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Nanostructured Polyimide Films by UV Excimer Laser Irradiation

Mariana-Dana DAMACEANU, Radu-Dan RUSU,
Mihaela OLARU, Iuliana STOICA, Maria BRUMA

"Petru Poni" Institute of Macromolecular Chemistry, Romanian Academy,
Aleea Grigore Ghica Voda 41A, Iaşi-700487, ROMANIA
E-mail: `damaceanu@icmpp.ro`

Abstract. Here we present a study of the polyimide films nanostructuring by KrF laser beam irradiation and the investigation of the mechanism of cone-like structure formation at two laser fluences, 57 and 240 mJ/cm^2. These films were prepared from fluorinated poly(naphthyl-imide)s containing oxadiazole rings, by casting polymer solutions onto glass plates and gradually heating. Their morphology before and after laser ablation was investigated by using various techniques such as infrared spectroscopy (FTIR), atom force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

Key words: poly(naphthyl-imide)s, oxadiazole ring, laser irradiation, cone-like structure, carbon layer.

1. Introduction

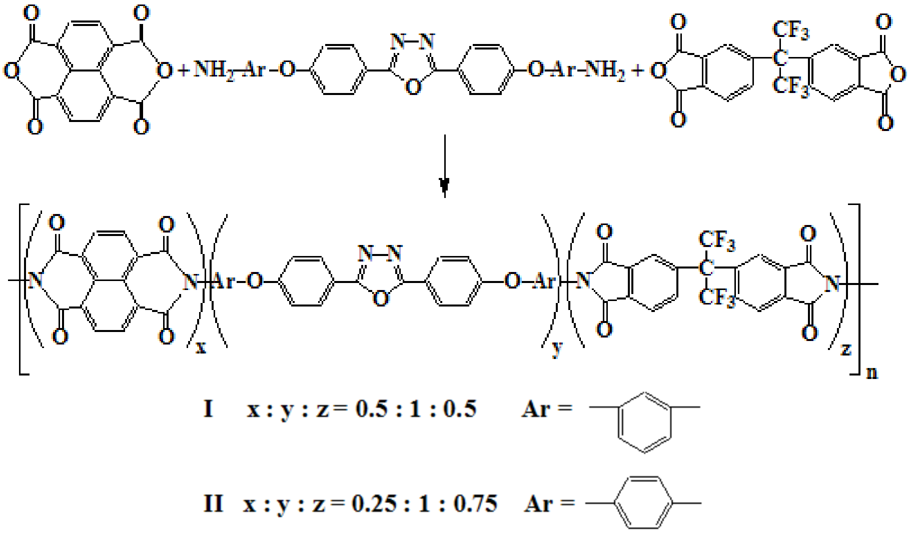
The direct structuring or laser ablation of polymers has generated considerable interest in research during the past two decades [1]. Excimer laser ablation of polyimides has attracted considerable attention, since these polymers possess outstanding key properties, such as thermooxidative stability, high mechanical strength, high modules, excellent electrical and optical properties, and superior chemical resistance, and are ideal for a variety of applications in the electrical and electronics industries [2–4]. Laser ablation studies showed clearly that this method caused clean etching of the material with micron size precision. Because of the importance of polyimides in numerous applications and the difficulty in etching these polymers by other means, such findings prompted intensive further research. Presently, laser ablation of polymers is a routine part in microelectronic packaging and fabrication of devices. In addition, laser irradiation is being explored as means of generating uniform thin polymer films [5,6]. Here, we present a study of thin films made from new fluorinated poly(naphthyl-imide)s containing oxadiazole rings upon irradiation with UV laser of various fluences and the investigation of their morphology before and after laser ablation.

2. Experimental

2.1. Synthesis of polyimides

Fluorinated poly(naphthyl-imide)s containing oxadiazole rings (**I** and **II**, Scheme 1) were prepared by solution polycondensation reaction at high temperature of equimolar amounts of 2,5-bis[4-(m-aminophenoxy)-phenylene-1,3,4-oxadiazole or 2,5-bis[4-(p-aminophenoxy)-phenylene]-1,3,4-oxadiazole with a mixture 1:1 or 2:1 of hexafluoroisopropylidene diphthalic dianhydride (6FDA) and naphthalene-1,4,5,8-tetracarboxylic dianhydride (NTDA), respectively, in N-methylpyrrolidone (NMP) as solvent and in the presence of benzoic acid as catalyst, at a concentration of 10–12% total solids [7].

Scheme 1. Synthesis of the polyimides.



2.2. Preparation of thin films

Thin films of these polyimides were prepared by casting a solution of 10–12% concentration of polymers in NMP onto glass plates, followed by gradual heating from room temperature up to 210°C, and kept at 210°C for 1 h. The resulting transparent films were stripped off the plates by immersion in hot water followed by drying in oven at 110°C. These films had the thickness in the range of 30–50 μm and were used for laser ablation.

2.3. Measurements

The infrared spectra of the polymers were recorded on FT-IR Bruker Vertex 70 Spectrophotometer in transmission mode, by using pristine or ablated thin films having the thickness of 5–6 µm.

Thermal stability of the polymers was evaluated by thermogravimetric analysis which was performed with a MOM derivatograph made in Budapest, Hungary.

Glass transition temperature was measured by differential scanning calorimetry with a DSC 12E calorimmeter.

Mechanical properties of the polymer films were analysed by tensile testing using an Instron 5566 apparatus. The samples were used in the form of strips having the thickness of 0.03 mm, gauge length of 25 mm and width of 15 mm. Stiffness, tensile strength and elongation-at-break were determined at 10 mm/min cross-head speed. The tensile stress (MPa) versus tensile strain (%) dependencies was recorded.

Static ablation of polyimide samples (i.e. the samples were not moved during the irradiation) was realized by using a COMPexPRO (Coherent) excimer laser operating at 248 nm (KrF), with pulse duration of 25 ns and an energetic stability of laser beam of minimum 1%. The experiments were performed after 30 pulses at laser fluence of 57 and 240 mJ/cm^2. The quality of free-standing thin films and of ablated thin films was investigated by atomic force microscopy (AFM) using a Scanning Probe Microscopy Solver PRO-M, NT-MDT equipment made in Russia, in semi-contact mode, semi-contact topography technique.

Surface chemical composition of both untreated and treated polyimide films were evaluated by XPS which was performed in a XPS microprobe instrument PHI Versaprobe (Physical Electronics, USA). The photoelectrons were detected with a hemispherical analyzer positioned at an angle of 45° with respect to the normal of the sample surface. The energy resolution was about 0.5 eV and survey-scan spectra were made at 187.85 eV. Individual high-resolution C1s, O1s and N1s spectra were taken and the concentrations of different chemical states were determined by fitting the curves with symmetrical Gauss–Lorentz functions. The spectra were fitted by using MultiPak v7.3.1 software from Physical Electronics, USA which was supplied with the spectrometer.

3. Results and discussion

Polycondensation reaction at high temperature (210°) of equimolar amounts of aromatic diamino-oxadiazoles with a mixture 1:1 or 1:2 of NTDA with 6FDA, in NMP, in the presence of benzoic acid as catalyst, yielded six-member polyimides containing oxadiazole rings **I** and **II** (Scheme 1). The resulting polymer solutions in NMP were used partly to cast thin films and partly to isolate the solid polymer by precipitation into water.

The poly(oxadiazole-naphthyl-imide)s **I** and **II** are soluble in aprotic amidic solvents such as NMP, dimethylacetamide or dimethylformamide, and even in less polar solvents as chloroform. The good solubility of these polyimides compared with that of related polyimides based only on NTDA, is explained mainly by the presence in the polymer chain of flexible hexafluoroisopropylidene groups (6F) that disturb the tight packing of the polymer chains and make the shape of the respective macromolecules to be far from a linear rigid rod which is characteristic to polyimides based only on NTDA where strong interchain interactions are present.

The good solubility makes the present polymers potential candidates for practical applications in spin-coating and casting processes. These polymers possess film forming ability. The polymer solutions (10–12%) in NMP were processed into thin films by casting onto glass plates. The free-standing films having the thickness in the range of tens of micrometers were flexible, tough, and maintained their integrity after repeated bendings. The values of tensile strength were in the range of 69–100 MPa, elastic modulus in the range of 2.26–2.59 GPa and elongation to break in the range of 5.12–7.51%. All these tensile data demonstrate that the films prepared from these copoly(naphthylimide)s containing oxadiazole moiety and flexible 6F linkages are though and can be used as advanced materials in microelectronic industry.

The polyimides **I** and **II** are highly thermostable, their initial decomposition temperature (IDT) being above 445°C (Table 1), temperature of 10% weight loss in the range of 490–512°C, and temperature of maximum decomposition rate (T_{max}) above 540°C. These data show that the present polyimides have high thermal stability, similar with that of five-member polyimides based on the same diamino-oxadiazoles, but without naphthalene units [8]. The glass transition temperature of the polymer **II**, containing only *para*-substituted phenylene rings, is the highest, 303°C, while that of the polymer **I**, containing some *meta*-substituted phenylene rings, is 265°C.

Table 1. Thermal properties of the polymers

Polymer	$\mathbf{T}_g$ [°C]	**IDT** [°C]	$\mathbf{T}_{10\%}$ [°C]	$\mathbf{T}_{max}$ [°C]
I	265	445	490	560
II	303	490	512	542

$\mathbf{T}_g$ = glass transition temperature, from DSC curve;
IDT = onset on the TG curve;
$\mathbf{T}_{10\%}$ = temperature of 10% weight loss on the TG curve;
$\mathbf{T}_{max}$ = temperature of maximum rate of decomposition.

The films prepared from copolyimides **I** and **II** have been subjected to static ablation by using excimer laser operating at 248 nm (KrF), at the laser fluence of 57 and 240 mJ/cm^2.

The **FTIR spectroscopy** was used to investigate the structural changes that appeared in the polymer films after laser ablation. In FTIR spectra, the sharp band at 3493 cm^{-1} was assigned to the N-H stretching vibration of polymer chain, to the end NH_2 groups or to NH groups in polyamidic acid incompletely imidized during polymer synthesis. The broad absorption at 3080 cm^{-1}belongs to the C–H stretching vibrations of the aromatic rings. The characteristic imide ring absorptions appeared at 1784 cm^{-1} (asymmetrical C=O imide stretching) and 1716 cm^{-1} (symmetrical C=O imide stretching). The sharp peaks at 1593 and 1483 cm^{-1} were assigned to the stretching vibrations of aromatic systems, *i.e.*, the 1,4-disubstituted phenylene rings. The broad absorption at 1371 cm^{-1} was assigned to C-N stretching in imide ring, while the band at 1242 cm^{-1} was assigned to asymmetric C$_{Ar}$-O-C$_{Ar}$ stretching vibration of diaryl ether group. Characteristic absorption peaks of 1,3,4-oxadiazole ring were identified at 1024 cm^{-1} and 983 cm^{-1} (=C–O–C= stretching). The sharp band at 731 cm^{-1} corresponds to the out-of-plane bending vibration of the imide ring. A decomposition of imide system under laser irradiation should be correlated with a decrease of carbonyl bands, of C–N stretching vibration, and of out-of-plane bending vibration of the imide system. Instead, even after irradiation with 30 pulses at a higher fluence of 240 mJ/cm^2, several bands have grown in intensity, i.e., 1784, 1716, 1483, 1371, 1242, 841 and 720 cm^{-1}, whereas only three bands have decreased, i.e., 3493, 2853–2921 and 1307 cm^{-1}. An increase of the absorption was also observed over the whole mid-IR region, denoted by the rising baseline. This increase of the baseline has been reported previously and was assigned to an accumulation of carbonaceous species in and surrounding the irradiated area [9]. The absorption bands characteristic to oxadiazole rings remained unchanged after irradiation, which proved the higher stability of oxadiazole ring compared with naphthyl-imide one.

Atomic force microscopy (AFM) was used to further examine the surface morphology, as well as the period and depth of the grooves. After 30 laser pulses at 57 mJ/cm^2 (slightly higher than the ablation threshold), the surface topography changed from an original more or less smooth surface, with irregular protuberances (Fig. 1) to a surface characterized by the appearance of cone-like structures (Fig. 2).

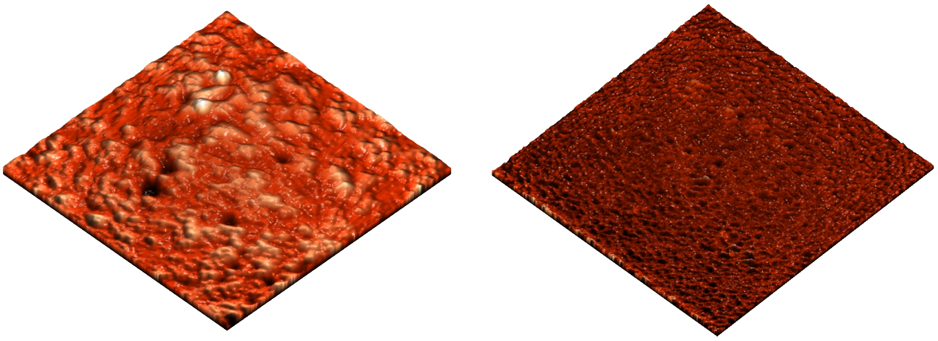
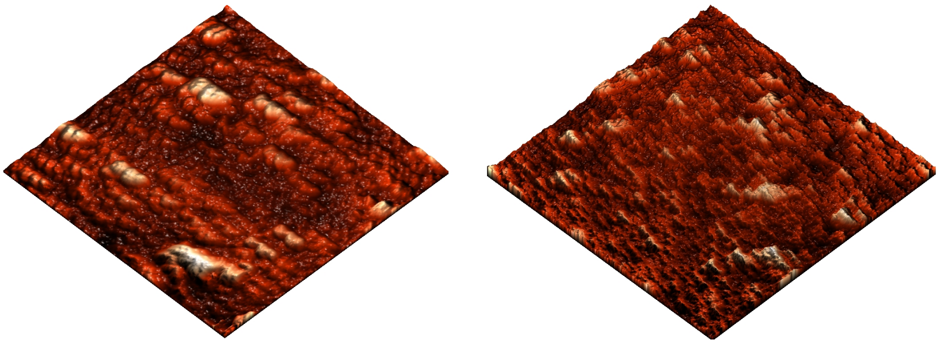

(a) (b)

Fig. 1. AFM images of thin films of polyimides **I** (a) and **II** (b), before laser-irradiation.

At low fluence (57 mJ/cm^2), the inital protuberances from polymer **I** surface evolved to densely packed cone-shaped structures that, at a certain level, lead to the formation of long periodic structures with a period of about 0.7 µm and 50 nm depth. In case of polymer **II** film, the laser irradiated area was characterized by closely packed cones of 50 nm heights. In addition, the number of cones and the base diameter decreased, as compared with the surface of polymer film **I**.

When laser fluence increased to 240 mJ/cm^2 (Fig. 3), sparsely distributed cones could be observed for polymer film **I**. Also, the decrease of cones number, as well as the increase of their height and base diameter with the increasing of laser fluence were registered.

The formation of conical structures at 57 mJ/cm^2 can be due to shielding by opaque impurities such as calcium- and phosphorous-containing which remained in the film during its preparation. These impurities are evenly distributed in the polymer film, having higher threshold fluence than the polymer itself. During irradiation, the impurity particles are not ablated, while the surrounding polyimide is removed. The remaining phosphorous- and calcium-containing particles shade the material underneath from the laser radiation, creating the observed conical structures. Moreover, self-organization of polyimide molecules and clusters under UV laser irradiation at a fluence above ablation threshold can be considered responsible for the formation of long periodic structures. The appearance of periodic structures on the laser-irradiated polymer film surface, such as polyethersulfone, was also reported by other authors [10].



(a) **(b)**

Fig. 2. AFM images of surface structure of polymer film **I** (a) and **II** (b) produced by KrF excimer laser at the laser fluence of 57 mJ/cm^2.

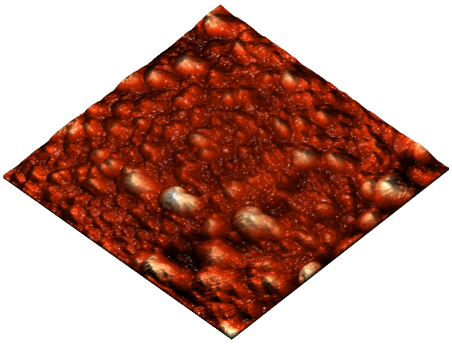


Fig. 3. AFM image of surface structure of polymer film **I** produced at the laser fluence of 240 mJ/cm^2.

From **XPS measurements**, carbon, nitrogen, oxygen, fluorine, silicon, sodium, calcium and sulfur atoms were detected at the surfaces of polyimide film **I** irradiated with laser fluence of 240 mJ/cm^2. The compositions (± 2.0 %) obtained from curve fitting for each core-level spectrum of the original and ablated polyimide film **I** are summarized in Table 2. The spectral features of the original polyimide **I** film are similar to those of previously reported spectra of polyimides, including Kapton film [11, 12].

The C 1s spectrum is composed of four components: the 284.8 eV component assigned to aromatic carbons in benzene rings not joined to oxygen or nitrogen, the 286.3 eV component assigned to carbon atoms single bonded to oxygen or nitrogen, the 287.7 eV component assigned to carbonyl carbons of the imide groups, and 288.9 eV component due to carboxylic carbon probably remained from an incomplete imidization process. Their contribution is different: 87%, 8%, 2% and 3%, respectively. Compared with the XPS spectra of Kapton film, shifts of about 0.2–1.1 eV are observed, which are probably due to NH_2 end groups of polymer chain and formation of -N=C=O or NO_2 groups. The O 1s spectrum is composed of two peaks at 532.2 eV and 533.6 eV, assigned to carbonyl oxygens and ether oxygens, respectively. The N 1s spectrum is composed of a single peak at 399.8 eV corresponding to nitrogens of the imide groups. The F 1s spectrum is composed of a single component at 688.3 eV corresponding to fluorine atoms of hexafluoroisopropylidene groups. Traces of silicon- sodium-, calcium- and sulphur-containing particles, which are impurities coming from the glass support (CaO, SiO_2) used in the manufacturing of polyimide **I** films were also detected.

Table 2. The compositions (± 2.0 %) obtained from curve fitting for each core-level spectrum of the original and ablated polyimide film **I**, at laser fluence of 240 mJ/cm^2

Original polyimide I film				**Ablated polyimide I film**			
Element	Atom %	Binding energy (eV)	Bond type	Element	Atom %	Binding energy (eV)	Bond type
C 1s	76.3	284.8 (87%) 286.3 (8%) 287.7 (2%) 288.9 (3%)	CH C-O C=O	C 1s	81.3	284.1 (14%) 284.8 (76 %) 286.3 (8 %) 287.7 (1 %) 288.9 (2 %)	C CH C-O C=O
O 1s	16.2	532.2 (90%) 533.6 (10%)	O=C O-C_{Ar}	O 1s	12.4	532.3 (82 %) 533.6 (18 %)	O=C O-C_{Ar}
Si 2p	4.7	102.2	glass (SiO_2)	Si 2p	3.2	102.2	glass (SiO_2)
N 1s	1.6	399.8	imide N	N 1s	1.9	399.7 (65 %)	imide N
F 1s	0.4	689.0	F-C	F 1s	0.5	688.3	F-C
Na 1s	0.4	1071.4	glass (Na_2O)	Na 1s	0.4	1071.1	glass (Na_2O)
Ca 2p	0.3	348.6	glass (CaO)	Ca 2p	0.2	348.6	glass (CaO)
S 2p	0.2	169.0	glass (SO_3)	S 2p	0.2	169.0	glass (SO_3)

The observed spectra of the surface irradiated with 30 pulses at laser fluence of 240 mJ/cm^2 show that modified bonding environments are produced on ablated surface, as well. In the case of polyimide film **I** surface, the C 1s spectrum is tentatively curve-fitted to four primary components (Figure 4, left). Compared with the C 1s spectrum of the original polyimide film **I** surface, the relative intensity of the peak assigned to aromatic carbons in benzene rings not joined to oxygen or nitrogen at 284.8 eV, carbonyl carbon component at 287.7 eV and carboxylic C at 288.9 eV decreases, while the relative intensity of carbon component single bonded to oxygen or nitrogen at 286.3 eV remains unchanged (cf. compositions of C 1s spectra presented in table 2). A new component at 284.1 eV (figure 4, right) can be assigned to carbon atom which suggests the formation of carbon-rich surfaces observed after irradiation, probably resulting from the preferential removal of imide groups in polyimide molecules, followed by chemical bond formation processes such as rearrangement and recombination. In N 1s spectrum, no obvious changes can be seen, except for a shoulder at higher binding energy side of the peak. In O 1s spectrum the relative intensity of the peak assigned to carbonyl oxygens 532.3 eV decreases while the component intensity at 533.6 eV due to ether oxygens increases. Overlay views of the unmodified and ablated regions of the polyimide **I** film shows that the ablation increases the overall levels of carbon and nitrogen, and decreases the amount of oxygen. The contribution of a reaction similar to combustion followed by leaving incompletely combusted hydrocarbons and redeposition and surface oxidation are suggested, similarly to previously reports on other polyimides [13].

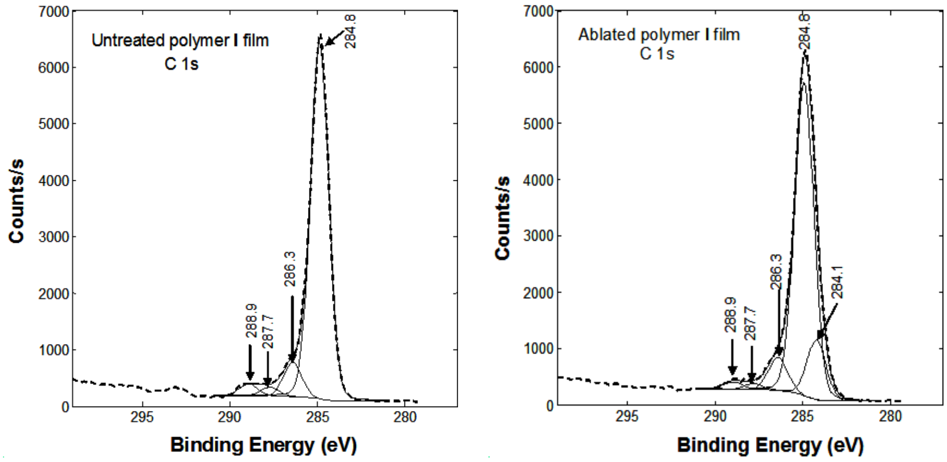


Fig. 4. XPS spectra (**C 1s**) of the original and ablated (at 240 mJ/cm^2) polyimide **I** films.

When laser fluence was 57 mJ/cm^2 similar features have been observed. In carbon spectrum, intensity is increased at ~285 eV, which is consistent with formation of aliphatic or aromatic C-C or C-H bonds, probably after loss of O and/or N. There is a loss of intensity around 286.5 eV, which is typical of C-O bonding of Ar-O-Ar links in the polymer. There is a change in shape at 287–289 eV, which indicates modification and, probably, a small loss of C=O and/or C=N units. The peak at 293 eV which is characteristic of C-F is reduced, and intensity is increased at 290–292 eV. This may indicate loss or migration of fluorine around the polymer, after liberation by laser pulses. Nitrogen looses intensity at ~402 eV, which is typical of highly oxidized organic species that may be a contaminant and are removed by ablation. The peak at ~400 eV characteristic to C-N/C=N bonds increases in intensity and broadens, indicating more variation in C/N chemistry. Oxygen looses intensity at higher binding energies, which is consistent with loss of C-O bonding and perhaps water.

4. Conclusions

Two fluorinated polymers having oxadiazole-naphthylimide structures have been prepared and processed into thin free-standing films having the thickness in the range of tens of micrometers. Irradiation of the films with KrF pulsed laser operating at 248 nm, at laser fluence of 57 mJ/cm^2 and 240 mJ/cm^2, was performed and the behaviour of these films before and after irradiation was investigated by using various techniques. FTIR spectroscopy evidenced a decomposition of imide rings under laser radiation and accumulation of carbonaceous species in/and around the irradiated area. The absorption bands characteristic to oxadiazole rings remained unchanged after irradiation. Atomic force microscopy showed that the film surface changed from a relatively smooth morphology to one having cone-like structure: at low laser fluence, of 57 mJ/cm^2, the film surface looked like a densely packed cone-shaped long periodic structure; at higher laser fluence, of 240 mJ/cm^2, the number of cones decreased while their height and base diameter increased. The formation of cone structure at low laser fluence is explained by the presence of opaque impurities which shade the material underneath from laser radiation, while the surrounding polyimide molecules self-organize under UV-laser radiation and lead to the formation of long periodic structure. XPS spectra of the films before laser irradiation revealed the presence of all atom species in the polymer chain and of sodium, calcium, silicon and sulfur impurities, so that the general aspect of such spectra are similar to those of conventional Kapton polyimide film. Overlay views of the unmodified and ablated regions of the polyimide **I** film shows that the ablation increases the levels of carbon and nitrogen, and decreases the amount of oxygen. After irradiation with high laser-fluence (240 mJ/cm^2) XPS spectra of the ablated film suggested the formation of carbon-rich surface.

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