Femtosecond laser induced index and relief gratings in polymer films

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A true single-step process suitable for fabrication of micro-periodic structure in polymer films by two-photon initiated photopolymerization and laser ablation is presented. By the right choice of the irradiation energy, the irradiated zone is modified or ablated in the 1.44-μm-thick film. The mechanism of grating generation and the potential application of the gratings in integrated optics are discussed.

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Planar grating waveguide structures (GWS) play a very important role in the construction of compact integrated optical devices. They are attractive for numerous optical applications such as narrow-band spectral filters[1], optical switches and modulators[2], high-reflectivity mirrors[3], distributed feedback (DFB) lasers[4], grating coupler biosensors[5], and so on.

Pressing demands for inexpensive yet reliable and efficient waveguide grating lead many researchers to consider polymers as an alternative basic material[1,4,6]. Many different approaches for the writing of gratings in polymers have been developed such as imprinting or embossing[7], laser ablation[1], holographic interference[8], ultraviolet (UV) irradiating lithography[9], and photoisomerisation[10]. At present, most methods are altering the surface profile of the films. These involve some photochemical process and/or some developing stages. Also some volume gratings have been reported in photoreactive polymers[10−12] where the refractive index of materials can be changed throughout the volume of the films. Unfortunately, all these methods can only realize one sort of gratings mentioned above in one step.

Two-photon initiated polymerization (TPIP) in organic materials has been shown to be a powerful tool for micro- and submicro-fabrication. Femtosecond laser induced TPIP gratings in polymer films have not been studied much so far. Several groups have investigated two-photon induced grating structures in bulk polymeric materials[13−15]. Under various conditions, volume-grating structures have been produced. But for practical application, especially in integrated optics, waveguide thickness is usually several micrometers related to the refractive index of substrate and waveguide layer. Therefore, it is necessary to investigate TPIP in polymer films for further application of phase gratings. In this letter, we report a true single-step process suitable for fabrication of phase gratings in polymer films. Index or relief gratings can be fabricated in one step according to practical applications by the irradiation of femtosecond lasers.

Effective initiators are key to TPIP. Since a high effective initiator for TPIP is not available commercially, an initiator 1-[(1E)-2-(4-{[4-((1E)-2-(4-[4-N,N-dimethylamino]phenyl)vinyl]phenyl}phenylamino)phenyl]-vinyl]-4-[4-N, N-di-methylamino]benzene (abbreviated as DPVMB) with D-π-A structure had been synthesized and used as a two-photon absorption sensitizer. The single-photon and two-photon absorption and fluorescence properties in various solvents had been studied in pervious work[16]. The maximum value of two-photon absorption cross-section is 20×10^{-50} cm^4·s·photon^{-1} molecule^{-1} at 800 nm.

Our resin consists of 1% photoninitiator, 70% monomer (Sartomer Product No.CN970E60), and 29% polymer binder (poly (methyl methacrylate)). The film of the copolymer was prepared on quartz substrate using a spin-coater. The quartz substrate with size of $40 \times 40 \times 33$ (mm) was polished and cleaned before spin coating. The refractive index of the substrate is 1.4569 (measured at the wavelength of 633 nm). Thin films of the polymer ($\approx 1-2$ μm) were prepared by spin coating, as described in detail elsewhere[17].

A film was prepared by spin coating on a quartz substrate under 1300 r/m for 30 s and soft-baking procedures. The 2010 prism coupling measuring system (made in Metricon, USA) was used to investigate the refractive index and thickness of polymer films[18]. The measured thickness and refractive index of the film are $d = 1.44$ μm and $n = 1.51$ at the wavelength of 632.8 nm.

The experimental setup is shown in Fig. 1. A mode-locked 76-MHz and ~200-fs pulses Ti:sapphire laser operating at 800 nm is used as an excitation source. The incident energy was attenuated with a half-wave plate before a polarizer. Then the laser beam was tightly focused by an optical microscopic objective with a high numerical aperture (NA) of 0.8 into the polymeric thin-film, yielding a focus diameter $d_{\text{focus}} = 1.22\lambda/\text{NA} = 1.22$ μm. The substrate was placed on a computer controlled three-axis translation stage.

Due to the superior spatial confinement on the longitudinal direction of TPIP, especially for low power,

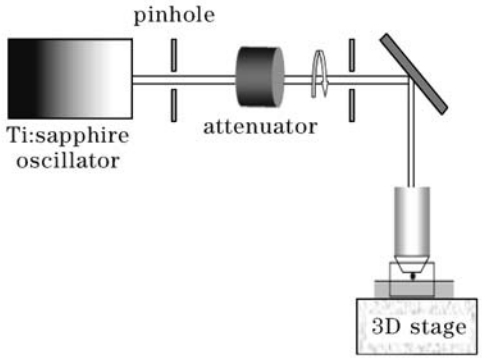

Fig. 1. Principle setup for the fabrication of planar waveguide gratings by two-photon polymerization.

two surfaces of both the polymer film and the substrate should be leveled strictly. Otherwise, the focus will easily deviate from the thin-film, which is different from stereo polymerization. So it is necessary to modulate the stage on the xy plane precisely. Also, the setup is susceptible to vibration and environmental changes. Slight shake of the translator, especially at high scanning speed will greatly affect the continuity of polymeric stripe in the situation of single or two modes waveguide. In our experiment, the scanning speed is 50 μm/sec. Lower scanning speed means longer time for fabricating process.

Femtosecond laser pulses periodically scan on the top of the thin-film and the polymerization process can be initiated upon the polymeric threshold through the thin film. In our experiment, the TPIP threshold was about 10 mW. Scanning electron microscope (SEM) analysis has revealed the existence of the polymerized stripe in the previous experiment. With the incident power of 30 mW, a thicker film was written for achieving several stripes and then the sample was submerged into 1,2-dichloroethane for several minutes. The unpolymerized monomer and inert component were extracted. The sample was dried in vacuum and coated with a thin layer of gold. The results are shown in Fig. 2. Line width of the stripes was about 0.8 μm.

Based upon the experimental results above, a refractive-index modulation grating was fabricated in the 1.44-μm-thickness film. The phase-contrast microscopic photo of the microstructure is shown in Fig. 3.

To characterize the morphology of grating region, the generation of surface profile was observed through an atomic force microscopy (AFM) section analysis, as shown in Fig. 4. The peak-to-peak modulation depth

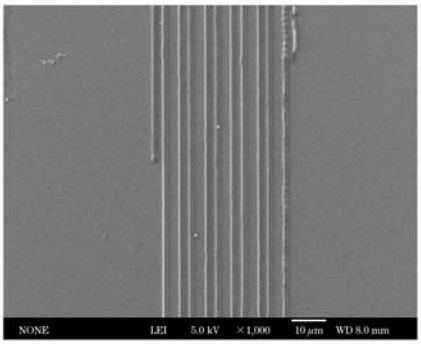

Fig. 2. SEM image of the stripes fabricated by TPIP.

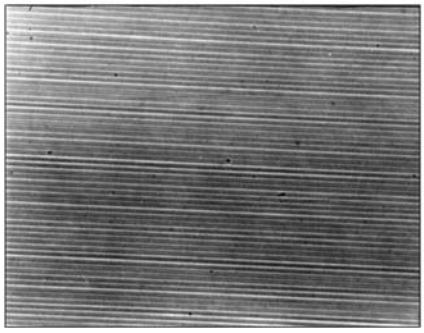

Fig. 3. Microscopic photos of microstructure with an incident energy of 30 mW in the 1.44-μm-thick film. The period of the grating is 2 μm.

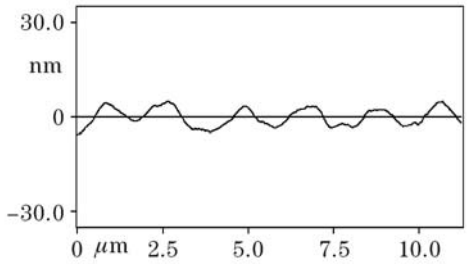

Fig. 4. AFM section analysis of the surface after irradiation by a laser power of 30 mW.

is about 7 nm. The surface of the grating is rough and uneven since in this case the photothermal influence cannot be totally neglected.

The surface profile of the induced grating structure depends on the incident energy. On a femtosecond scale, thermal diffusion into the material is nearly negligible. Roll of the surface is little. Therefore while the incident energy is below the ablation threshold, there will be only TPIP occurring in the film.

Increasing the incident energy can distinctly alter the modulation amplitudes of the surface to form relief gratings. Various sinusoidal gratings exhibiting different grating amplitudes were generated in the polymer films by applying different laser powers just above the ablation threshold. An example of a typical surface relief grating written in the former film at an incident power of 50 mW is shown in Fig. 5. In comparison with the first volume-grating sample (produced by 30 mW), a quai-sinusoidal grating surface with homogeneous periodicity attests to the good quality of the laser-generated grating. The quality of the groove edges of the surface gratings is very high and the peak-to-peak modulation depth is about 40 nm. This arises from the fact that the polymer

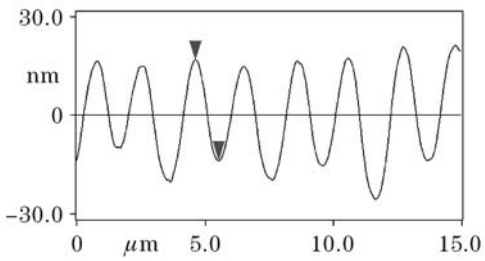

Fig. 5. AFM section analysis of the surface after irradiation by a laser power of 50 mW.

produces gaseous products, which do not condensate on the surface. The surface profile attributed to ablation but not the strong heating effect of the pulsed lasers that lead to swell, as written portions of the film are lower than the unwritten ones. It is pertinent to note that TPIP still occurs in the case of ablation. As TPIP volume and laser ablation surface relief gratings are totally transparent, both are phase gratings, not amplitude gratings.

For phase gratings, the Δn is defined as the refractive index difference between the irradiated and non-irradiated zones. Δn of TPIP gratings is the order of $\sim 10^{-3}$[13], less than that of the surface relief gratings. Δn of the latter is $\Delta n_{\rm surf} = n_{\rm film} - n_{\rm air} = 1.51 - 1 = 0.51$, where $n_{\rm film}$ is the refractive index of the film and $n_{\rm air}$ the refractive index of the air. As a diffractive element, obviously the relief grating would play a dominating role.

In conclusion, one-step relief and index gratings can be generated in polymer films with different incident powers by fs-laser induced multi-photon absorption. The index gratings may be used in organic DFB laser, especially for electrically pumped DFB laser, which usually needs a field-effect electrode to inject electrons and in narrow-band spectral filters and nonlinear optical switch. The smooth surface in grating region would be benefit for the further process. The further study for integrated optics devices such as input/output coupler (index and relief gratings), filters and polymeric DFB laser is under progress.

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