



# Spectroscopic investigations of femtosecond laser irradiated polystyrene and fabrication of microstructures

K.L.N. Deepak<sup>a,1</sup>, R. Kuladeep<sup>a,1</sup>, V. Praveen Kumar<sup>a,1</sup>, S. Venugopal Rao<sup>b,1</sup>, D. Narayana Rao<sup>a,\*</sup>

<sup>a</sup> School of Physics, University of Hyderabad, Hyderabad-500046, India

<sup>b</sup> Advanced Center of Research in High Energy Materials (ACRHEM), University of Hyderabad, Hyderabad-500046, India

## ARTICLE INFO

### Article history:

Received 14 September 2010

Received in revised form 2 February 2011

Accepted 2 February 2011

Available online 17 February 2011

### Keywords:

Emission

Bond-scission

Polymers

Free radicals

Femto second laser irradiation

Electron spin resonance

## ABSTRACT

We report microfabrication of structures in bulk and thin films of polystyrene (PS) using femtosecond (fs) laser pulses. For the first time to our knowledge, we report emission from the fs laser modified regions of bulk and thin films of PS when excited at 458, 488, and 514 nm. Moreover, we report the existence of peroxide type free radicals, for the first time, in fs laser irradiated bulk PS. We observed the suppression of Raman modes in case of structures fabricated at higher energies and the same effect was noticed in central portion of the structures fabricated. No appreciable broadening was observed in the case of structures fabricated at low energies. Possible applications resulting from such structures are discussed briefly.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

The discovery of mode-locked Ti: sapphire laser has enabled the production of stable femtosecond (fs) pulses, (sub-ten fs pulses are now a commercial reality) opening up the possibility of achieving GW and TW peak power pulses by passing them through a regenerative amplifier system. These pulses find wide applications not only in ultrafast spectroscopy but also in micro- and nano-machining. The fs laser pulse has become a promising tool for micromachining primarily due to its superior advantages over continuous wave (CW) and long pulse lasers [1–3]. With CW and long pulse lasers, substantial heat diffusion occurs during the laser-material interaction, resulting in a relatively large volume of heat affected zone around the laser focus. However, the pulse duration of a femto second pulsed laser is of the order of several tens of femto seconds, which is much shorter than the electron-ion energy transfer time [4]. Before heat can diffuse away, the target material at the focus is evaporated during the laser pulse interaction. Owing to the minimal and negligible heat diffusion, the structures fabricated are limited to the spot size of the focused beam and damage threshold [1,4]. As pulses produce extremely high peak intensities, they are capable of breaking down almost all materials including the optically transparent materials. This unique and ubiquitous nature of fs pulses has stimulated the interest in the

fabrication of two-dimensional or three-dimensional integrated optics, in which optical devices, such as gratings [5], waveguides [6,7], couplers [8], etc., are fabricated on a single substrate/crystal.

## 2. Experimental

In all experiments, microstructures 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 all X, Y, and Z directions. Laser energy was varied using the combination of half wave plate and a polarizer. We have used 40× (Numerical Aperture (NA) of 0.65) and 20× (NA of 0.4) microscope objectives in our experiments for focusing. Bulk PS was purchased from Goodfellow, UK. These bulk samples were cut and polished. In our study, microstructures were fabricated in thin films and bulk of PS. Before irradiating with fs pulses, these samples were sonicated for one hour in distilled water to remove dust and unwanted polishing powder. Solution of PS was prepared by mixing 1 g of polystyrene beads (ACROS) in 8 ml toluene and stirred for 48 h for complete miscibility. We prepared thin films of PS on a glass plate by spin coating the solution of PS. Theoretical spot sizes were estimated using the formula  $D = 1.22 \lambda / NA$  where D is the spot size, and  $\lambda$  is the wavelength used. The spot size was estimated to be 1.5  $\mu\text{m}$ /2.4  $\mu\text{m}$  (40×/20× objective).

\* Corresponding author. Tel.: +91 40 23134335; fax: +91 40 23011230.

E-mail address: [dnrsp@uohyd.ernet.in](mailto:dnrsp@uohyd.ernet.in) (D.N. Rao).

<sup>1</sup> Tel.: +91 40 23134335.

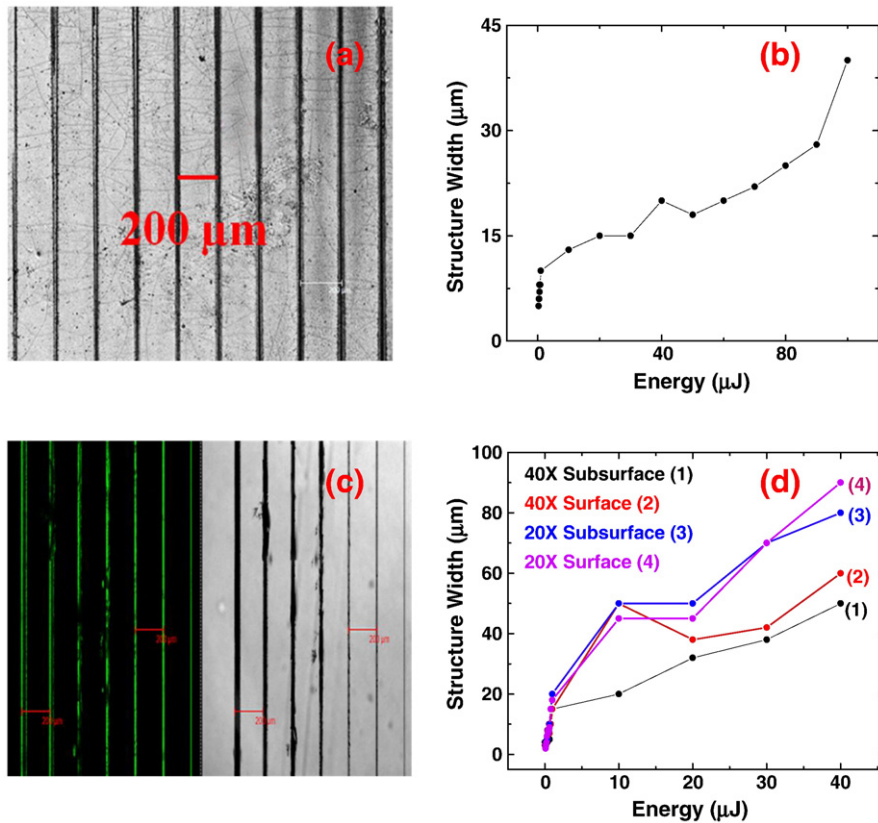
### 3. Results and discussion

Initially, structures were fabricated in thin films of PS with 40× objective in single scan method. Fabricated structures were found to be increasing in width with energy. Fig. 1(a) shows the confocal images of fabricated structures in PS thin films and Fig. 1(b) shows the plot of structure width with energy. However, the energy values reported here are measured at the laser and do not take in to account of the reflection losses at different surfaces. Similar studies were performed in bulk PS also on the surface and subsurface using 40× and 20× microscope objectives. We have found structure width increasing with 20× because spot sizes obtainable with 20× (2.4 μm) are more compared with spot sizes obtained with 40× (1.5 μm). Furthermore, structures fabricated at a particular energy on the surface were found to possess more width compared to the structures fabricated inside the surface with 40× lens, while with 20× lens the structure widths are nearly same. This could be attributed to the difficulties in exact positioning of focal point on the surface while the subsurface writing does not have this problem.

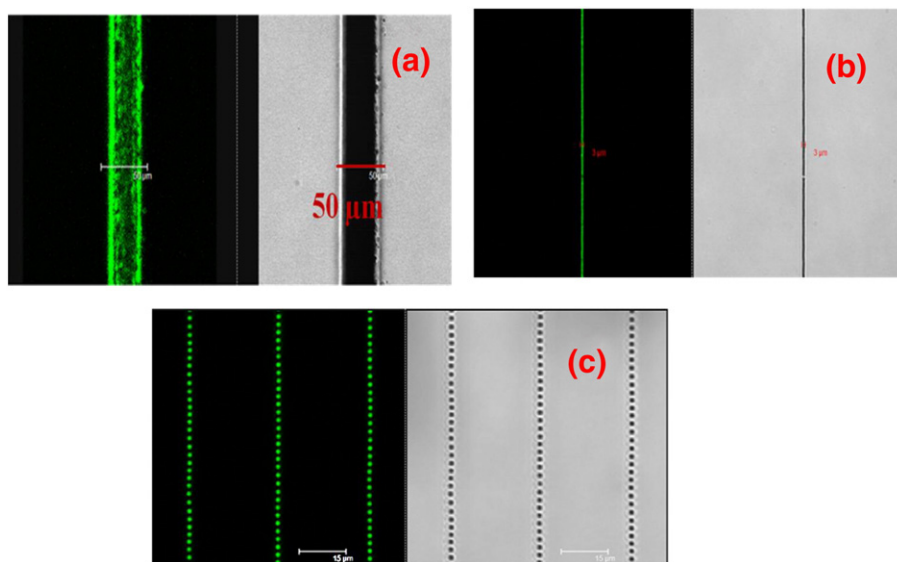
The third order nonlinear susceptibility [ $\chi^3$ ] of PS is  $1.15 \times 10^{-12} \text{ cm}^2/\text{W}$  [9,10] while the refractive index ( $n_0$ ) of PS is 1.55 [11]. The nonlinear refractive index ( $n_2$ ) calculated using the formula  $n_2 = (3\pi\chi^3)/n_0$  is  $\sim 7 \times 10^{-12} \text{ cm}^2/\text{W}$ . The negative third order nonlinearity of PS will cause defocusing of ultrashort laser pulses at high irradiances [11]. In our experiments the input energy was varied from 10 nJ to 100 μJ, which corresponds to peak intensities ranging from  $1 \times 10^{11} \text{ W/cm}^2$  to  $1 \times 10^{15} \text{ W/cm}^2$  (with 40× objective lens). The estimated spot size with 40× NA is 1.5 μm. However, we observed that the smallest structure widths obtained in our studies was  $\sim 3 \mu\text{m}$  at energy of 10 nJ. Due to  $n_2$  and the peak intensities involved the

material induces considerable divergence of input beam. This accounts for the observed size larger than the calculated values for the spot size. When pulse energy is increased to 1 μJ or higher (up to 100 μJ in our case) the material starts melting and since each position of the material experiences 2–3 pulses the second and third pulses experience a different medium altogether. A mixture of molten solids, released gasses contribute to the scattering of the laser beam near focus leading to a large change in beam diameter at the focal point. The observed increase in structure width [see Fig. 1(a)–(d)] with energy can be attributed to these effects.

In this paper, we report emission from the fs laser modified structures for the first time when excited at 458, 488 and 514 nm in both thin films and bulk PS polymers. Fig. 2(a) shows a microstructure fabricated in bulk PS at 40 μJ energy with 1 mm/s speed while Fig. 2(b) shows a similar structure fabricated at 63 nJ energy. In the case of structures fabricated at higher energies, emission (pseudo green color seen in confocal microscope images) was found to be at the edges of the central portion of the structure was influenced by large intensities of the incident Gaussian fs pulse resulting in void formation. By making emission as bit 1, one can fabricate several craters (micron sized) towards realization of memory based devices. Fig. 2(c) shows a grating fabricated in bulk PS using 40× objectives with 33 nJ energy with 3 mm/s scanning speed. Since the repetition rate of the laser is 1 kHz, and scanning speed of 3 mm/s which was high, we expect minimal cumulative effects. This resulted in a 2 μm crater spaced at almost 2 μm. There was therefore, no formation of a channel at this speed and energy. This demonstrates the possibility of fabricating memory bits, 2D and 3D photonic crystal structures in bulk PS using fs laser direct writing technique. Preparation of photonic crystals in PS by chemical routes such as vertical deposition method has been



**Fig. 1.** (a) Confocal microscope image of micro structures fabricated in thin films of PS with different energies using scanning speed of 1 mm/s. (Right to left structures written at 100 μJ to lower energies in steps of 10 μJ, Scale bar is 200 μm); (b) plot of structure width with energy; (c) microstructures fabricated on the surface of bulk PS from 40 μJ to 10 μJ in steps of 10 μJ and 1 μJ, 798 nJ energies (From left to right). Pseudo green color shows emission from the modified regions when excited at 488 nm (Scale bar is 200 μm); (d) structure width versus energy in case of 40× and 20× objectives on surface and subsurface of bulk PS.



**Fig. 2.** (a) Confocal microscope image of a structure fabricated inside bulk PS with 40  $\mu\text{J}$  energy with 1 mm/s speed, and 50  $\mu\text{m}$  width (Scale bar is 50  $\mu\text{m}$ ); (b) confocal microscope image of a structure fabricated inside bulk PS with 63 nJ energy with 1 mm/s speed, and 3  $\mu\text{m}$  width; (c) energy used 33 nJ, 3 mm/s scanning speed, 40 $\times$  objective (Scale bar is 15  $\mu\text{m}$ ).

already reported in the literature [12–15]. Preparation of photonic crystals takes only few hours of time with fs laser direct writing technique compared to long duration through chemical routes. This shows the efficiency of laser writing technique superior to other techniques. Gratings and 2D structures fabricated in Poly Methyl Methacrylate (PMMA) and Poly Dimethyl Siloxane (PDMS) were reported by us earlier [16].

We observed and recorded emission by exciting at three different wavelengths 458, 488 and 514 nm in bulk PS using confocal microscope. Similar trend was noticed in the case of the structures fabricated on the surface of bulk PS and thin films of PS. Fig. 3(a)–(c) shows emission plots for the structures excited at 458, 488 and 514 nm wavelengths using confocal microscope. We found emission intensity increasing with the energy used for fabricating the structures from all the emission plots at different excitation wavelengths as structures fabricated with more energy were modified more compared with the structures fabricated at low energy. We also observed that the emission peaks were different for different excitation wavelengths from plots Fig. 3(a)–(c). Nurmukhametov et al. have shown the fluorescence from PS when irradiated with 248 nm UV laser and concluded the presence of optical centers being responsible for fluorescence behavior [17]. In their case, the fluorescence band ranges from 330 nm to 520 nm while absorption band ranges from 290 nm to 460 nm. They noticed change in the fluorescence peak position when excited at different wavelengths. They established different optical centers being responsible for such a behavior and hypothesized their results more close to the spectrum of diphenylbutadiene (DPBD). In our case PS was modified mainly due to 800 nm (infrared) laser through multi-photon absorption process. Fs laser irradiation leads to bond scission thereby leading to a large number of defects that act as optical centers for emission. Excitation at different wavelengths leads to the excitation of different optical centers and hence the shift in the emission peak. Low temperature studies are in progress to understand the emission more precisely.

Moreover, we observed for the first time ESR signal for the fs irradiated PS. Fig. 4 shows the ESR signal of fs irradiated bulk PS. Pristine PS did not show any free radicals and or paramagnetic centers. After fs irradiation, bulk PS has shown peroxide type free radical. We found that ESR signal becomes stronger with the incident energy as high energy irradiation modifies more compared to the low energy case. The ESR peak is attributed to peroxide type free radical in fs irradiated PS with g

value of 2. This result exactly matched with our earlier work in case of fs irradiated PDMS which showed similar peroxide radical [16]. M. Velter-Stefanescu et al. have similar radicals in electron beam irradiated PMMA at the magnetic field value of 326.5 mT [18].

Watanabe et al. have reported luminescence and defect formation by visible and near-infrared irradiation of vitreous silica describing the paramagnetic nature of defects formed after fs exposure [19]. The present work concentrates on polymers along with the observation of luminescence and paramagnetic behavior. These observations lead us to the conclusion that luminescence and paramagnetic defects generally follow laser irradiation in most of the materials such as glasses and plastics.

We collected the confocal micro-Raman spectra from the modified regions of thin films of PS in order to predict the effect of fs pulses on Raman modes of PS. Fig. 5(a) shows Raman spectra collected for a structure fabricated at 90  $\mu\text{J}$  energy, 1 mm/s speed using 40 $\times$  objective. The spectra were collected from the middle portion and edge portion of the microstructure as shown in Fig. 5(b). The circles shown in Fig. 5(b) depict the middle and edge portions of the structure where Raman spectrum was collected. We used 50 $\times$  objective with 0.75 NA to collect Raman with excitation wavelength 514 nm. Hence, the spot size of the 514 nm beam is approximately 836 nm. But, size of the circles is shown slightly larger in Fig. 5(b) just for clarity only (Even though the scale bar is 65  $\mu\text{m}$  width).

In polystyrene 1001  $\text{cm}^{-1}$  corresponds to ring breathing mode. We found suppression of Raman modes for the structures fabricated at higher energies. Also, similar trend has been noticed in the middle of the structure as it is influenced by the central portion of the incident Gaussian pulse which has more intensity resulting in larger stress or void formation. In Fig. 5(c) since, the microstructure was fabricated at lower energy; there was no appreciable change in ring breathing mode in both the regions (middle and edge) of the microstructure.

We plan to take this work further towards fabricating waveguide devices, grating couplers in bulk PS for applications in integrated optics. Detailed and systematic study on the optical centers responsible for emission behavior is under progress.

#### 4. Conclusions

In this paper we presented fabrication and characterization of different micro structures fabricated in thin films and bulk of PS. We

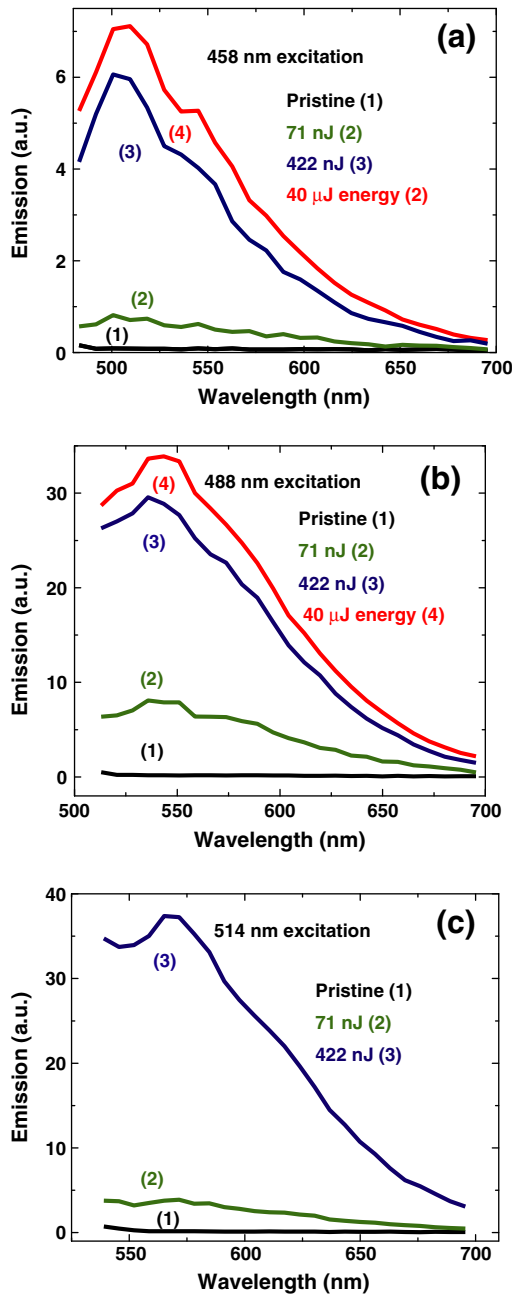


Fig. 3. (a) Plots of emission when structures fabricated at 40 μJ, 422 nJ, 63 nJ and pristine region of PS excited at 458 nm; (b) plots of emission when structures fabricated at 40 μJ, 422 nJ, 63 nJ and pristine region of PS excited at 488 nm; (c) plots of emission when structures fabricated at 422 nJ, 63 nJ and pristine region of PS excited at 514 nm.

showed increment in structure width with focusing optics (40× and 20×) and energy of the pulses. Also, we studied the spectroscopic properties of the modified structures in thin films and bulk of PS. We reported emission from the fs laser modified structures of PS for the first time in both thin films and bulk that opened doors for applications in memory based devices. Also, we reported for the first time existence of peroxide type free radicals in the fs irradiated bulk PS. We showed suppression of Raman modes in the case of structures (thin films of PS) fabricated at high energies and the effect was found to be more especially in the middle portion of the structures fabricated. No appreciable change was observed in case of structures fabricated at low energies.

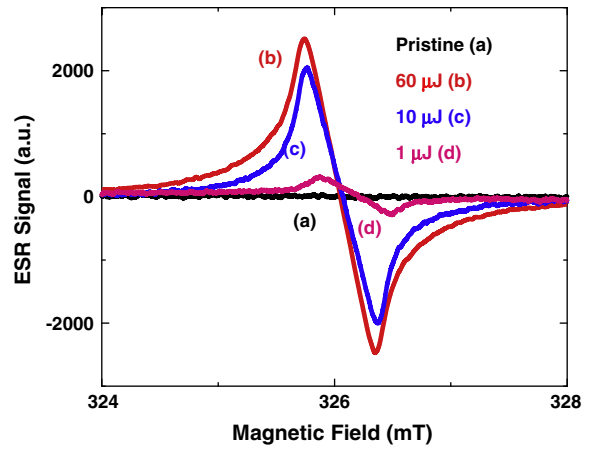


Fig. 4. ESR spectrum recorded for fs-irradiated bulk PS at different energies 1, 10 and 60 μJ.

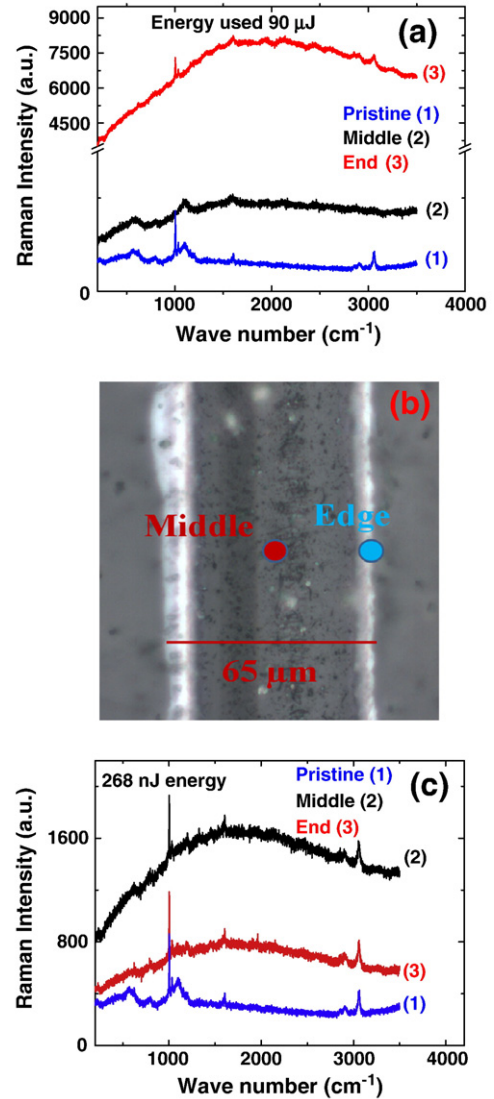


Fig. 5. (a) Raman spectra collected from a microstructure fabricated in PS thin film using 40× objective with energy 90 μJ, 1 mm/s speed; (b) 65 μm width (Scale bar) structure obtained with 90 μJ energy. The spot sizes used to collect Raman are 836 nm (For clarity spots are shown in bigger size); (c) Raman spectra recorded for similar structure fabricated with 268 nJ energy in PS thin film.

## Acknowledgements

K. L. N. Deepak acknowledges the senior research fellowship from Council of Scientific and Industrial Research (CSIR), India. D. Narayana Rao and S. Venugopal Rao acknowledge financial support from the CSIR and Department of Science and Technology, India through a project SR/S2/LOP-11/2005. This research is performed in the framework of ITPAR Phase II FaStFal 2007–2010 project.

## References

- [1] K.M. Davis, K. Miura, N. Sugimoto, K. Hirao, *Opt. Lett.* 21 (1996) 1729.
- [2] K. Yamada, W. Watanebe, T. Toma, K. Itoh, J. Nishii, *Opt. Lett.* 26 (2001) 19.
- [3] R. Osellame, S. Taccheo, M. Mariangoni, R. Ramponi, P.L. Laporta, D. Polli, S.D. Silvestri, G. Cerullo, *J. Opt. Soc. Am. B* 20 (2003) 1559.
- [4] C.B. Schaffer, A. Brodeur, J.F. Garcia, E. Mazur, *Opt. Lett.* 26 (2001) 93.
- [5] L. Shah, A.Y. Arai, S.M. Eaton, P.R. Herman, *Opt. Express* 13 (2005) 1999.
- [6] D. Homoelle, W. Wielandy, A.L. Gaeta, N.F. Borrelli, C. Smith, *Opt. Lett.* 24 (1999) 1311.
- [7] C.R. Mendonca, L.R. Cerami, T. Shih, R.W. Tilghman, T. Baldacchini, E. Mazur, *Opt. Express* 16 (2008) 200.
- [8] K. Minoshima, A.M. Kowalevicz, E.P. Ippen, J.G. Fujimoto, *Opt. Express* 10 (2002) 645.
- [9] Y. Liu, F. Qin, Z.Y. Wei, Q.-Bo Meng, D.Z. Zhang, Z.Y. Li, *J. Appl. Phys.* 95 (2009) 131116-1.
- [10] F. Qin, Y. Liu, Z.M. Meng, Z.Y. Li, *Appl. Phys. Lett.* 108 (2010) 053108-1.
- [11] E.G. Gamaly, S. Juodkazis, K. Nishimura, H. Misawa, B.I. Davies, L. Hallo, P. Nicolai, V.T. Tikhonchuk, *Phys. Rev. B* 73 (2006) 214101-1.
- [12] G.A. Ozin, S.M. Yang, *Adv. Funct. Mater.* 11 (2001) 95.
- [13] A. Polman, P. Wiltzius, *MRS Bull.* (2001) 608.
- [14] A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John, S.W. Leonard, C. Lopez, F. Meseguer, H. Miguez, J.P. Mondia, G.A. Ozin, O. Toader, H.M. van Driel, *Nature* 405 (2000) 437.
- [15] Liu Ye, Zheng Zhong Yu, Fei Qin, Fei Zhou, Zhou chang Zhu, Dao-Zhong Zhang, Qing-Bo Meng, Zhi-Yuan Li, *Chin. Phys. Lett.* 25 (2008) 4019.
- [16] L.N. Deepak Kallepalli, D. Narayana Rao, S. Venugopal Rao, *Appl. Opt.* 49 (2010) 2475.
- [17] R.N. Nurmukhametov, L.V. Volkova, S.P. Kabanov, *J. Appl. Spectrosc.* 73 (2006) 55.
- [18] M. Velter-Stefanescu, O.G. Duliua, N. Preda, *J. Optoelectron. Adv. Mater.* 7 (2005) 985.
- [19] M. Watanabe, S. Juodkazis, H.-B. Sun, S. Matsuo, H. Misawa, *Phys. Rev. B* 60 (1999) 9959.