, which could be applied in the fabrication of organic semiconductor lasers[1−4]. In the past few years, optically pumped polymer lasers have been demonstrated with various resonant-cavity configurations[5,6]. In order to reduce lasing threshold to realize electrically driven lasing, low-loss organic resonator can be adopted. Distributed feedback (DFB) structure is believed as one of the most promising ways[7].

Many techniques have been developed to fabricate DFB-organic solid lasers (DFB-OSLs)[8−17]. One of the methods is to etch one-dimensional (1D)[9,10] or two-dimensional (2D)[11,12] DFB grating on silica substrate surface first, then form organic thin film by spin-coating. Another is to use soft lithography[13−15] or photoisomerization reaction[16] to form grating on the polymer films directly. In the former case, complicate fabrication techniques are required, while in the latter case, some complicate fabrication techniques are needed to stabilize the refractive index changes. Both of them lead to considerable complexity in fabrication process. Moreover, all the approaches mentioned above manifest a surface relief as high as several tens of nanometers to several hundreds of nanometers[9−11,13−16], which could cause some difficulties in the later steps toward the fabrication of DFB polymer laser.

Monroe *et al.*[18,19] developed series of photosensitive polymer to fabricate holographic diffraction grating by ultraviolet (UV) polymerization reaction. Its refractive index modulation can be achieved around 0.01. However, only samples with fixed grating period of about 1 μm were investigated in their reports. To fabricate the low-order gratings generally used in DFB lasers, it is necessary to study the application of photopolymer for short period gratings. In addition, the maximum absorption wavelength of the photo-initiator system used in Monroe's is at about 477 nm and it is insufficiently sensitive to 355-nm UV light used in our experiment. So we developed a photopolymer formulation sensitive to 355-nm UV light and compatible with spin-coating process to fabricate low-order polymer DFB grating by UV polymerization reaction.

Photosensitive polymer materials are composed of a polymer binder, a liquid monomer, and photo-initiator system. The nonvolatile additives of the coating solutions contain 51.2% poly(methyl methacrylate)(PMMA), 45.6% 2-phenoxyethyl ester acrylate (POEA), 2.5% benzophenone, 0.7% 4,4'-bis (dimethylamino) benzophenone (Michler's ketone), and 0.01% 2,6-di-t-butyl-4-methylphenol (BHT). In this formulation, PMMA was used as binder, while POEA acted as monomer. Benzophenone combined with Michler's ketone is an efficient photo-initiator system for 355-nm UV light, and BHT was used for antioxidation. The solvent was chlorobenzene, which has a good solubility for PMMA as well as appropriate low volatility, making it possible to form polymer film with excellent uniformity by spin-coating process. The total concentration of solution is 18% (by weight).

The photosensitive polymer solution was spin-coated onto transparent glass substrates at 1500 rpm to form sample films. A frequency-tripled picosecond Nd:YAG laser was used to excite photopolymerization. Figure 1 shows the interference exposure configuration. Using Lloyd mirror can form a good interference pattern on photopolymer sample and adjusting the angle of the mirror can change the polymer grating period. Before UV exposure, the samples were pre-baked at 70 °C for 2 − 5 min, and then exposed in interference UV light whose intensities were about 4 mW/cm^2 for 2 min. After exposing the film under a laser beam to polymerize the residual monomer, the samples were post-baked at 100 °C for 30 min. During the course of both exposures, the polarization of the laser beam was kept parallel to the

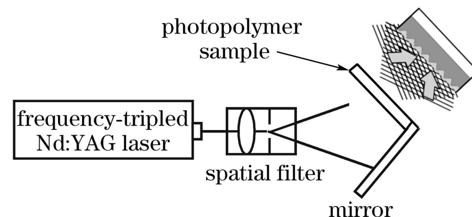

Fig. 1. Schematic configuration for UV interfering exposure.

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interference fringes. All above processing were carried out in N_2 environment to reduce influence of air, O_2 and H_2O molecules.

The diffraction efficiency of the gratings was measured with a He-Ne laser with output wavelength of 632.8 nm. The sample was held at Bragg angle with the laser beam, and the diffraction efficiency η was calculated as follows

$$\eta = \frac{I_\mathrm{d}}{I_\mathrm{d} + I_\mathrm{t}}, \quad (1)$$

where I_t is the intensity of the radiation passing through the sample and I_d is the intensity of the radiation diffracted. According to Kogelnik's coupled-wave theory[20], the diffraction efficiency for grating is given by

$$\eta = \sin^2\left(\frac{\pi \Delta n d}{\lambda \cos\theta_0}\right), \quad (2)$$

where Δn and d are the refractive index modulation and the grating thickness, respectively. $\lambda = 632.8$ nm is the wavelength of the probe radiation, while θ_0 is the Bragg angle within the polymer, which can be calculated by

$$\theta_0 = \arcsin\frac{\lambda}{2n_\mathrm{eff}\Lambda}, \quad (3)$$

where Λ is the grating period, and n_eff is the effective refractive index of the polymer film, which was measured to be about 1.5 with MF-1000 ellipsometer.

In interference exposure conditions, a polymerization reaction take places in monomer, and the monomer migrates from non-reaction regions to reaction regions, while the binder migrates from reaction regions to non-reaction regions, ultimately forms material cycle distribution, and thus the refractive index modulation. Theoretically, grating index modulation Δn should be unrelated to the film thickness d. From Eq. (2), we can see sine-squared relations between the diffraction efficiency η of grating and the film thickness d. Therefore, we can measure the grating diffraction efficiencies of the samples with same grating period and different film thicknesses to determine the refractive index modulation amplitude Δn.

We measured grating diffraction efficiencies of six group samples with the Λ = 1000, 800, 600, 500, 400, 350 nm, and obtained each refractive index modulation amplitude. Figure 2 shows the dependence of refractive index modulation Δn on the period Λ of the gratings.

By fitting the experimental data with the results given by coupled-wave theory[20], the maximum refractive index modulation Δn was found to be 0.012, much higher than 0.008 reported by Monroe for a similar photopolymer formulation composed of PMMA binder and POEA monomer[19].

We measured the surface morphology of the polymer gratings with atomic force microscope (AFM). The sample was spin-coated at 1500 rpm, resulting in a film thickness d of about 12 μm. A typical grating ($\Lambda = 1000$ nm) surface of the AFM image is shown in Fig. 3. The grating surface relief depth Δh was about 12.5 nm. It was found that the surface relief depth Δh decreases with the grating period Λ, as shown in Fig. 4.

Being of a small molecular structure, monomer can shuttle between polymer chain gaps freely. While being of a macromolecular chain structure, polymer binder migrates more slowly than monomer does. Especially when the polymerization reaction takes to a certain extent that monomer depletes greatly, the migration of polymer binder will encounter greater resistance and more gather in reaction regions, so the film thickness of reaction regions is slightly larger than both sides, forming the surface relief depth.

The phenomenon that the film surface relief depth decreases with the grating period can be explained as follows: on the one hand, because of internal defects scattering of the film, the smaller the grating period is, the worse extinction ratio of interference light is, and the more gentle space distribution is. Such make the film internal modulation of refractive index range and the surface relief depth decrease with the grating period. On the other hand, the smaller the grating period is, the

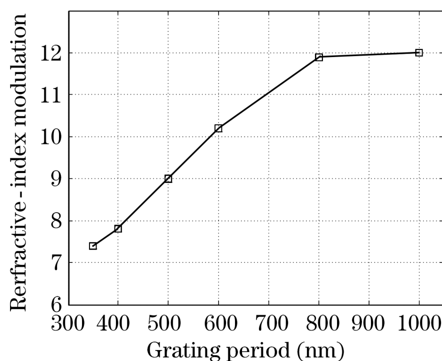

Fig. 2. Refractive-index modulation decreases with grating period.

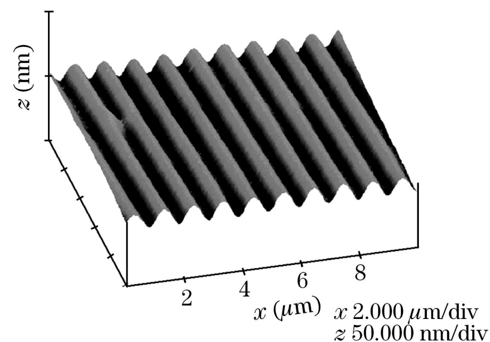

Fig. 3. AFM image of the DFB gratings ($\Lambda = 1000$ nm).

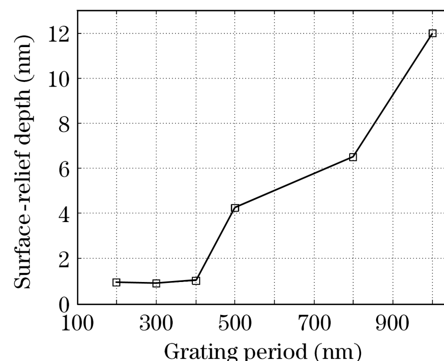

Fig. 4. Surface-relief depth Δh decreases with the grating period Λ.

shorter the migration distance is, so the polymer binder can quickly migrate to interference extinction regions, which will help to reduce grating fluctuations.

For samples with a grating period less than 400 nm, Δh was only about 1 nm. Such a smooth surface is of significant advantage compared with other polymer grating fabrication techniques. After forming grating on silica substrate surface, we can then form organic films by spin-coating or by vacuum thermal deposition to fabricate organic DFB lasers conveniently.

In summary, we have developed a photopolymer formulation that is sensitive to 355-nm UV light and can be used to form polymer films by spin-coating process. A very low surface relief depth ranging from 12.5 to about 1.0 nm has been demonstrated with a refractive index modulation Δn of about 0.012. Such polymer gratings show promising potentials for the fabrication of low-order DFB organic semiconductor lasers.

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