Nuclear Instruments and Methods in Physics Research B 267 (2009) 3606–3610

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Atomic force microscopy and Raman scattering studies of femtosecond laser-induced nanohillocks on CR-39

Shazia Bashir [a], M. Shahid Rafique [a,*], Wolfgang Husinsky [a], Alison Hobro [b], Bernhard Lendl [b]

[a] Institut für Allgemeine Physik, Vienna University of Technology, Vienna, Austria
[b] Institut für Chemische Technologien und Analytik, Vienna University of Technology, Vienna, Austria

ARTICLE INFO

Article history:
Received 16 July 2009
Received in revised form 28 August 2009
Available online 12 September 2009

PACS:
61.82.Pv
68.37.Ps
79.20.Ds
61.80.Ba

Keywords:
Ti:sapphire laser
AFM
Nanohillocks
Raman spectroscopy

ABSTRACT

The phenomenon of nanohillock-like defect formation on the surfaces of CR-39 by ultra-short laser irradiation is investigated using an Atomic Force Microscope (AFM) and Raman Scattering. A polymer CR-39 target was exposed to Ti:sapphire 25-fs laser pulses with a central wavelength at 800 nm. Samples were irradiated for different laser fluences both in air and vacuum. Detailed surface topographical features of the bombarded samples were characterized by atomic force microscopy in contact mode in air at room temperature. AFM reveals that the growth of nanohillocks and their features are strongly dependent on the ambient condition, target position from focus, and irradiation fluence. The appearance of these nanohillocks in the range 1–20 nm in height and 10–90 nm in diameter are regarded as typical features for fast electronic processes (correlated with existence of hot electrons) and are explained on the basis of Coulomb explosion. These nanostructures due to localization of laser energy deposition in small areas provide a possible pathway from dense electronic excitation to atomic motion causing permanent structural modification which are well correlated to structural alterations, like crosslinking and chain scissions, inferred from Raman spectroscopy.

1. Introduction

The study of interaction of ultra-short lasers with polymers is a topic of interest mainly due to their importance for many advanced technological applications. These applications include, microfabrication, two-photon polymerization, ionizing radiation detection, optical information recording, electroluminescence properties, optoelectronics, nanoelectronics and sensor devises [1,2].

For polymers, both ion implantation and photo irradiation phenomena are comparable as both can modify the polymer structure by carbonization, chain scission, crosslinking, free radical formation, polymerization [3,4], etc. Such radiation induced effects are responsible for the changes in structural, optical, electrical, and mechanical properties of polymeric materials, which may provide an opportunity to tailor the properties of the polymers according to the different requirements [3–7]. To investigate nanostructures by ultra-short laser is also a fundamental challenge due to its similarity with the process of surface modification by the impact of highly charged ions [8].

Substantial work is reported on femtosecond laser ablation of polymers [2,9–11]. The interaction of ultra-short laser radiation with matter is caused by several processes. In particular, we can distinguish between more conventional thermal processes and electronic processes. These two process categories can be distinguished during laser sputtering by varying the pulse duration, laser fluence and number of pulses [12], which are regarded as the key parameters that govern the laser-induced ablation process. Fast electronic processes can cause Coulomb explosion (CE) in different materials [13–17]. Nonthermal ablation often would be considered as "gentle ablation" or "nanoablation" since it occurs around the ablation threshold and tends to result in surface removal controllable on the nanometer scale [18,19]. To explore the role of Coulomb explosion for nanostructuring of material surfaces is the subject of considerable interest. Some good examples in which surface modification of different materials by femtosecond laser irradiation is explained on the basis of CE are: the hillock-shaped damage, formed on a glass surface by femtosecond pulses of 180 fs with energy of 5 nJ/pulse at 800 nm wavelength is reported by Vanagas et al. [20]. The lateral crosssection of the hillocks observed was 115–155 nm with a height of 40–70 nm. According to the authors the formation of hillocks without obvious melting and crater pitting proves that material starts to leave the surface before melting or vaporizing and is attributed to a Coulomb explosion of the exposed material. In another example ultrafast melting of graphite is observed by Raman spectroscopy, atomic force microscopy as well as time of flight mass spectrometry. A displacive motion between the topmost surface layers is attributed to

* Corresponding author. Tel.: +92 300 4178639.
E-mail address: shahidrafiq@uet.edu.pk (M.S. Rafique).

0168-583X/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2009.09.004

Coulomb explosion [21]. Recently the identification of the unique appearance of individual, localized nanohillocks, typically a few nm in height and with a few tens of nm in diameter after interaction of ultra-short laser radiation with surfaces of metals, dielectrics and semiconductors are regarded as characteristic for a strong localized potential energy deposition to the electronic system resulting in Coulomb explosion [22].

Thermal ablation processes, on the other hand, results in a slow particle emission (typically picoseconds time scale for energy deposition) with a non-localized surface topographic features like craters [23], larger bumps [24].

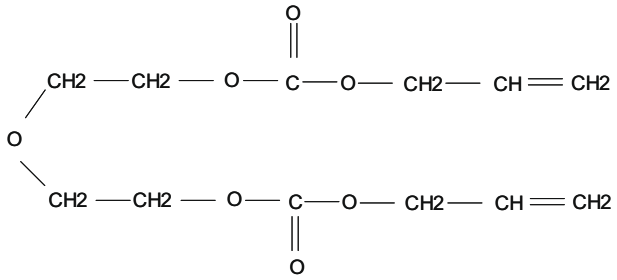
A CR-39 nuclear track detector has been well demonstrated to have an excellent track registration property and used widely in various fields by many authors [3,5,25]. A few studies, however, have been performed to obtain the fundamental information on laser irradiation effects on this detector [7,26].

In the present investigations AFM and Raman spectroscopy is employed for surface and structural characterization of the polymer after irradiation by an ultra-short laser around the ablation threshold. The purpose of surface analysis is to investigate nanostructures produced by localized laser energy deposition by a single shot on CR-39 surfaces and to understand possible physical mechanism responsible for the formation of nanohillocks. The structural and chemical changes, like bond breaking, bond weakening, crosslinking, polymerization, appearance of new disorder bands revealed by Raman spectroscopy measurements are correlated with surface analysis by AFM exhibiting the transition from electronic processes (nanoablation) to thermal processes with an appearance of a more disturbed polymer surface with increasing laser fluence.

2. Experimental details

A polymer CR-39 target is irradiated with laser pulses both in air and in UHV (10^{-9} torr) by a multipass CPA Ti:sapphire amplifier seeded from a mode-locked Ti:sapphire oscillator. The system operating at a repetition rate of 1 kHz provides laser pulses with a central wavelength around 800 nm and a typical pulse length of 25 fs.

A CR-39 by Pershore Mouldings has been used in the experiments. It is an Allyl diglycol carbonate with basic monomer structure as



The target (20 mm × 20 mm × 1 mm) was mounted on a *xyz*-manipulator with a spatial resolution of 5 μm in each direction for a precise positioning of sample for each exposure. The laser beam, after focusing through a 36 cm focal length lens, was incident perpendicular to the surface of the target placed 5 mm away from focus giving a spot diameter of 100 μm. The irradiation fluence was varied from 0.06 to 1.5 J cm^{-2}. In order to perform AFM measurements, a surface area of approximately 1 mm × 1 mm was irradiated by overlapping individual laser spots. A beam profiler (Laser Cam-HR Coherent) was used to monitor the laser beam (intensity) profile. Investigation of the topography of the laser irradiated CR-39 were performed with a MFP-3D scanning force microscopy (Asylum Research, USA) in contact mode under ambient conditions.

The Raman spectroscopy is performed by a Raman spectrometer Lab Ram HR-800 (Horiba Jobin-Yvon). A He–Ne laser is used as an excitation source with 8 mW power, at 632.8 nm. A 20× objective lens is used for laser focusing, resulting in a spot size of ~20 μm. The spectral data were accumulated at a fixed grating position and collected using an air-cooled CCD camera.

3. Results and discussion

3.1. AFM measurements

Formation of nanohillocks on a CR-39 surface with increasing laser fluences is shown by AFM surface topography images in air (Fig. 1) and under vacuum (Fig. 2). In case of air the surface structures are observed for fluences ranging from 0.25 to 2.5 J cm^{-2} whereas in vacuum, the structures are observed for fluences ranging from 0.06 to 0.5 J cm^{-2}. The major characteristic feature observed in Fig. 1a is the development of two nanohillocks, which are visible as small protrusions with typical diameter of 10–30 nm and height 2–6 nm. We define a nanohillock as a clearly identified and isolated surface bump, with height typically from 1 up to 20 nm and diameter from 10 up to 100 nm. Under ambient condition, the threshold value of the fluence to develop nanohillocks is found to be 0.25 J cm^{-2}. Fig. 1b shows the appearance of several numbers of nanohillocks with the average height of 6 nm and average diameter of 40 nm, when the polymer was exposed to a fluence of 0.5 J cm^{-2}.

In addition to these localized protrusions, some smaller pores with average depths of 3 nm and average diameters of 40 nm are also seen on the irradiated surface for this fluence. Fig. 1c shows that the average number, diameter and height of nanohillocks are significantly enhanced when CR-39 is exposed to a fluence of 1.5 J cm^{-2}. The average heights of 8 nm and average diameters of 70 nm are observed for this fluence. If the laser fluence is further increased to 2.5 J cm^{-2}, the entire surface is severely disturbed with no localized nanostructures as shown in Fig. 1d.

Fig. 2a is AFM view of nanohillock-formation with average height of 5 nm and diameter 40 nm at the threshold fluence, i.e. 0.06 J cm^{-2}. Fig. 2b shows that at the fluence 0.12 J cm^{-2} a larger number of hillocks as compared to Fig. 2a appears with an average

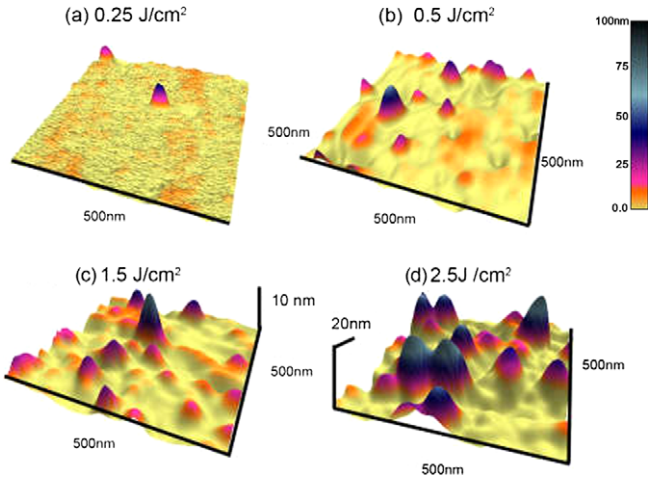


Fig. 1. AFM Topographic images of nanohillocks formation on CR-39 surface (scan area 500 nm × 500 nm) after 25 fs laser irradiation in air at fluence (a) 0.25 J cm^{-2} (b) 0.5 J cm^{-2} (c) 1.5 J cm^{-2} (d) 2.5 J cm^{-2}.