Femtosecond laser micro fabrication in polymers towards memory devices and microfluidic applications

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Abstract

We have investigated femtosecond laser induced microstructures, gratings, and craters in four different polymers: poly methyl methacrylate (PMMA), poly dimethyl siloxane (PDMS), polystyrene (PS) and poly vinyl alcohol (PVA) using Ti:sapphire laser delivering 800 nm, 100 femtosecond (fs) pulses at 1 kHz repetition rate with a maximum pulse energy of 1 mJ. Local chemical modifications leading to the formation of optical centers and peroxide radicals which were studied using UV-Visible absorption and emission, confocal micro-Raman and Electron Spin Resonance (ESR) spectroscopic techniques.

Keywords Diffraction grating, Electron spin resonance, Emission, Free radicals, Laser direct writing.

1. Introduction

Different materials including polymers and semiconductors have been tried for fabricating different micro- and nano-patterns by laser ablation method [1, 2]. The ablation of polymers after interaction with fs laser pulses is a subject that has been studied in detail [3, 4]. The interaction mechanism is slightly different in case of fabricating structures inside bulk samples. Nonlinear absorption takes place while transferring the energy from laser pulse to the material of interest as photon energy is less than the band gap of the material. Each 800 nm photon has 1.55 eV energy while band gap of the most of the transparent polymers lie in between 4 to 7 eV. There are three different nonlinear ionizations that take place when femtosecond (fs) pulses interact with materials namely tunneling, intermediate and avalanche ionizations which can be predicted by Keldysh parameter [5]. X. Liu et al. have shown that for 100 fs pulses, the dominant absorption process is avalanche ionization which produces an exponential increase in conduction band electrons. As this requires seed electrons in the conduction band [6], thermally excited carriers from defects and/ or traps form the necessary seed electrons. At large intensities as in the present case, multiphoton absorption leads to ionization to seed the avalanche ionization [5, 7]. The

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multiphoton ionization and avalanche ionization are strongly dependent on intensity. These two ionizations, MPI and avalanche, are strongly intensity dependent. Here, we present some of our results on the structures obtained through fs laser interaction with different polymers.

2. Sample Preparation

Bulk samples of PMMA and PS are purchased from Goodfellow, USA and Goodfellow, UK. PDMS was home made. These samples were cut into 1 cm × 1 cm dimensions and sides are polished using alumina powder and polishing sheets of different fine grades. Before micro fabrication experiments carried out, these samples are sonicated in distilled water to remove unwanted dust and polishing powder. Solution of PS was prepared by mixing 1 gram of polystyrene beads (ACROS) in 8 ml toluene and stirred for 48 hours for complete miscibility. Solution of PVA was prepared by adding 100 ml water to 8.6 grams of PVA (ACROS Organics-88% hydrolyzed) and stirred. Initially, PVA solution was heated for an hour at 70°C to dissolve PVA beads and stirring is continued further.

3. Experimental Details

Microstructures, diffraction gratings and 2-dimensioal grids (for ESR analysis) are fabricated using a Ti: sapphire oscillator amplifier system operating at a wavelength of 800 nm delivering ~100 fs pulses, ~1 mJ output energy pulses with a repetition rate of 1 kHz. The near-transform nature of the pulses was confirmed from the time-bandwidth product. Three translational stages (Newport) were arranged three dimensionally to translate the sample in X, Y, and Z directions. Laser energy was varied using the combination of half wave plate and a polarizer. We have used 40X (Numerical Aperture (NA) of 0.65) and 20X (NA of 0.4) microscope objectives in our experiments for focusing.

4. Results and Discussion

Microstructures, microcraters, and diffraction gratings are fabricated in these polymers using typical experimental set up as shown in figure 1. Red color line shows the laser beam path which is made to fall vertically on the sample holder of 3-dimensional stage micro fabrication setup using mirrors M1, M2, and M3. These beams were aligned straight by introducing apertures in pairs in the path of the beam. The beam was viewed through the CCD camera after focusing using either 40X or 20X microscope objective lenses. A white spot (plasmon) was clearly observed at the focus of the objective. The Z axis of the stage is slowly moved upwards so that it

touches the surface of the substrate. Plume was observed through CCD imaging system as debris was removed from the surface of the material.

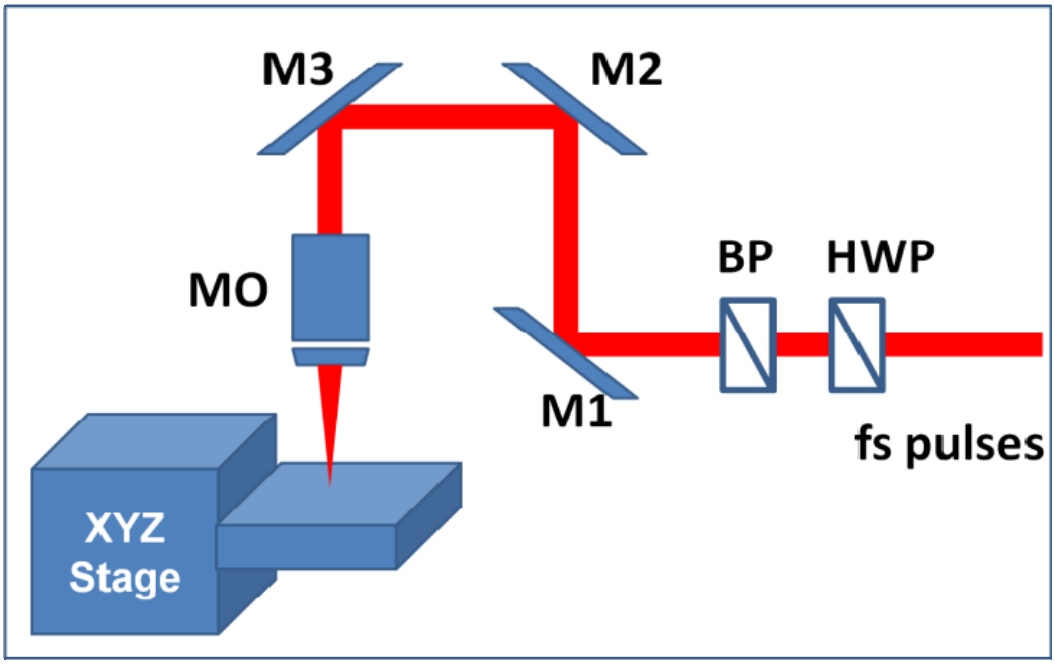

Figure 1 Experimental setup used for fs laser microfabrication of different structures in polymers.

By translating the stage along X, Y, and Z directions at different scan speeds, we obtained microstructures. We observed structure width increasing with the energy, number of scans, scan speed and focusing [8-14]. By increasing energy, and number of scans the irradiated region is exposed to more irradiation dose that results in increased structure width. By reducing the scan speed also, one would expect similar result as the region is exposed to more irradiation dose. The spot sizes obtainable with microscope objectives is obtained using the relation $D = 1.22\lambda/NA$, where D is the spot size, λ is the wavelength of the laser used, and NA is the numerical aperture of the objective. 40X and 20X microscope objectives with NA of 0.65 and 0.2, respectively, were used for the experiments. Thus, the minimum spot sizes obtainable with 800 nm laser beam were 1.5 and 2.4 μm respectively. From this we can conclude that higher NA objectives lead to minimum spot sizes. However, the effect of pulse width and laser intensities also plays a major role. Typical confocal microscope image of the fabricated structures in PVA is illustrated in the figure 2(a). Figure 2(b) shows the plot of structure width versus the input energy. These structures were fabricated in single scan, 1 mm/s speed and with 40X microscope objective. Similar trend is noticed with other polymers also.

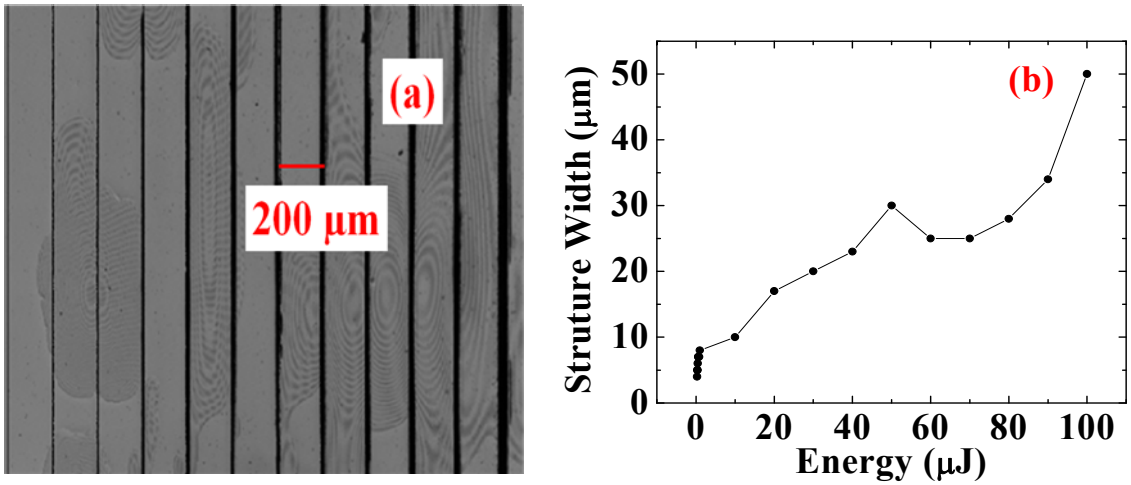

Figure 2 (a) Left to right: Structures were fabricated from 1 µJ to 100 µJ in steps of 10 µJ (scale bar is 200 µm), speed 1mm/s, 40X objective lens. (b) Plot of variation of structure width with energy.

The investigated polymers are transparent to UV-visible light and hence do not undergo any kind of modification. However, when 800 nm IR laser beam is focused, nonlinear absorption takes place at the focus which leads to polymer chain scission. The energy of an 800 nm photon corresponds to 1.55 eV, while the optical band gap of pure PMMA being 4.58 eV. Most of the investigated polymers have wide band gap of more than 4 eV which imply that the nonlinear process involving at least three photons is responsible for structural modification at the focal volume [15]. In addition to three photon absorption, it has been shown [16] that there are three possible mechanisms viz. tunneling, intermediate, and multi-photon ionizations that take place when transparent material interacts with femtosecond pulses. The Keldysh parameter, which tells us the mechanism that is dominant, is defined as $\gamma = (\omega/e)\,(m \times c \times n \times \varepsilon_o \times E_g/I)$ where 'ω' is the laser frequency, 'I' is the laser peak intensity at the focus, 'm' and 'e' are the reduced mass and charge of the electron, respectively, 'c' is the velocity of light and n is the refractive index of the material, E_g is the band-gap of the material and ε_0 is the permittivity of free space. For our studies the Keldysh parameter was <1 illustrating tunneling as responsible mechanism for structures written using 40X and 20X microscopic objectives for our investigated polymers.

Sparse reports are available on emission of polymers as they contain different functional groups such as ketone and aldehyde etc [17-18]. Pristine polymers neither show any absorption or emission in visible region. However when these polymers are treated with ionizing radiation such as UV, they show emission. When these polymers are treated with ionizing radiation, bond scission takes place. This bond scission leads to formation of different optical centers and defects [8-14, 17-18]. Moreover, we observed similar emission in mechanically scratched/disturbed polymers. Some of these results were reported by our group [8-14]. This opened doors for the

use of fs irradiated polymers towards memory based devices. One can fabricate micro-craters using fs laser direct writing technique. The crater due to fs irradiation treatment show emission which can be treated as bit one for memory based applications.

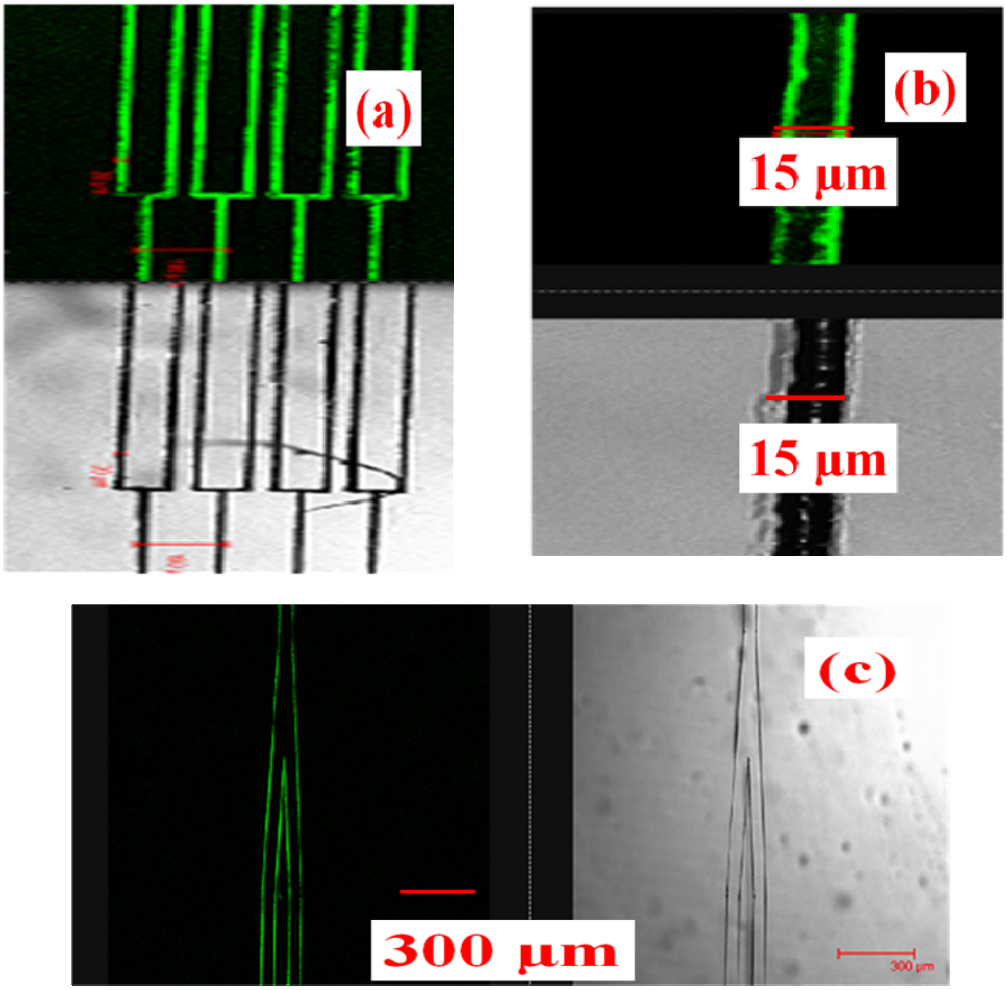

Figure 3 40X objective lens used (a) Part of 1:8 splitter in PMMA (15 µJ with 0.05 mm/s). Pseudo green color represents emission when excited at 488 nm. Width of structure is 15 µm. Since image is large, part of the structure is shown. (b) Same 1:8 splitter in PMMA (15 µJ with 0.05 mm/s). Scale bar is 15 µm. (c) Y coupler fabricated inside PMMA with 1 µJ energy, 1 mm/s speed. Pseudo green color represents emission when excited at 488 nm. Scale bar is 300 µm. Since image is large, part of the structure is shown.

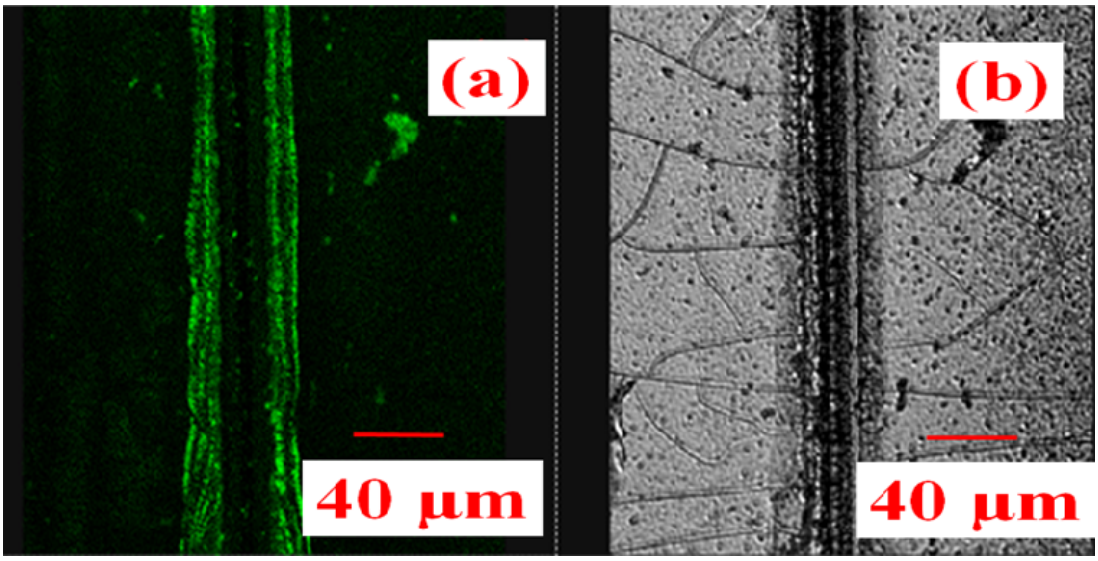

Figure 4 (a) Emission from the channel when excited at 488 nm in PS thin film fabricated at 100 µJ energy, 1mm/s speed, 40X objective lens used. Scale bar is 40 µm. (b) Transmission Image

Figures 3 (a) to (c) show the emission in PMMA (pseudo green color) when excited at 488 nm. We observed emission coming from only from the edges as the middle portion of the Gaussian pulse resulted in void formation and tail portion of the Gaussian pulse changes the refractive index of the material smoothly. It is depicted clearly in the figures 3 (b), 4 (a) and 4(b). The emission intensity was found to be more for the structures fabricated with more energies as the material undergoes more structural modifications.

A microfluidic structure was fabricated on the surface of PMMA at 1 µJ energy with mm/s speed. Rhodamine B solution was injected into the structure and we observed the flow of Rhodamine B into the structure through its emission. Figure 5 shows the confocal microscope image of the fabricated structure (Right). Left side of the figure shows the emission (pseudo color) coming from the structure due to Rhodamine B. Further studies are in progress to carry out detailed microfluidic studies.

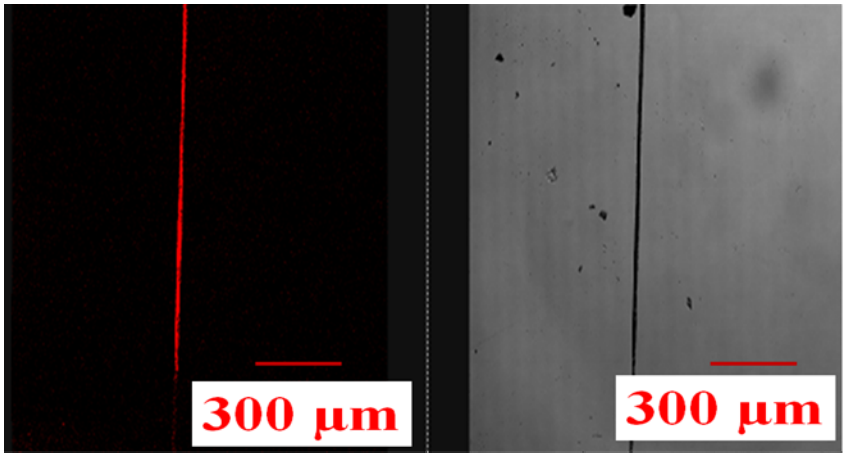

Figure 5 A confocal microscope image of a fabricated microstructure on the surface of PMMA (Right) and emission from the microstructure due to the injected Rhodamine B solution (Left).

We had earlier fabricated several microstructures, micro craters and diffraction gratings in PMMA, PDMS, PS and PVA [8-14] using 800 nm laser pulses. All these fabricated structures showed emission when excited at 458, 488, and 514 nm wavelengths. Interestingly, the emission peak was found to be changing with excitation wavelength though the excitation spectra at different emission monitoring wavelengths remain unchanged. Figures 6 (a) and (b) show the emission of fs laser irradiated polymers at maximum absorption. This maximum absorption corresponds to the transitions involved with in the functional groups such as $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ etc as these polymers contain aldehyde, ketone groups and double bonds. Figure 6 (c) shows the shift in emission peak with the excitation wavelength. This is the well known red edge effect. Different excitation wavelengths locally excite different optical centers and conformers leading to the shift in the emission peak.

Different research groups have worked on ESR of polymers [19-21]. However, reports on ESR analysis of fs laser irradiated polymers are sparse as the field has gained momentum recently and many theoretical and experimental results need to be explored further. In our endeavor towards understanding ESR of fs irradiated polymers, we fabricated two dimensional grids to increase effective area of irradiation for ESR analysis. We observed peroxide type free radicals when these polymers were treated with fs laser. Pure polymers such as PMMA are not paramagnetic substances and hence do not contain any paramagnetic centers. So, there were no peaks observed in ESR spectrum. However, when polymers PMMA, PDMS, and PS are treated with fs laser, they showed ESR signal which is an indication of existence of peroxide type free radicals. Figure 7 (a) shows ESR signal in PMMA and (b) shows the same in PS. In case of PS, the radicals are alkoxy radicals as reported in literature [22].

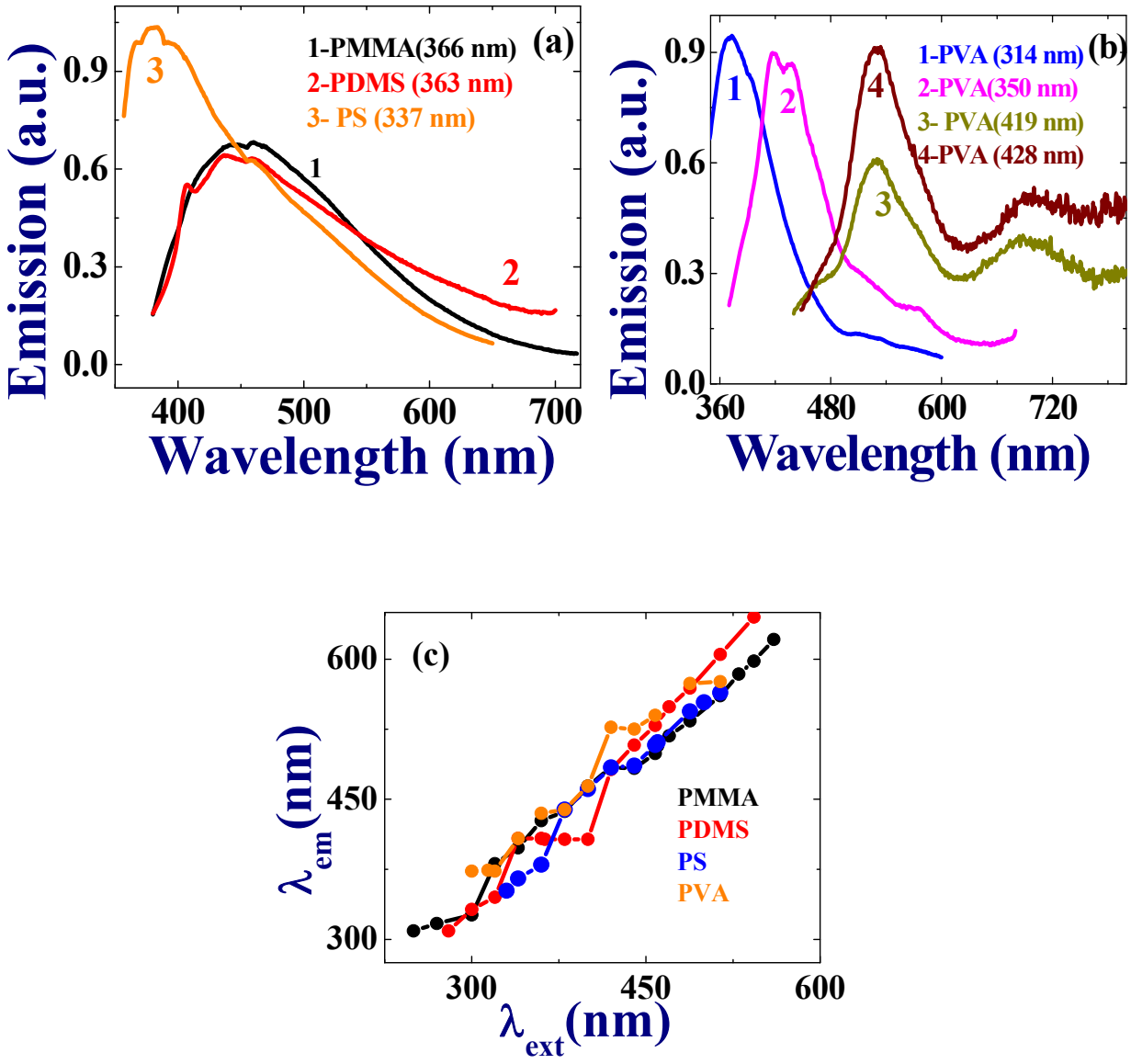

Figure 6 Emission plots of (a) PMMA, PDMS, and PS (b) PVA. (c) Plot of emission and excitation wavelengths in different polymers investigated.

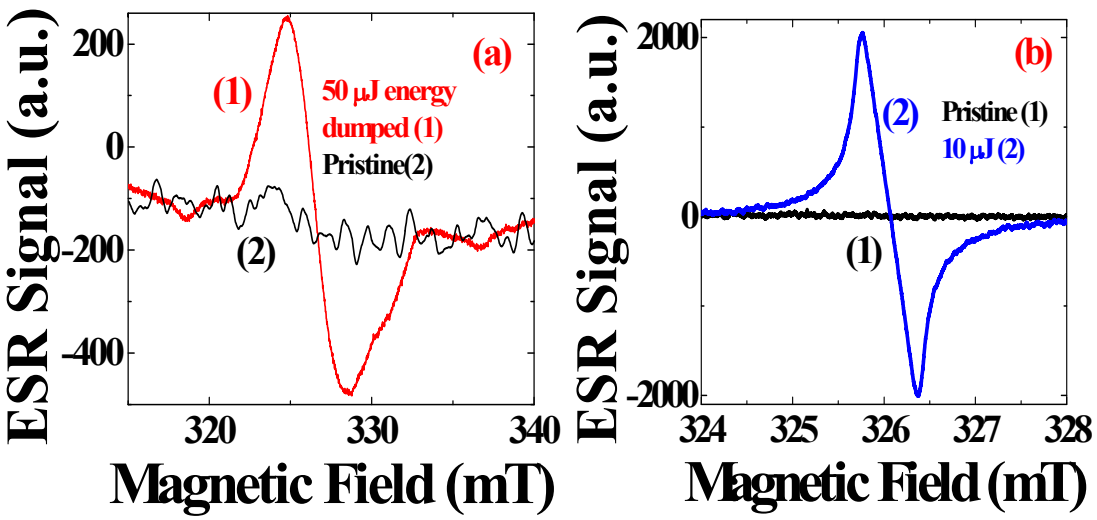

Figure 7 ESR spectrum of fs irradiated (a) PMMA (b) PS.

Further, confocal micro-Raman studies were carried out for the fabricated structures in the channels. Formation of defects such as optical centers and free radicals lead to broadening of Raman peaks and reduction in Raman intensity due to high intense shock waves formed at the center of the Gaussian pulse. In order to study the local effect, a microstructure was fabricated on the surface of PDMS at 15 μJ energy with 0.05 mm/s speed. The structure width is 50μm as shown in figure 8 (a). Figure 8 (b) shows the Raman signal collected at different points across the structure using Raman mapping technique. The Raman peaks at 2903 and 2963 cm^{-1} indicate symmetric and anti-symmetric stretching modes of CH_3. Broadening and reduction in intensity can be easily seen from figure 8 (b) which is a clear indication of the formation of defects such as optical centers and free radicals. Figure 8 (c) is a plot of position of the focused spot with in the microstructure with the Raman intensity for 2903 cm^{-1} Raman mode. It almost resembles Gaussian kind of profile. From this observation, we conclude that the formation of defects lead to broadening and suppression of Raman intensity and the stress generated locally depends on the local intensity due to incident Gaussian laser pulse.

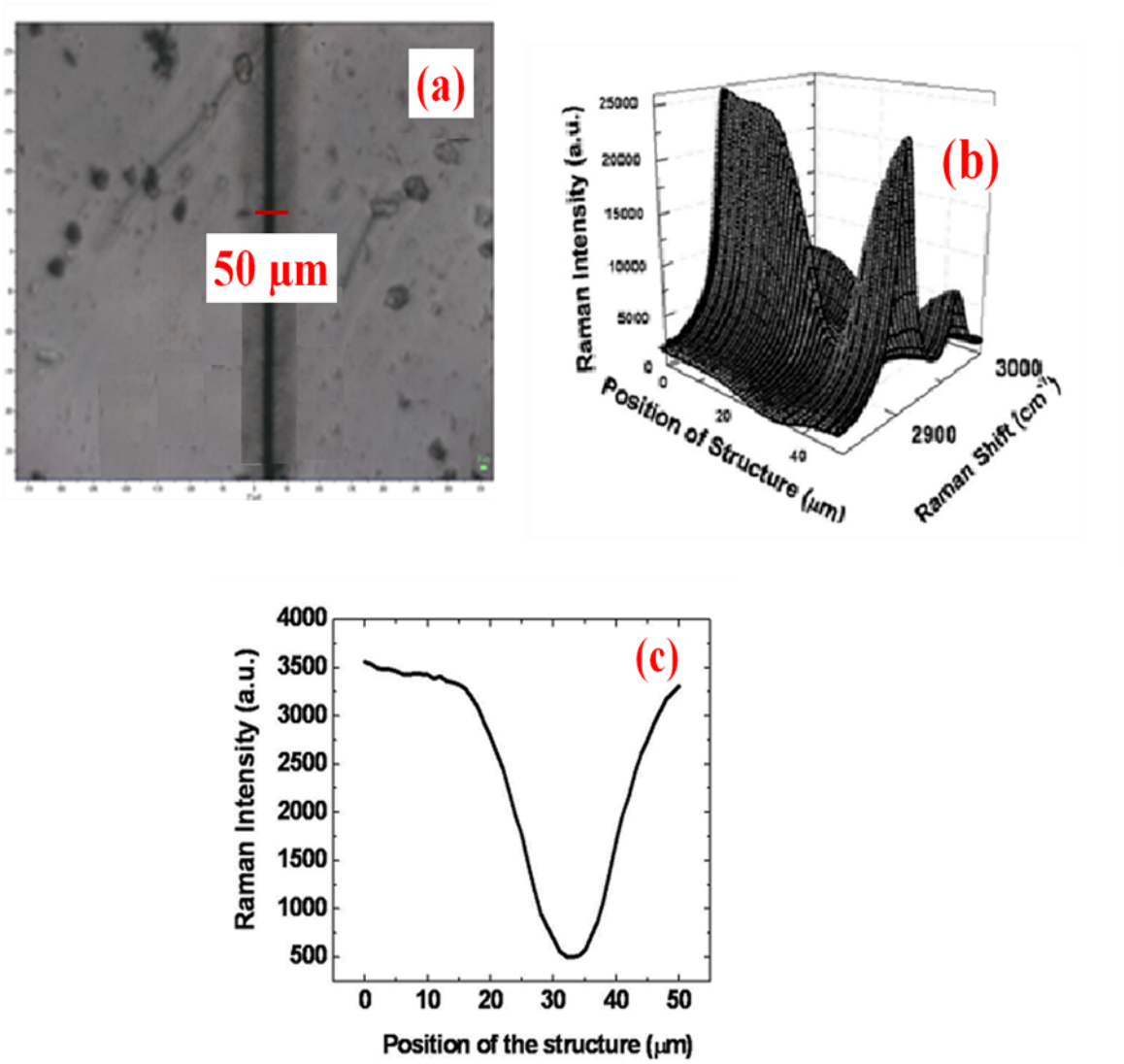

Figure 8 (a) Microscope image of a surface microstructure in PDMS (b) Raman mapping signal across the structure (c) Plot of position of structure with Raman Intensity.

5. Conclusions

We fabricated several microstructures and diffraction gratings in the bulk and thin films of polymers PMMA, PDMS, PS and PVA and observed emission from the fs laser modified regions in these polymers which can be used as a tool towards memory based devices. The emission is attributed to the formation of optical centers. We demonstrated some of the possible applications of laser direct writing towards waveguides, Y couplers, and memory based devices. Formations of defects such as optical centers which lead to the observed red edge effect and paramagnetic free radicals such as peroxide are investigated. Raman mapping studies carried out across the structure revealed that formation of defects due to the local stress generated due to fs laser pulse.

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