Physico-chemical Insights on Tuning the Morphology of a Photosensitive Polyimide by UV Laser Irradiation

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An aromatic photosensitive polyimide is prepared from 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 4,4'-diaminodiphenyl methane and its structuring ability upon UV-laser exposure is investigated. Surface modification is performed at two laser fluences, i.e. 89 and 244 mJ/cm^2, and different number of pulses. The changes of the surface morphology, induced by the employed patterning technique, are examined. According to atomic force microscopy data cone-like structures are formed and their appearance mechanism is analyzed taking into account the laser irradiation conditions. Surface wettability tests reveal an intensification of hydrophobic character, which may be ascribed to the formation of a thin carbon-enriched layer at the polyimide surface.

Keywords: polyimide, laser, morphology, wettability

The ability to pattern functional polymers at different length scales has generated considerable interest in various research fields including tissue engineering, optics and microelectronics. Among the reported surface patterning techniques, pulsed laser micromachining has emerged as a powerful tool used to modify, functionalize and etch materials with high resolution (at micrometer scale) due to the low wavelength of the source [1,2]. Excimer laser ablation of polyimides (PIs) has attracted considerable attention because these polymers possess excellent thermal, mechanical and electrical properties [3]. Laser induced periodic structures (LIPS) on PIs were initially prepared by using Nd:YAG laser as the light resource at an energy lower than the ablation threshold [4]. Other studies have analyzed the mechanism of the LIPS formation, revealing that it is mainly determined by the absorption characteristics of the PI film to the incident laser [5,6]. Considering the difficulty in etching these polymers by other means recent reports are mostly focused on the preparation of LIPS on different PI films [7-9]. According to the literature on laser ablation of PIs, doping of small molecules, which show absorbance at incident laser, is helpful to the laser ablation process [10]. From this viewpoint it can be considered that the utilization in PI synthesis of monomers containing photosensitive groups represents a better alternative. It is widely known that inherent photosensitive PIs are prepared by the polycondensation of benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA) and various diamines [11].

The present research article presents original data concerning the UV-laser micromachining of an aromatic PI prepared from BTDA and a diamine containing a flexible methylene sequence. The prepared structure is confirmed by infrared spectroscopy and the impact of the employed laser patterning conditions on the PI surface properties are investigated by atomic force microscopy (AFM) and contact angle measurements.

Experimental part

Materials and film preparation

Benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA, Aldrich) is recrystallized from acetic anhydride and vacuum dried before use. 4,4' diaminodiphenylmethane (DDM, Sigma) is recrystallized from ethanol solution. N-methyl-2-pyrrolidone (NMP, Aldrich) is purified by distillation under reduced pressure and stored over 4A° molecular sieves.

Film preparation

PI films are obtained by thermal imidization of poly(amic acid) (PAA) film cast on a glass substrate, which are placed overnight in an 80°C oven to remove most of the solvent. The semidried PAA films are further dried in an oven and transformed into the corresponding PI, by the following heating program: 120, 160, 180, 210 and 270 °C for 1 h at each temperature. After stripping the films in hot water, the resulting samples are dried at 65 °C in a vacuum oven for 24 h. The film thickness is around 50 μm.

Characterization

Infrared spectrum is recorded with a Bruker Vertex 70 spectrometer in transmission mode, at 24 cm^{-1} resolution, by using precipitated polymers ground in potassium bromide pellets.

Static ablation of polyimide samples is made on a LPX 220 excimer laser operating at 308 nm (XeCl), with pulse duration of 25 ns and an energetic stability of laser beam of minimum 1%. The experiments are performed after 5, 10, 15, 30 pulses at two laser fluences of 89 mJ/cm^2 and 244 mJ/cm^2.

The water static contact angles are measured by the sessile-drop method, with a CAM-101 (KSV Instruments, Finland) system equipped with a liquid dispenser, video camera, and drop-shape analysis software, at room temperature.

Atomic force microscopy (AFM) measurements are performed on a scanning probe microscope Solver Pro-M (NT-MDT, Russia), in air, at room temperature, in tapping mode. A rectangular silicon cantilever NSG10 (NT-MDT, Russia), with a typical force constant k_N = 11.8 N/m and 161 kHz resonance frequency is used. The tip curvature radius and height was 10 nm and 14–16 μm, respectively. The scan areas are 1 x 1 μm^2 and 2 x 2 μm^2.

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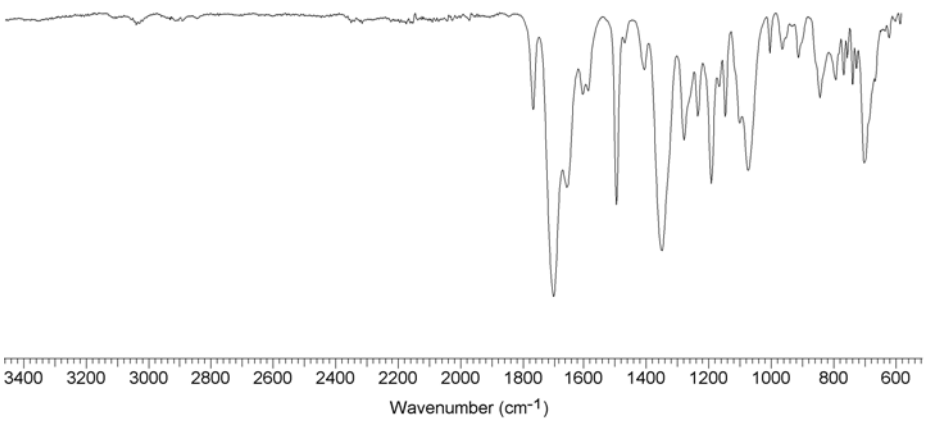

Fig. 1. FTIR spectrum of poly(BTDA-DDM)

Results and discussion

Structural characterization of the PI

The PI, here under investigation, is synthesized via a two-step process by thermal imidization method in solution. An equimolar ratio is maintained between BTDA and DDM monomers. The first step of the reaction consists in the preparation of the PI precursor in N-methyl-pyrrolidinone (NMP) (15 %wt). Secondly, the polymer solution is heated to perform cyclodehydration of PAA to the corresponding PI.

The chemical structure of the investigated PI is confirmed by Fourier-Transformed Infrared Spectroscopy (FTIR). Figure 1 presents the FTIR spectrum of the BTDA-DDM polymer. Characteristic imide absorption bands are observed at around 1775 cm^{-1} (attributed to the C=O asymmetrical stretching vibrations of imide groups), 1712 cm^{-1} (attributed to the C=O symmetrical stretching vibrations of imide groups), 1370 and 720 cm^{-1} (assigned to C–N stretching and C–N bending, respectively, in imide groups). An additional band, at 1670 cm^{-1}, corresponds to C=O stretch of benzophenone. The bands at around 2935 and 2860 cm^{-1} are assigned to the CH_2 vibration of aliphatic units, while, the C–H linkage of aromatic rings shows a peak at about 3050 cm^{-1}. The broad absorption band at 3350–3450 cm^{-1} characteristic of NH amidic and the narrow absorption peak at 1650–1660 cm^{-1} due to C=O group in amide linkage disappear entirely, indicating the completion of thermal imidization process and confirms the synthesis of poly(BTDA-DDM).

Morphological Changes Induced by Pulsed Laser Exposure

In order to understand the mechanism of UV laser structuring, first the pristine poly(BTDA-DDM) film morphology is examined by AFM method. For AFM imaging in semi-contact mode, the AFM tip is positioned over the sample and the scanning is made at a constant frequency of 1.01 Hz. The typical forces between the tip and the samples are maintained constant by a feedback control. In figure 2 it can be observed that the untreated poly(BTDA-DDM) film reveal a uniform and flat surface, covered with nanometric pores. The analyzed surface shows a small root-mean-square roughness, *Sq*, of 0.5 nm - value comparable with those obtained for other PIs [12,13]. The surface topography and roughness of the PI film derive mainly from the characteristics of the polymer chains that govern aggregation and molecular ordering, which occur during drying and the thermal imidization processes [14].

For surface structuring the laser fluence used in surface patterning should be chosen in relation to the ablation threshold [15,16]. If the laser fluence exceeds the ablation threshold (which depends on the PI structure), the process leads to the formation of deposited ablation products on the surface because of photodecomposition, which sometimes are useful for functionalization of the PI surface. When the polymer surface is irradiated by an excimer laser at fluence below the ablation threshold a photochemical reaction could also take place [17].

In this work, PI fluence threshold for ablation is determined from the plasma emission intensity plot as a function of laser fluence. Above the ablation threshold, plasma emission is recorded with a fast intensified charge coupled device (ICCD) camera (iStar DH740-18U-03) at different laser energies, keeping the laser focalization spot constant (fig. 3). This method is not reported yet, so for its validation a commercial polymer with known value of fluence threshold is taken in discussion, namely polyethylene terephthalate (PET). In order to have a good signal to noise ratio and also to avoid detector saturation, relatively large acquisition time values have been selected: 244 μs for PET and 500 ns for studied PI plasma plume recordings. Vertical cross-sections through the centre of the two-dimensional images, presented in figure 3, are further used to get the maximum emission from the plasma as a function of laser fluence (fig. 4). By performing a linear fit, the fluence threshold is determined at the intersection with the fluence-axis. Thus, it results a fluence threshold value of 186 mJ/cm^2 for PET, which is quite close to the value reported in literature, *i.e.* 170 mJ/cm^2 [18]. This confirms the method used subsequently for PI

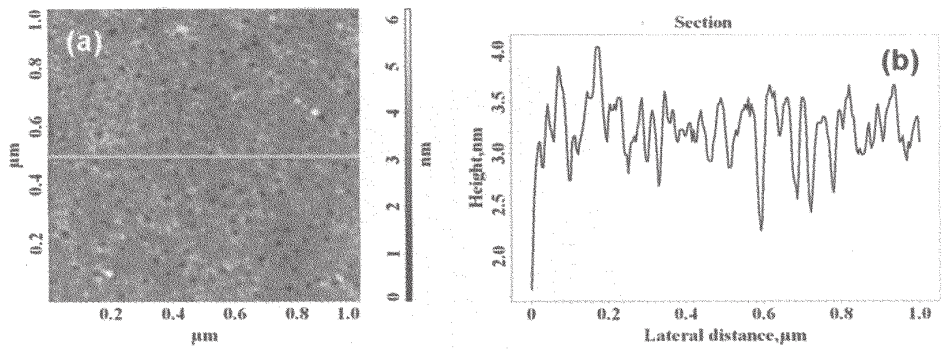

Fig. 2. The height 2D AFM image (a) and cross-section profile (b) of pristine poly(BTDA-DDM)

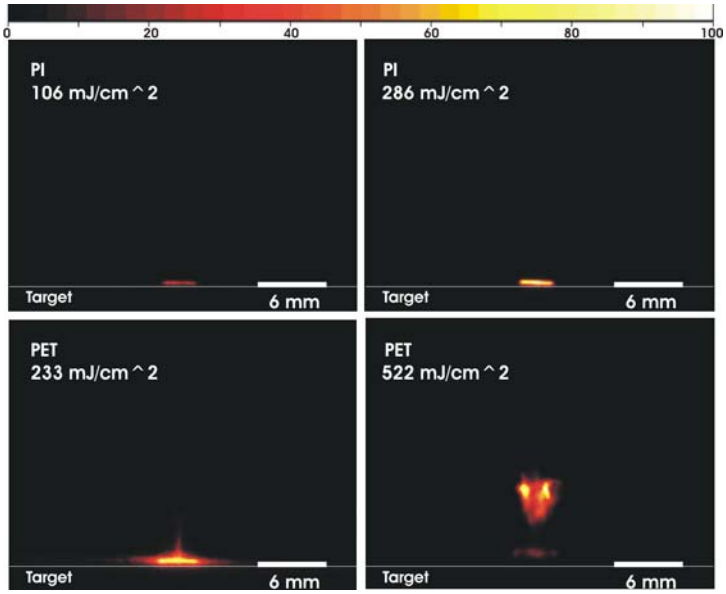

Fig. 3. Plasma plume images recorded by ICCD fast imaging.

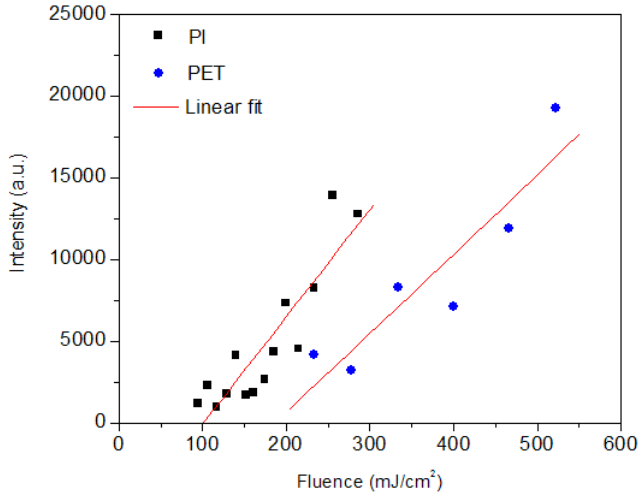

Fig. 4. Laser fluence threshold for ablation determined from the maximum emission intensity *versus* laser fluence

threshold determination. Following the same procedure the PI fluence threshold value is found to be 101 mJ/cm^2.

The fluences used for this experiment are below and above the ablation threshold: 89 and 244 mJ/cm^2, respectively; and the number of pulses are varied for both fluencies, namely 5, 10, 15 and 30 pulses. As shown in figures 5 and 6, for all UV-laser exposure conditions, the surface topography of poly(BTDA-DDM) is modified from an original smooth surface, with some irregular features, to a surface characterized by the appearance of cone-like structures with closely packed cones that, at a certain level, lead to the formation of long periodic structures.

According to the AFM data, it can be observed that the diameter and height of the cone-shaped structural formations depend on the laser irradiation conditions, as shown in table 1. At the fluence of 89 mJ/cm^2 and 5 laser pulses (fig. 5(a)) individual cones are periodically placed on the PI surface. By increasing the number of pulses to 10 (fig. 5(b)) the periodicity is slightly decreased and cone average diameter and height of the cones are reduced. At 15 pulses (fig. 5(c)) structural formations are bigger and uniformly distributed, but not in a repetitive fashion. At 89 mJ/cm^2 and 30 pulses (fig. 5(d)) the cones are agglomerated and become again arranged periodically.

When the laser fluence was increased to 244 mJ/cm^2 (fig. 6), cones with higher height could be distinguished. In this case there is no ordering and agglomeration tendency, but the cones are distributed more uniformly. At 5 and 10 laser pulses (fig. 6(a), (b)) the surface formations exhibit a bumpy aspect, with the height increasing with the pulses number. Further augmentation of the pulses leads to a change of the cones shape from globular to a cliff-like one (fig. 6(c)), with bigger dimensions. At 30 pulses, cone-like formations are noticed, but the surface is non-uniform and exhibits degradation tendency (fig. 6(d)).

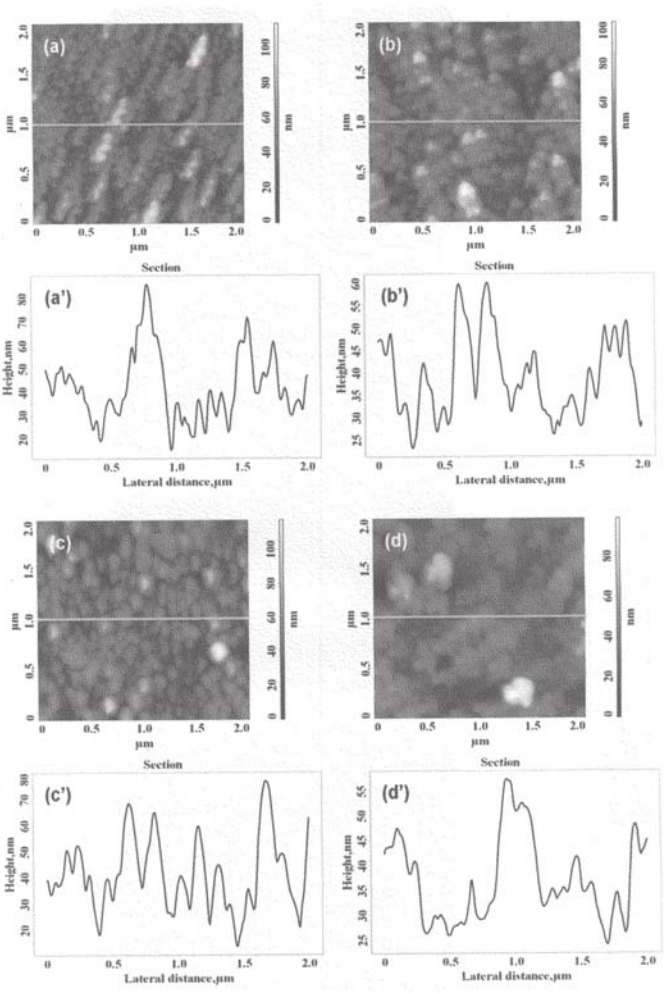

Fig. 5. The 2D AFM images of poly(BTDA-DDM) after UV-laser exposure at 89 mJ/cm^2 and the corresponding cross-section profiles at different number of pulses: (a, a') 5 pulses, (b, b') 10 pulses, (c, c') 15 pulses and (d, d') 30 pulses.

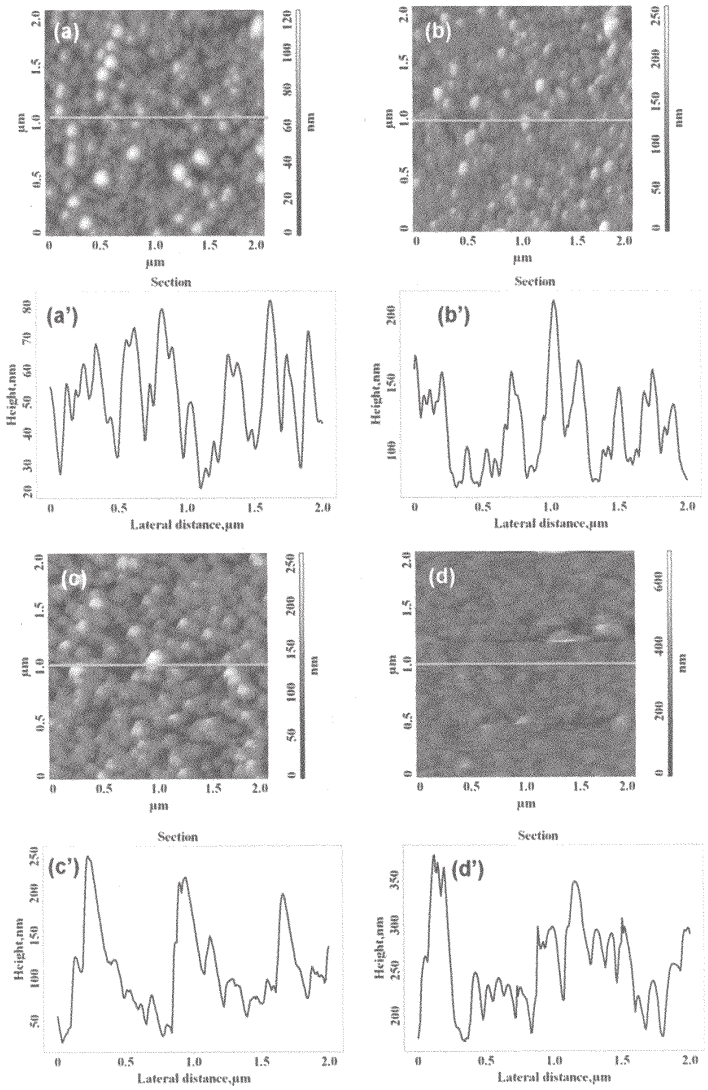

Fig. 6. 2D AFM images of poly(BTDA-DDM) after UV-laser exposure at 244 mJ/cm^2 and the corresponding cross-section profiles at different number of pulses: (a, a') 5 pulses, (b, b') 10 pulses, (c, c') 15 pulses and (d, d') 30 pulses.

No.	Fluence, mJ/cm^2	Number of laser pulses	Period of cones, nm	Diameter of cones, nm	Height of cones, nm
1.	89	5	200	78	60
2.	89	10	150	50	30
3.	89	15	-	130	60
4.	89	30	260*	250*	55*
5.	244	5	-	128	80
6.	244	10	-	80	100
7.	244	15	-	130	150
8.	244	30	-	110	100

* period and dimensions for agglomerated cones

Table 1
DIMENSIONS OF THE SURFACE CONE FORMATIONS AT TWO LASER FLUENCES AND DIFFERENT NUMBER OF PULSES

To explain the reaction mechanism between the excimer laser beam and polyimides, several theories have been introduced: the presence of particulate impurities, differences in the etch rates of crystalline and amorphous domains, stress release, surface scattered waves, photochemical bond breaking and thermal reaction [19-21]. It is generally agreed that the mechanism is mainly photothermal, with additional photochemical processes. Which one dominates depends on the laser-ablation fluence: at a low fluence, the photochemical mechanism dominates, while the photothermal one becomes significant at high fluence values. It is believed that in the case of the studied PI, the laser-induced periodic structures may be generated by the interference between the laser-induced surface electromagnetic waves and the incident laser beams or by the Fresnel diffraction in the laser beam causing intensity modulation of the transverse intensity profile, thus inducing distinct local heating of the surface.

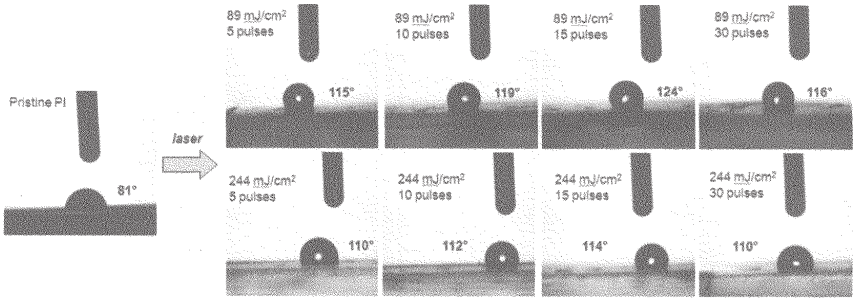

Fig. 7. Water contact angles on poly(BTDA- DDM) before and after laser treatment.

Surface wetting changes upon UV-laser exposure

The pulses laser micromachining of PI film affects not only the morphology, but also the chemistry of the surface as reflected in the changes recorded on the wettability. The contribution of chemical modifications to the wetting response of laser treated PI surfaces constitutes the subject of many papers [7,22,23]. An important characteristic of PI ablation is formation, within a certain fluence range, of a carbon-enriched layer on the irradiated film surface, the carbonized material being different from the material deposited in the surrounding ablation crater. The carbonization usually enhances the electrical conductivity. The carbonized material is formed from amorphous carbon and graphite derivates [24,25]. Also, it has been shown that UV laser pyrolysis of PI produced gaseous products such as carbon monoxide, carbon dioxide, methane and hydrogen cyanide, while thermal pyrolysis of PI only showed carbon monoxide and carbon dioxide. Therefore, the UV laser ablation is characterized by a different decomposition route compared to simple thermal pyrolysis.

Water contact angle values on untreated poly(BTDA-DDM) film and those treated with 5-30 pulses at 89 and 244 mJ/cm^2 are recorded. The projected image of a water droplet casted on a flat PI film surface, before and after laser treatment is shown in figure 7. It can be remarked that the initial hydrophobic character of the studied sample is intensified from 5 to 15 pulses as a result of the formation of carbon layer on the surface. Conversely, for both fluences at 30 laser pulses the value of the water contact angle decreases close to the value obtained for 5 pulses. This might be explained by the partial destruction of the carbon-enriched coating formed at the surface.

Conclusions

A photosensitive polyimide is prepared by polycondensation reaction of BTDA and DDM. Infrared spectroscopy confirms the fully transformation of PAA into the corresponding PI structure. The resulted PI film is processed by pulsed UV-laser micromachining at two fluences (89 and 244 mJ/cm^2) and different number of pulses.

The surface properties of the polymer before and after laser treatment are investigated by AFM and contact angle methods. Cone-like structural formations of different dimensions appear on the polymer surface for all applied laser exposure conditions. At 89 mJ/cm^2 the ordering tendency of the cones is observed, with a period of 200, 150, 260 for 5, 10 and 30 pulses, respectively. By increasing the fluency to 244 mJ/cm^2, the cones from the PI surface become more uniformly distributed and no packing or ordering is noticed.

The carbon condensation occurring during ablation of PI film at the applied fluences is useful for the production of vertical interconnections in high density printed circuit boards. Also, the oriented surface structuring obtained at 89 mJ/cm^2, 5 and 30 pulses, can be used as hydrophobic layers for guided cell growth in tissue engineering.

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