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Atomic force microscopy, Raman spectroscopy and nonlinear absorption properties of femtosecond laser irradiated CR-39

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Abstract Investigations have been performed to explore ultrashort laser irradiation effects on the surface topography as well as structural and nonlinear absorption properties of a polymer CR-39. For this purpose, a CR-39 target was exposed in air to 25 fs, 800 nm Ti:sapphire laser radiation at fluences ranging from 0.25 $\mathrm{J\,cm^{-2}}$ to 3.6 $\mathrm{J\,cm^{-2}}$. The surface features, structural changes and nonlinear absorption were explored by AFM, Raman Spectroscopy and a Z-scan technique, respectively. Several topographical structures like bumps, explosions and nano cavities have been observed on the irradiated surface. Raman spectroscopy reveals changes in the fundamental structure of the polymer after the irradiation. Nonlinear absorption data contained by the Z-scan technique predict the dominance of three-photon absorption in case of pristine CR-39. Furthermore, nonlinear absorption (three or two photon) increases with increasing laser fluences and is well correlated with surface and structural changes revealed by AFM and Raman spectroscopy.

1 Introduction

CR-39 (allyl diglychol carbonate) is a popular polymer, which is known as an excellent material for a number of industrial, medical and optical applications. A CR-39 nuclear track detector has the track registration property and is widely used in various fields [1–3] like fusion research, nuclear science and astrophysics [2, 4]. Recent work shows that the irradiation of high-energy particles and photons on a CR-39 induces changes in its morphological, structural and optical properties [2, 4–7]. Work with regard to the nonlinear optical properties of composite CdSe/CR-39 [8] and pure CR-39 has also been reported [9]. A very few studies, however, have been performed to obtain fundamental information on laser irradiation effects on this detector (material) [10, 11]. CR-39 has good optical transparency and structural stability. The purpose of this study is to explore the optical and structural stability after the irradiation with an ultrashort laser pulse. The work presented in this paper is dedicated to explore the surface, structural and chemical changes induced by femtosecond laser irradiation at different fluences and to correlate the effect of these changes with alterations of the nonlinear absorption properties of CR-39.

2 Experimental details

A polymer CR-39 (20 mm × 20 mm ×1 mm) has been irradiated in air with 800 nm, 25 fs Ti:sapphire laser radiation. The laser beam, after passing through a 36 cm focal length lens, was incident perpendicular to the surface of the target placed 5 mm away from the focal point resulting in a spot size of 100 µm. The irradiation fluence was varied from 0.25 $\mathrm{J\,cm^{-2}}$ to 3.6 $\mathrm{J\,cm^{2}}$. In order to expose the target uniformly to perform AFM measurements, a surface area of approximately 1 mm ×1 mm was irradiated by overlapping individual laser spots. For this purpose, the target was mounted on a xyz-manipulator with a spatial resolution of 5 µm in each direction for a precise positioning of the target after individual exposure. Investigations on the topography were performed with a MFP-3D (Asylum Research USA)

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AFM. Raman spectroscopy was done by a Raman spectrometer Lab Ram HR-800 (Horiba Jobin-Yvon) with a resolution of 3 cm^{-1}. A He–Ne laser operated at 632.8 nm with 8 mW is used as an excitation source. The spectral data were accumulated at a fixed grating position for one minute and were collected using an air-cooled CCD camera.

In order to correlate changes induced by irradiation in the surface topography and Raman spectra with the nonlinear absorption, an open aperture Z-Scan technique [12] has been employed. In this technique, the irradiated CR-39 was scanned by the femtosecond laser (800 nm, 25 fs) operated at 1 KHz with a scanning energy of 100 nJ. This technique allows determining the nonlinear absorption coefficients (Two-Photon Absorption (TPA) or Three-photon Absorption (ThPA)) of the material [9].

3 Results and discussion

3.1 AFM measurements

Figure 1 presents AFM images (displayed area 5 µm × 5 µm) of an ultrashort laser irradiated CR-39 target at a fluence of (a) 0.25 $J\,cm^{-2}$, (b) 0.5 $J\,cm^{-2}$, (c, d) 1.5 $J\,cm^{-2}$, (e) 2.5 $J\,cm^{-2}$ and (f) 3.6 $J\,cm^{-2}$. Gradual growth (with increase in the laser fluence) of localized nano structures in the form of bumps is clearly seen on the irradiated surface. In addition to these bumps, explosion like features forming nano cavities with a diameter ranging from 50–100 nm and depths 1–5 nm at the top of the bumps (Fig. 1d) are observed for laser fluences of typically 1.5 $J\,cm^{-2}$. The formation of various features (bumps, etc.) provides clear evidence for a significant change in the surface morphology of the irradiated polymer. The physical mechanisms responsible for bump formation are thermal stresses produced by fast laser heating [13].

3.2 Raman spectroscopy

Raman spectra of unexposed and exposed CR-39 for different laser fluences are shown in Fig. 2. In a pristine CR-39 target various peaks observed confirm its basic monomer structure [7]. Intensity peaks around 2913 cm^{-1} and 2958 cm^{-1} are assigned to $-CH_2-$ symmetric and asymmetric stretching modes of unexposed CR-39 respectively [7]. The intensity of theses peaks reduces significantly after exposure at lower laser fluences (0.25 and 0.5 $J\,cm^{-2}$) and is almost negligible at higher laser fluences (1.5, 2.5 and 3.6 $J\,cm^{-2}$). At lower laser fluences broadening of these bands is also observed with a Raman shift of 4 cm^{-1} in the symmetric stretching mode.

The intensity of other significant peaks appearing at 1737 cm^{-1} (C=O band), 1643 cm^{-1} (C=C band),

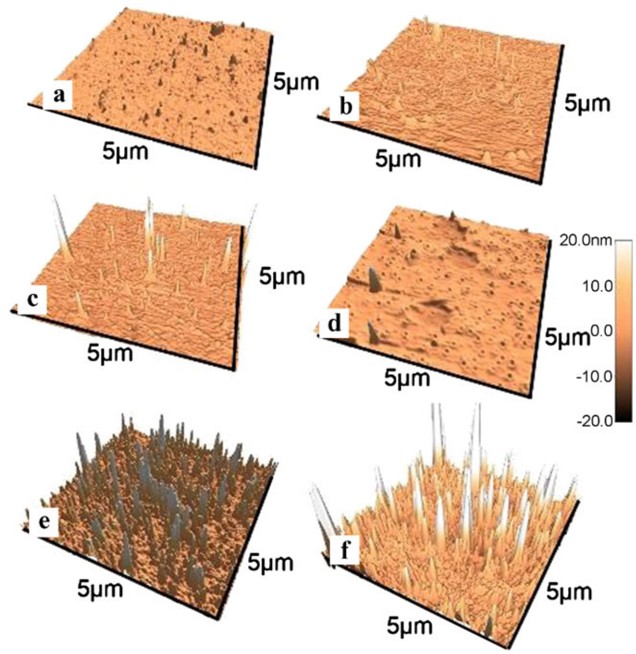

Fig. 1 AFM images (5 µm × 5 µm) of a femto second laser (800 nm, 25 fs) irradiated CR-39 at fluence (**a**) 0.25 $J\,cm^{-2}$, (**b**) 0.5 $J\,cm^{-2}$, (**c**) 1.5 $J\,cm^{-2}$, (**d**) 1.5 $J\,cm^{-2}$, (**e**) 2.5 $J\,cm^{-2}$, and (**f**) 3.6 $J\,cm^{-2}$

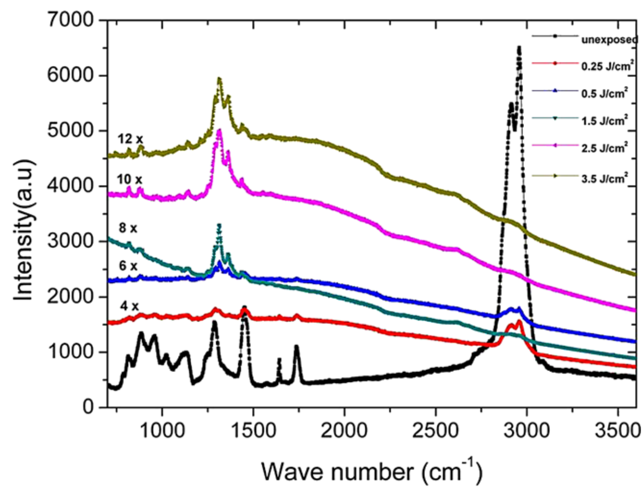

Fig. 2 Raman spectra of the virgin and laser irradiated CR-39 (25 fs, 800 nm) in air for different fluences after background subtraction

1451 cm^{-1} (–C–H– bending mode) is either reduced after the exposure or has totally disappeared depending upon the irradiation fluence. The observed band at 1287 cm^{-1} for unexposed target corresponds to C–O stretching mode. For a fluence of 0.25 $J\,cm^{-2}$ a Raman shift of 4 cm^{-1} and for fluences of 0.5–3.6 $J\,cm^{-2}$ a shift of 7 cm^{-1} has been observed. Two additional peaks are identified at 1314 and 1363 cm^{-1}. The peak at 1314 cm^{-1} corresponds to the C–O stretching mode and is attributed to oxidation of CR-39 due to its exposure in air. The results indicate, that the damage in CR-39 has been produced through radiation-induced oxi-

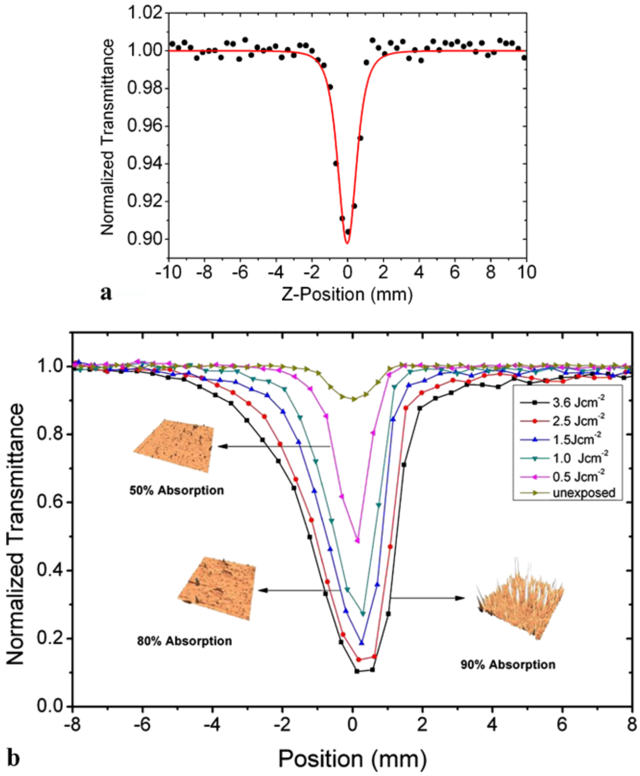

Fig. 3 (**a**) Z-scan (nonlinear absorption) measurements for an unexposed CR-39 and the corresponding fitting curve. (**b**) Normalized transmittance measured by Z-scan technique of a laser irradiated CR-39 at different fluences along with surface micrographs pertaining to the respective fluence

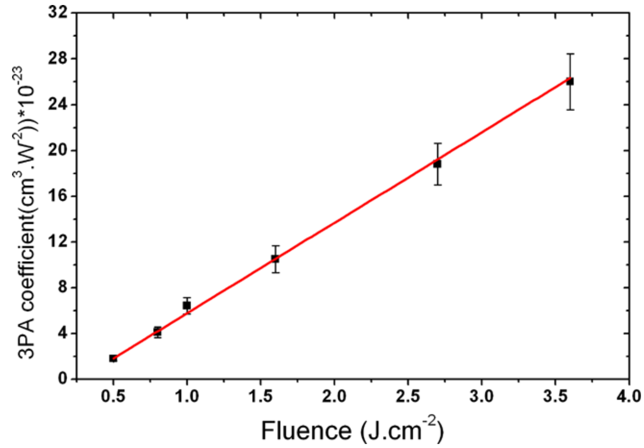

Fig. 4 Three photon absorption coefficient of femtosecond laser irradiated CR-39 for different fluences

dation [14]. The appearance of additional peaks in the spectrum indicates the enhancement of radiation effects, which lead to the formation of more active chemical bonds increasing the degree of cross linking. The relative changes of the peaks (weakening, strengthening, broadening, shifting) and the appearance of additional peaks observed in the exposed CR-39 suggest a significant change of the chemical structure of the polymer.

3.3 Z-scan measurements

Figure 3(a) shows the experimentally obtained Z-scan data of pristine CR-39: the corresponding absorption curve and the fit assuming three-photon processes to dominate. This turns out to be in good agreement with other experimental data, clearly indicating the dominance of three-photon absorption in the pristine CR-39. This is quite reasonable, because the CR-39 band gap (3.6 eV indirect and 4.2 eV direct) [2] is higher than twice the photon energy at 800 nm (1.5 eV).

Figure 3(b) shows a Z-scan measurement for irradiated CR-39 at different laser fluences. It is evident that nonlinear absorption of the polymer increases with increasing laser fluence. Gradual formation of bumps (see Fig. 1a–e) and changes in chemical structure (Fig. 2) of CR-39 causes the increase in nonlinear absorption with the increase in the laser fluence. Femtosecond laser induces structural irregularities or defects in the polymer in the form of stress distributions, local melting and scission of polymer chains, which are responsible for a change in the nonlinear absorption of the irradiated polymer.

The graph in Fig. 4 shows that the three-photon absorption coefficient (obtained by fitting) also increases from 1.8×10^{23} (cm^3/W^2) to 26×10^{-23} (cm^3/W^2) with the increase of the irradiating laser fluence from 0.5 $J\,cm^{-2}$ to 3.6 $J\,cm^{-2}$. The Z-scan data indicate the existence of three-photon absorption. However, the contribution of two-photon absorption can be assumed for the irradiated polymer due to several morphological changes and modifications of the polymerization state as becoming evident from the AFM and Raman measurements. These irradiation-induced defects can cause changes in the bandgap energy of the polymer leading to enhanced absorption [2, 15]. These effects could possibly lead to the formation of absorption centers with an energy cut off lower than the three-photon energy and thus to increased two-photon absorption. Therefore, the occurrence of both two- and three-photon absorption processes is probable for the irradiated target.

4 Conclusions

Thermal stresses are responsible for ultrashort laser irradiation-induced morphological features, like, bumps, explosions and nano cavities. Multiphoton absorption properties of CR-39 are strongly influenced by surface modifications, as well as structural and chemical changes induced by ultrashort laser radiation. Three-photon absorption is found to be the dominant process in the pristine CR-39. The nonlinear absorption increases with the increase of the laser fluence. Enhanced nonlinear absorption is observed because of gradual growth of nano bumps and occurrence of explosions and nano cavities. Bond breaking, chain scission and cross linking caused by the energy deposited during ultrashort laser irradiation are also major causes of significant increase in the nonlinear absorption properties of CR-39.

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