Femtosecond-laser direct writing in polymers and potential applications in microfluidics and memory devices

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Abstract. We have investigated femtosecond-laser-induced microstructures (on the surface and within the bulk), gratings, and craters in four different polymers: polymethyl methacrylate, polydimethylsiloxane, polystyrene, and polyvinyl alcohol. The structures were achieved using a Ti:sapphire laser delivering 100-fs pulses at 800 nm with a repetition rate of 1 kHz and a maximum pulse energy of 1 mJ. Local chemical modifications leading to the formation of optical centers and peroxide radicals were studied using ultraviolet-visible absorption and emission, confocal micro-Raman and electron spin resonance spectroscopic techniques. Potential applications of these structures in microfluidics, waveguides, and memory-based devices are demonstrated. © 2012 Society of Photo-Optical Instrumentation Engineers (SPIE). [DOI: 10.1117/1.OE.51.7.073402]

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1 Introduction

A variety of materials including polymers and semiconductors have been successfully used in fabricating different micro- and nano-patterns using the laser ablation method.1,2 The ablation of polymers (after interaction with ultrashort laser pulses) is a subject that has been studied in detail over the last few years.3,4 The interaction mechanism is slightly different in the case of fabricating structures inside the bulk. Nonlinear/multiphoton absorption results in the transfer of energy from laser pulse to the material, since single photon energy is less than the band gap of the material. Each 800-nm photon has 1.55 eV energy, while the band gap of the most of the transparent polymers lies in the range of 4 to 7 eV. There are three different nonlinear ionization mechanisms that occur when femtosecond (fs) pulses interact with materials—namely tunneling, intermediate, and avalanche ionizations, which can be predicted through the Keldysh parameter.5 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. Since this requires seed electrons in the conduction band,6 thermally excited carriers from defects and/or traps form the necessary seed electrons. At large peak intensities (as in the present case) multiphoton absorption leads to ionization to seed the avalanche ionization.5,7 Multiphoton ionization (MPI) and avalanche ionization are strongly dependent on the peak intensity of the laser pulses. These two ionizations, MPI and avalanche, are strongly intensity dependent. Herein we present some of our results on the structures obtained through fs-laser interaction with different polymers such as polymethyl methacrylate (PMMA), polydimethylsiloxane (PDMS), polystyrene (PS), and polyvinyl alcohol (PVA). Some of these structures find impending applications in the fields of microfluidics and optical memories. Advantages of this technique compared to other microfabrication techniques are presented.

2 Sample Preparation

Bulk samples of PMMA and PS were purchased from Goodfellow, USA and Goodfellow, UK. PDMS was homemade. These samples were cut into 1 x 1-cm dimensions and sides were polished using alumina powder and polishing sheets of different fine grades. Before microfabrication experiments were being carried out, these samples were sonicated in distilled water to remove unwanted dust and polishing powder. Solution of PS was prepared by mixing 1 g of polystyrene beads (ACROS Organics) in 8 ml toluene and stirring for 48 h for complete miscibility. Solution of PVA was prepared by adding 100 ml water to 8.6 g 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 was continued until the solution was clear without any bubbles or agglomerates.
3 Experimental Details

Microstructures, diffraction gratings, and two-dimensional (2-D) grids [particularly for Electron Spin Resonance (ESR) analysis] were 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 used 40× (numerical aperture (NA) of 0.65) and 20× (NA of 0.4) microscope objectives in our experiments for focusing the laser beam. Emission from the structures was recorded using Fluorolog Horiba JOBIN YVON fluorescence spectrometer and Leica TCSSP2AOBS laser-scanning confocal microscope. ESR spectra were collected using JES-FA 200 ESR spectrometer (JEOL) with X-band unit. Raman spectra were collected using HR 800 Horiba Jobin Yvon confocal micro-Raman spectrometer.

4 Results and Discussion

Microstructures, microcraters, and diffraction gratings were fabricated in these polymers using the experimental setup as shown in Fig. 1. The red line indicates the laser beam path which was incident vertically on the sample holder of three-dimensional (3-D) stage in the microfabrication setup using mirrors M1, M2, and M3. These beams were aligned in a straight line by introducing apertures in the beam path. The beam was viewed through the CCD camera after focusing using either 40× or 20× microscope objective lenses. A white spot (plasma) was clearly observed at the focus of the objective. The z-axis of the stage was slowly moved upwards so that it touched the surface of the substrate. Plume was observed through the CCD imaging system as debris was removed from the surface of the material.

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. By increasing energy and number of scans, the irradiated region was exposed to a higher irradiation dose, which resulted in increased structure width. By reducing the scan speed also, one would expect similar results as the region was exposed to more irradiation. The minimum spot sizes achievable with microscope objectives were calculated using the relation $D = 1.22 \frac{\lambda}{NA}$, where $D$ is the spot size, $\lambda$ is the wavelength of the laser used, and NA is the numerical aperture of the objective.

The minimum spot sizes attainable with and 800-nm laser beam were 1.5 $\mu$m for 40× and 2.4 $\mu$m for 20×, respectively. From this we can conclude that the 40× NA objective led to minimum spot size. However, the effect of pulse width and laser intensities also plays a major role. A typical confocal microscope image of the fabricated structures in PVA is illustrated in Fig. 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 40× microscope objective. A similar trend was noticed with structures observed in other polymers also.

The investigated polymers are transparent to ultraviolet (UV)-visible light and hence do not undergo any kind of modification due to UV light. However, when 800-nm IR-laser pulses are focused, nonlinear absorption transpires at the focus, a phenomenon which leads to polymer-chain scission. The energy of a 800-nm photon corresponds to 1.55 eV, while the optical band gap of pure PMMA is 4.58 eV. Most of the investigated polymers have wide band gap of more than 4 eV, which implies that the nonlinear process involving at least three photons is responsible for structural modification at the focal volume. In addition to three-photon absorption, it has been shown that there are three possible mechanisms viz. tunneling, intermediate, and MPIs that take place when transparent material interacts with fs pulses. The Keldysh parameter, which tells us which mechanism is dominant, is defined as $\gamma = \frac{(\alpha/e)(m \times c \times n \times \epsilon_r \times E_g)}{I}$ where $\alpha$ is the laser frequency, $I$ is the laser peak intensity at the focus, $m$ and $\epsilon_r$ are the reduced mass and charge of the electron, respectively, $\epsilon_r$ is the velocity of light, $n$ is the refractive index of the material, $E_g$ is the band gap of the material, and $E_g$ is the permittivity of free space. For our studies the Keldysh parameter was less than one, illustrating that tunneling was the responsible mechanism for structures written using 40× and 20× microscopic objectives for our investigated polymers.

Sparse reports are available on emission of polymers as they contain different functional groups such as ketones and aldehydes. Pristine polymers show neither absorption nor emission in the visible region. However, when these polymers are treated with ionizing radiation such as UV, they exhibit 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. Interestingly, we observed similar emission in mechanically scratched/disturbed polymers. Some of these results were reported earlier by our group. This opened doors for the use of fs-irradiated polymers for...
memory-based devices. One can fabricate microcraters on the surface of a polymer using an fs-laser direct writing technique. The craters due to fs irradiation demonstrate emission which can be treated as bit ‘one’ for memory-based applications. Nie et al. have successfully demonstrated 3-D optical memory utilizing emission in fs-modified PMMA. They could achieve a high signal-to-noise ratio without any crosstalk. We used a fixed 1-kHz-repetition-rate laser and therefore the same area was exposed to multiple laser shots, leading to incubation effects resulting in larger features. In our case we could obtain 1-μm structures in these polymers. On the other hand, if a single-shot laser is used, one would obtain the smallest features. Alternatively one could utilize higher NA objectives and lower energies to obtain smaller features. Furthermore, parameters such as pulse width and thermal diffusion length cannot be ignored. In our case the pulse width was estimated to be ~100 fs. One needs to optimize the writing speed, spot size at focus, and appropriate energies to be used in order to achieve structures useful for memory applications. Further detailed studies are imperative to identify the mechanisms to increase the data-storage capacity produced by the fs-laser direct writing technique, when compared to the potential of CD and/or DVD technology. The advantage of fs-laser direct writing is that one can easily fabricate truly 3-D features, as the modification takes place exactly at the focus due to nonlinear processes. A large-area (1-in²) wafer could be processed within a few hours. Parallel processing with multiple beams (since the energies required for polymer modification are little) could reduce the time by an order of magnitude. Moreover, fs lasers lead to minimal thermal damage hence minimal structure widths.

We have also attempted fabrication of structures to be used in waveguide applications. Figure 3(a) to 3(c) shows the waveguide channels fabricated. The usefulness of fs-laser direct writing lies in its ability to fabricate complex structures such as Y-couplers and beam splitters. The exact mechanism that leads to index change in the modified regions is still not apparent. We are exploring the losses such as bending losses and transmission losses for the structures fabricated. Figure 3(a) to 3(c) shows the emission in PMMA (pseudo-green color) when excited at a wavelength of 488 nm. We observed emission appearing only from the edges as the central portion of the Gaussian pulse resulted in void formation and the tail portion of the Gaussian pulse changed the refractive index of the material smoothly. It is depicted clearly in Figs. 3(b), 4(a), and 4(b). The emission intensity was found to be superior for the structures fabricated with higher energies, since the material undergoes further structural modifications.

A microfluidic structure was fabricated on the surface of PMMA at 15-μJ energy with 0.05-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 side). The 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. We are in the process of performing further experiments to understand the behavior of liquid/liquid flow in such microchannels.

We had earlier fabricated several microstructures, microcraters, and diffraction gratings in PMMA, PDMS, PS, and PVA using 800-nm laser pulses. All these fabricated structures showed emission when excited at 458, 488, and

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**Fig. 3** (a) Part of 1:8 splitter in PMMA (15 μJ with 0.05 mm/s). Width of structure is 15 μm. (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. Scale bar is 300 μm. Pseudo-green color represents emission when excited at 488 nm. Since image are large only part of the structures are shown. 40x objective lens was used for the structures fabricated.

**Fig. 4** (a) Emission from the channel (excited at 488 nm) in PS thin film fabricated at 100-μJ energy, 1-mm/s speed, 40x objective lens used. Scale bar is 40 μm. (b) Confocal microscope image of the structure.

**Fig. 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).
514-nm wavelengths. Interestingly, the emission peak was established to be changing with excitation wavelength, though the excitation spectra at different emission-monitoring wavelengths remain unchanged. Figure 6(a) and 6(b) illustrates 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 $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, as these polymers contain aldehyde, ketone groups, and double bonds. Figure 6(c) shows the shift in emission peak with the excitation wavelength, and the phenomenon was well reported as 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. However, reports on ESR analysis of fs-laser-irradiated polymers are sparse. The field has gained momentum recently, and many theoretical and experimental results are being explored. In our endeavor toward understanding ESR of fs-irradiated polymers we fabricated 2-D grids to increase the effective area of irradiation for ESR analysis. We observed peroxide-type free radicals when these polymers were treated with a fs laser. Pure polymers such as PMMA are not paramagnetic and therefore do not hold any paramagnetic centers. Thus, no peaks were observed in the ESR spectrum of pure samples. However, when these polymers (PMMA, PDMS, and PS) were treated with fs-laser pulses they showed an ESR signal, which is an indication of the existence of peroxide-type free radicals. Figure 7(a) shows the ESR signal in PMMA and (b) shows the same in PS. In the case of PS the radicals are identified to be alkoxy radicals (also reported in the literature).

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 led to the
broadening of Raman peaks and reduction in Raman intensity due to high-intensity 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, as shown in Fig. 8(a), was 50 μm. Figure 8(b) illustrates the Raman signal collected at different points across the structure using the Raman mapping technique. The Raman peaks at 2903 and 2963 cm\(^{-1}\) designate symmetric and antisymmetric stretching modes of CH\(_3\). Broadening and reduction in intensity can be easily seen from Fig. 8(b), which offers 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 within the microstructure with the Raman intensity of 2903-cm\(^{-1}\) Raman mode. It resembles a Gaussian kind of a profile. From this observation we concluded that the formation of defects led to broadening and suppression of Raman intensity and the stress generated locally depends on the local intensity due to incident Gaussian laser pulse.

Our earlier works on laser direct writing in glasses produced waveguides and gratings.\(^{23,24}\) Waveguides in polymers have been successfully reported earlier.\(^{5,25}\) In the present work we tried to understand the interaction mechanism of fs pulses with polymers leading to structural and chemical changes. Our future work will focus on achieving low-loss waveguides in these materials.

5 Conclusions
We fabricated several microstructures and diffraction gratings in the bulk and thin films of polymers PMMA, PDMS, PS, and PVA. We observed emission from the fs-laser-modified regions in these polymers, a conclusion which can be used as a tool toward developing memory-based devices. The maximum absorption is attributed to the transitions arising from various functional groups of the polymers, which was identified to be the cause for emission. We demonstrated some of the possible applications of laser direct writing to 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 and alkyloxy radicals were investigated. Raman mapping studies carried out across the structure revealed that formation of defects is due to the local stress generated by the fs-laser pulse.

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References

Lakshmi Narayana Deepak Kallepalli obtained his BS honors and MS in physics, with specialization in photonics, from Sathya Sai Institute of Higher Learning, Puttaparthi, India. He received his PhD at the University of Hyderbad, School of Physics, Hyderabad, India in 2012. Currently, he is working as postdoctoral researcher at Laboratoire LP3, Aix-Marseille Univ., ParcScientifique et Technologique de Luminy, 163 Avenue de Luminy, 13288 Marseille cedex 9, France. He won the Dr. K. V. Rao Young Scientist Award (first prize) in May 2010 for his paper entitled “Fabrication and optical characterization of microstructures in poly methyl methacrylate (PMMA) and poly dimethyl siloxane (PDMS) using femtosecond pulses for photonic
and micro fluidic applications." His poster entitled “Electron spin resonance (ESR), laser confocal and micro-Raman studies of the femtosecond laser modified regions in poly (methyl methacrylate) (PMMA) and poly (dimethyl siloxane) (PDMS)” was adjudged one of the five best papers presented during the 9th DAE-BRNS National Laser Symposium, BARC, Mumbai, January 13th to 16th, 2010.

Venugopal Rao Soma has over 17 years of experience in the field of experimental nonlinear optics and photonics. After obtaining his MS and PhD from the University of Hyderabad, India, he worked at the University of St. Andrews, Scotland, investigating semiconductor hetero-structures for nonlinear frequency conversion using different phase-matching schemes with femtosecond pulses. He was later associated with the Centre for Ion Beam Applications as a research fellow in the physics department at the National University of Singapore. He was assistant professor in the physics department, Indian Institute of Technology, Guwahati, for a short time. Since 2007, he has been associated with the Advanced Centre of Research on High Energy Materials (ACRHEM), University of Hyderabad, working toward understanding the interaction of nanosecond, picosecond, and femtosecond laser pulses with high-energy materials using various time-resolved spectroscopic techniques. He has published more than 190 well-cited publications in refereed international journals and conference proceedings.

Narayana Rao Desai, currently professor of physics at the University of Hyderabad, obtained his PhD in physics from IIT Kanpur. He has been working in the field of lasers and nonlinear optics for the last three decades. He has published nearly 150 papers in international journals. His current interests are optical limiting, photonic crystals, femtosecond laser direct writing, spectral interferometry, and NLO studies of organic, inorganic, and semiconductor nanoparticles.