Femtosecond Laser Direct Writing and Spectroscopic Characterization of Microstructures, Craters, and Gratings in Bulk/Thin Films of Polystyrene

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Abstract. We present our experimental results obtained from the microfabrication of structures in thin films and bulk of polystyrene (PS). Different microstructures, craters, and gratings were fabricated and detailed physical/optical studies on these structures are presented. Diffraction gratings using 40X microscope objective lens in bulk PS exhibited a maximum diffraction efficiency of 10%. The observation of free radicals including luminescent centers and paramagnetic centers are presented in detail using the data collected with UV-Visible spectrometer and Electron Spin Resonance Spectrometer (ESR). Raman analysis of the microstructures is also discussed.

INTRODUCTION

Polymer optical components have been widely used for a number of applications because of their favorable characteristics including cost performance, flexibility/processability, and low weight. Among the optical components available, diffractive optical elements have attracted a great deal of interest [1-2]. Femtosecond lasers allow the fabrication of integrated photonic devices in three dimensions. Focused femtosecond laser pulses can induce structural changes in a localized volume inside transparent materials due to nonlinear absorption. Several reports of the use of this technique to fabricate waveguide devices and diffractive elements in a wide variety of glasses, polymers such as PMMA have appeared in the literature. In all these reports, the refractive index in the laser focus area increased relative to that before the irradiation. However, the reason for the observed changes in refractive index is not yet clear [3-5].

EXPERIMENTS AND RESULTS

Experiments were carried out using 100 fs pulses with 1 mJ energy (800 nm, 1 kHz). Half wave plate and polarizer combination was used to change the energy. 40X and 20X microscope objectives were used to fabricate structures in bulk and thin films of PS. Three Newport nano-positioner stages stacked together was used to control the fabrication process. PS bulk was purchased from Goodfellow, UK and is cut 1cm × 1cm square area pieces with edges polished and later sonicated to remove the debris and unwanted polishing powder. Solution of PS was prepared by mixing 1 gram of polystyrene beads (ACROS) in 8 ml distilled water and stirred for 48 hours for complete miscibility. We prepared thin films of PS on a glass plate by spin coating the solution of PS. Structures and gratings were fabricated in thin films and bulk of PS with 40X objective in single scan method. Fabricated structures were found to be increasing in width with energy. The energy values reported here are measured at the laser and do not take in to account of the reflection losses at different surfaces. Furthermore, structures fabricated at a particular energy on the surface were found to be having more width compared to the structures fabricated beneath the surface. There is a possibility for styrene molecules that they can be bonded with each other by "head to head" and "tail to tail" rather by usual bonding "head to tail" of monomer molecules. This unwanted bonding leads to the formation of defective units in the PS long chain. One would observe emission as these bonds are weak

and can be modified through bond breakage process, due to photo degradation.

Nurmukhametov et al. [6] have observed the changes in absorption and luminescent properties of PS thin films and solutions when exposed to UV light. In their analysis, they observed formation of optical centers resulted in UV (λ=248 nm) exposure that exhibited absorption band from 280-460 nm and fluorescence band from 330-520 nm. We used 800 nm laser corresponding to 1.55 eV energy. The band gap of PS is 4.36 eV [7] which requires minimum of three photons absorbed for photo chemical modification.
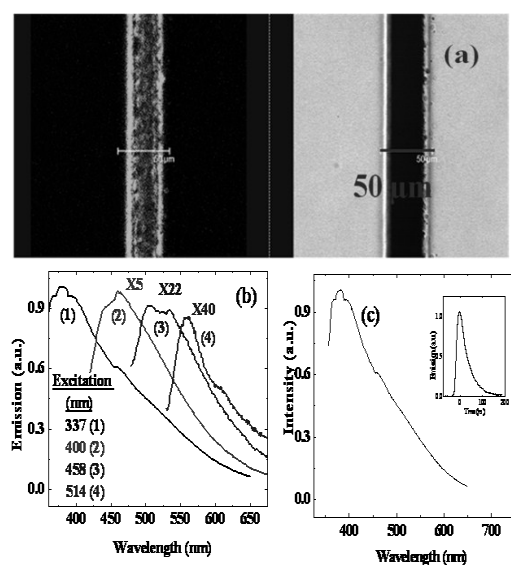

FIGURE 1(a) Confocal microscope image of a structure fabricated inside bulk PS [40 µJ energy, 1 mm/s speed, 50 µm width] Scale bar is 50 µm. Pseudo green color represents emission from the modified structure when excited at 488 nm wavelength. **(b)** Emission spectra recorded for PS Grating (1 µJ, 0.5 mm/s speed with 30 µm period) excited at different wavelengths. Emissions with longer wavelength excitations are enhanced for clarity **(c)** Emission spectrum of irradiated PS with excitation at 337 nm (Peaks at 383 and 458 nm). Inset of 1(c) shows the lifetime of optical center around 40 ns for the emission collected at 536 nm).

In microfabrication experiments since the laser energy is focused using microscope objective it is easy to achieve nonlinear absorption in different materials as the multi-photon absorption cross section depends on the intensity raised to the power 'n' where 'n' is minimum number of photons required to match the band gap. The results thus obtained under IR exposure become similar to the results obtained under UV exposure through multi-photon absorption. We

observed emission from fs laser modified PS when excited with 458, 488 and 514 nm wavelengths. The emission peak obtained with each excitation is different which indicates the formation of myriad optical centers. The excitation spectra recorded showed the same at different monitoring wavelengths which indicates partially that the optical centers resulted in the polymer chain breakage are from the same monomer. The maximum absorption or excitation occurred at 337 nm which indicates the presence of trans-stilbene in the emission spectrum that has peak at 367 nm. The broad emission peak around 383 nm is due to diphenylbutadiene (DPBD). The excitations at 337 and 400 nm showed the peak around 458 nm which is interpreted as due to diphenylhexatriene (DPHT) optical center. We estimated the life time of the emission using third harmonic of Nd:YAG laser at 355 nm, 10 Hz repetition rate with 6 ns pulses as the maximum absorption falls near the third harmonic of Nd:YAG. The emission was collected at 90° to the excitation and observed with a spectrometer and PMT attachment. Inset of figure 1(c) shows the life time of emission occurring at 536 nm with life time around 40 ns.
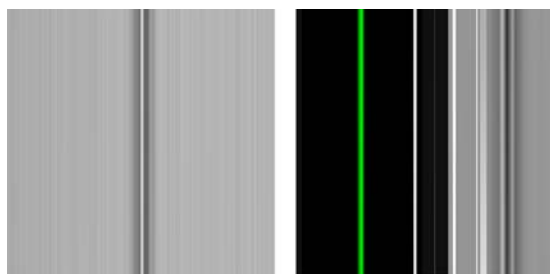

FIGURE 2(a) Confocal micro scope image of a buried single micro structure in PS fabricated at 1 µJ energy and 1 mm/s speed. Structure width 12 µm. **(b)** Confocal microscope image of micro craters in PS. Pseudo green color represents emission from the micro-craters. Scanning speed increased is 3 mm/s. Model used to fabricate micro- craters is shown in middle.

The formation of micro-craters occurred at lower energies and higher scanning speeds owing to minimal overlap of pulse to pulse. Figure 2(a) shows a confocal microscope image of a buried structure fabricated at 1 µJ and 1mm/s speed and (b) shows with 3 mm/s speed at the same energy. The pseudo color represents the emission from the modified structures. Each fluorescent crater can be treated as bit 1 and thus its applications can be realized in memory devices. A model to fabricate micro-craters is depicted in the

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figure 2 (b). The pitch p which is the distance from center to center can be varied by setting the scanning speed according to the relation **p=s/f** where **s** is scanning speed and **f** is laser repetition frequency which is 1 kHz in our case. L_0 is the overlap region between two consecutive focused spots which is (d-p) where d is the diameter of the spot that is 1.55 μm for 40X. Diffraction gratings are fabricated using repetitive scan method in bulk PS and efficiency is measured using He:Ne laser operating at a wavelength of 633 nm. First order diffraction efficiency is measured as the ratio of power diffracted into first order with transmitted power. Table 1 shows different gratings thus fabricated and their diffraction efficiencies. We obtained maximum DE of 10 % for a particular type of grating termed as PSG9 [1 μJ energy, 1 mm/s speed, 30 μm period]. Also, we observed peroxide type free radicals in fs laser irradiated regions of PS. Figure 3 (a) shows ESR spectra recorded for different irradiation doses in PS. Pristine PS as shown in (1) does not show any ESR signal. However, the same PS exhibits paramagnetic behavior when treated with fs laser. The g value calculated is 2 which indicate the formation of peroxide radicals. We collected the Raman signal from the central and edge portions of the structure for PSG1 grating. The intensity of Raman modes are suppressed in case of fs laser irradiated PS. We observed the intensity of two main Raman modes affected drastically, probably, due to stress waves generated in the fs laser irradiated regions. 1001 cm^{-1} and 1603 cm^{-1} modes of PS correspond to ring breathing and C=C vibrational modes [8-9]. The two modes 2980 and 3004 cm^{-1} which represent SP^3 and SP^2 CH groups disappeared completely in case of fs laser irradiated PS. Though we expect voids in the central portions of the fabricated structures, there could be ablated debris resettled in the middle portion of the structures which contribute to the Raman signal. We used confocal geometry to collect Raman signal from subsurface of PS that includes lower portion of the void structure. Raman mapping performed across the structure indicates that the stress induced in the material is different which resulted in intensity change across one of the single structures in PSG1 grating. The two modes depicted in figure 3(c) indicate ring breathing mode and styrene group band. We have fabricated such several structures in other polymers such as PMMA, PDMS, and PVA. In all these polymers we observed the formation of free radicals that exhibit

emission upon fs laser irradiation and paramagnetic behavior (except for PVA) [10-14].

S. No.	Terminology	Energy (μJ)	Speed (mm/s)	Period (μm)	Width (μm)	1st order DE
1	PSG1	1	0.5	30	16	8.30
2	PSG2	0.635	0.5	30	21	7.95
3	PSG3	0.033	0.5	30	3	0.26
4	PSG4	0.033	3	30	2	0.19
5	PSG5	1	3	30	4	0.13
6	PSG6	1	2	50	11	3.65
7	PSG7	1	0.5	100	20	6.63
8	PSG8	1	2	30	5	3.68
9	PSG9	1	1	30	12	**10.0**
10	PSG10	1	1	20	11	6.80
11	PSG11	1	1	50	12	1.79

FIGURE 3. Summary of diffraction gratings

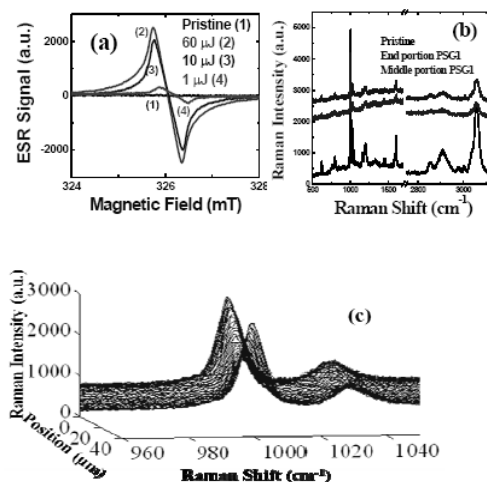**FIGURE 4(a)** ESR spectra of pristine and irradiated PS **(b)** Raman plot of pristine PS and fs irradiated grating PSG1 in middle and end regions **(c)** Raman mapping of PSG1 grating across the structure.

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