Gold coatings on polyethyleneterephthalate nano-patterned by F$_2$ laser irradiation

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Received 1 March 2007; received in revised form 15 November 2007; accepted 27 November 2007
Available online 3 December 2007

Abstract

In this work we present periodic surface structures generated by linearly polarized F$_2$ laser light (157 nm) on polyethyleneterephthalate (PET). Atomic force microscopy was used to study the topological changes induced by the laser irradiation. The laser irradiation induces the formation of periodic ripple structures with a width of ca 130 nm and a height of about 15 nm in the fluence range 3.80–4.70 mJ/cm$^2$ and the roughness of the polymer surface increases due to the presence of these periodic structures. Subsequently, the laser modified PET foils were coated with a 50 nm thick gold layer by sputtering. After Au deposition on the PET foils with ripple structure, the roughness of surface decreases in comparison to PET with ripples without Au coating. For 50 nm thick Au layers, the ripple structure is not directly transferred to the gold coating, but it has an obvious effect on the grain size of the coating. With considerably thinner Au layers, the ripple structures are smoothened but preserved.

Keywords: Polyethyleneterephthalate; F$_2$ laser; Polymer modification; Surface topology; Periodic surface structure; Sputtering

1. Introduction

Surface modification of polymers is an important application of laser radiation. Several studies have shown that the illumination of polymers by polarized UV-laser beam induces self-organized ripple structure formation within a narrow fluence range well below the ablation threshold [1–5]. The properties of these periodic structures have been frequently studied since the first report about them [6]. However, the ripples induced by 157 nm laser irradiation presented here are the smallest reported so far and no systematic investigations have been published on the structure-transfer of ripple nanopatterns into metal coatings.

The period of the ripples depends on the laser wavelength and on the angle of incidence of the radiation, and their direction is related to the direction of the laser beam polarization [7]. The spacing of the structures can be described by

$$\Lambda = \frac{\lambda}{n \sin(\theta)}$$

where $\Lambda$ is the spacing of the structures, $\lambda$ the wavelength of the excitation laser light, $n$ the effective refractive index of the material and $\theta$ is the angle of incidence of the laser beam [7].

These structures develop on the original material surface having a small roughness, as a result of treatment with one laser beam with an uniform intensity distribution. It is known that the interference between the incoming and the surface scattered waves plays an important role in the structure formation [8]. The interference causes an inhomogeneous intensity distribution, which together with a feedback mechanism results in the enhancement of the modulation depth [3]. However, the whole mechanism is complex and different processes have been reported as responsible for ripple formation [1,3,9,10] such as thermal and non-thermal scissoring of polymer chains, amorphization of crystalline domains, local surface melting, photooxidation and material transport. These ripple structures may be used to improve surface properties such as adhesion and friction [11,12], to attach and orient chemical and biological objects [13,14] or for liquid crystal alignment [15].

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Polyethyleneterephthalate (PET) is widely used due to its balanced thermomechanical and chemical resistant properties. Metallized polymers including PET are used extensively in magnetic recording media, microelectronics, photonic devices, medical implants and biosensors [16–18]. For many of these applications, the nano-patterned metal features are already frequently used or would open up new application fields. Examples are or could be small magnetic domains, quantum dots, photonic crystal structures or nano-engineered surfaces for enhanced biocompatibility.

Gold is an excellent candidate for metallization of electronic or photonic components, because of its resistance to electromigration, high electrical and thermal conductivity, high operation temperature and plating properties [19].

In this work we investigated the structure formation on PET induced by F2 laser irradiation and the changes in surface topology and roughness induced by the laser irradiation. The modified polymer was then coated with Au and we analyzed the surface topology with special emphasis to nano-patterns, i.e., ripple or grain formation and also the sheet resistance of the resulting Au layers. We compared the results obtained for pristine PET, pristine PET coated with Au, laser modified PET and laser modified PET coated with Au.

2. Experimental

2.1. Polymer modification

We performed experiments on oriented PET foils with a thickness of 50 μm ($T_m = 260 ^\circ C$, $T_g \approx 80 ^\circ C$, Goodfellow Ltd.). For modification of PET samples we employed a F2 laser (Lambda Physik LPF 202), that operates at a wavelength of 157 nm, with a pulse duration of 15 ns, and we applied a repetition rate of 5 Hz. We performed the irradiation at fluences well below the ablation threshold of PET ($29 \pm 6 $ mJ/cm$^2$ at 157 nm [20]). The light was polarized linearly with a Rochon prism and for the homogeneous illumination of the samples we used an aperture of 10 mm × 3.5 mm. The samples were mounted onto a translation stage and scanned at a speed of 6.25 μm/s and they were irradiated with 5600 pulses per area. We carried out the experiments in a flow box purged with nitrogen at a pressure of 110 kPa.

2.2. Gold deposition

We deposited Au layers from an Au target (99.999%) by means of a diode sputtering technique (BAL-TEC SCD 050 equipment) onto pristine and modified PET. The time elapsed between the laser modification of the polymer foils and the deposition of Au layers was several weeks. Typical parameters of sputtering were room deposition temperature, deposition time 300 s, total argon pressure of about 4 Pa, electrode distance of 50 mm and current of 20 mA. For thickness measurement, we deposited a Au layer under the same conditions on a Si(1 0 0) substrate.

2.3. Analytical methods

2.3.1. Surface topology

We examined the surface topology of pristine, irradiated (tapping mode) and metallized samples (contact mode) by AFM using MultiMode Digital Instruments NanoScopeTM Dimension IIIa set-up. By repeated measurements of the same region we certified that the surface topology did not change after five consecutive scans. The mean roughness value ($R_a$) represents the arithmetic average of the deviations from the centre plane of the sample.

2.3.2. Thickness measurements

We determined the thickness of Au layers on control Si substrate by investigation of scratches measured with AFM. We measured three scratches and we repeated the measurements five times on every sample. We obtained a value of 51.6 ± 0.5 nm for the Au layer thickness.

2.3.3. Sheet resistance

We examined the sheet resistance of Au layers by a two-point technique with a picoamperemeter KEITHLEY 487. The measurements were performed at a pressure of about 1 kPa.

3. Results

3.1. Polymer modification

Fig. 1 shows AFM pictures of laser modified PET for different values of the laser fluence. A change in the surface topology of modified PET is apparent between 2.80 and 3.80 mJ/cm$^2$. Laser irradiation induces the formation of ripple-like periodic structures on PET surface in a laser fluence range from 3.80 to 4.70 mJ/cm$^2$. The measured period of the structures is about 130 nm and as shown in Fig. 2, it does not depend on laser fluence. Fig. 2 also shows the height of the periodic structures as a function of the applied laser fluence. It can be observed that an increase of the laser fluence leads to a slight decrease in the height of the ripples.

3.2. Characterization of the gold layers

3.2.1. Surface topology and roughness

Fig. 3 shows the AFM images corresponding to the surface topology of laser modified PET and laser modified PET coated with Au layers. After coating with Au, the roughness of modified PET without periodic structures increases (Fig. 3A') in comparison to the uncoated polymer. In the case of PET with ripples (Fig. 3B), after Au deposition (Fig. 3B') roughness decreases. We evaluated surface roughness $R_a$ from the AFM data. In Fig. 4, we show the results as a function of the laser fluence. $R_a$ of pristine PET and pristine PET coated with Au are also shown for comparison. Laser modification of PET below a fluence of 3.60 mJ/cm$^2$ leads to a decrease of $R_a$. For laser fluences above 3.80 mJ/cm$^2$ for which ripple formation is observed (see Fig. 1), the value of $R_a$ increases sharply, due to the formation of these periodic structures. As mentioned above,
when these structures are coated with Au the value of $R_a$ decreases.

The 50 nm thick Au layers on flat PET and PET with ripples have comparable $R_a$ values (see Fig. 4), but there is an obvious change of the grain size as can be seen in Fig. 3. The grain size in Fig. 3A is approximately 50 nm, while the grain size in Fig. 3B is approximately 100 nm corresponding to the typical structure of the uncoated substrate in Fig. 3B. The grain size tends to increase with the laser fluence up to the values of Fig. 3B, while for higher fluences than about 3.8–4.0 mJ/cm² (corresponding to a more complete and regular filling of the area with the ripple pattern) the grain size decreases again. In this range the grains in some cases are oriented along the ripple direction. An example for this is shown in Fig. 3C.

3.2.2. Sheet resistance

We determined the sheet resistance of Au layers deposited on pristine PET and PET with ripples. Measurements were performed on four samples of each type and no significant differences were observed. The average value is $(22.2 \pm 0.8) \Omega$. From this value we conclude, that a continuous Au layer is formed in all the cases.

4. Discussion

The period of the ripples depends on the irradiation wavelength as described by Eq. (1). According to this and considering $\Lambda = 130$ nm, the effective refractive index is $n \approx 1.21$. This value is smaller than that of bulk PET.
However, this value was not derived for a light wavelength of 157 nm (but typically for the visible range where PET is transparent). Additionally, the surface degradation due to UV-laser irradiation may also lead to a change of the refractive index [21]. Some authors have introduced the idea of a selvedge region, a thin upper layer of the polymer where the refractive index is some type of average between the bulk index of the polymer and ca 1 (the index of the air) [22].

As we showed in Fig. 2, the periodicity of the ripples remains constant in the range of fluences at which these structures are formed, while its height slightly decreases when increasing the fluence. As proposed by other authors [23] ripple

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**Fig. 2.** Dependence of the width and the height of the ripple-like periodic structures formed on irradiated PET on laser fluence.

**Fig. 4.** Dependence of surface roughness ($R_a$) of laser modified PET and Au layer sputtered on laser modified PET on the laser fluence. $R_a$ of pristine PET and Au sputtered on pristine PET are also shown.

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**Fig. 3.** Surface topology of laser modified PET and modified PET coated with Au layer. The modification of PET was done with different laser fluences: 1.90 mJ/cm$^2$ (A), 3.80 mJ/cm$^2$ (B) and 4.70 mJ/cm$^2$ (C). The same samples with Au layers are (A'), (B') and (C'). $R_a$ is surface roughness in nm. The vertical scale is 50 nm.
The formation involves the melting of a thin layer of the polymer and the upper limit of the fluence region suitable for ripple generation corresponds to the value for which the depth of the molten layer reaches the modulation depth of the fully developed periodic surface structure. Then, the laser illumination removes all the modulation built up during the previous pulse. In the range of fluences presented in Fig. 2, we did not reach this upper limit, but probably the thickness of the layer that was affected by the laser irradiation increased with fluence, and this fact could be responsible for the lower height of the ripples that were formed.

In the results shown herein we observed that the values of \( R_a \) for the samples irradiated at fluences below 3.80 mJ/cm\(^2\) decreased slightly in comparison to the pristine PET. This effect could be explained as laser polishing as already observed in the irradiation with F\(_2\) laser of PTFE at low fluences [24]. This effect is attributed to the removal of scattering centres from the surface, probably based on a transient temperature rise of several hundred degrees at the irradiated area, accompanied by surface melting and surface decomposition. The mechanisms responsible for this polishing process have been described previously [7].

At the first glance, there seems to be a contradiction between the sharp increase of \( R_a \) at laser fluences above 3.80 mJ/cm\(^2\) due to ripple formation (Fig. 4) and the slight decrease of the ripple height with increasing fluence (Fig. 2). However, the increase of \( R_a \) can mainly be attributed to a more complete and regular filling of the whole area by the ripple pattern at higher fluences. In any case, the \( R_a \) value of an ideal sinusoidal pattern is not reached, which would be the (peak-valley) structure height multiplied by \( \pi/4 \).

The polymer foils modified by F\(_2\) laser irradiation were coated with 50 nm thick Au layers. As a result of the coating we observed a difference in the value of \( R_a \). While \( R_a \) increased in the case of Au deposited on pristine PET and modified PET without periodic structures (irradiated at low fluences), it decreased in the case of Au deposited on PET with surface ripples. One possible explanation for this effect is that Au was deposited preferentially in the valleys of the periodic structures. The formation of the Au layers takes place by clusters growth that finally form a continuous layer. Fig. 5 shows an AFM picture corresponding to PET with ripples coated with Au by sputtering during a time of 130 s. The thickness of this Au layer is approximately three times smaller than the typical thickness of the samples presented in this work. From this image it can be seen that ripples remain even if the thickness of the gold layer is comparable to the corresponding ripple height. This could indicate a difference in growth rates on convex and concave areas, as smoothing effect is more pronounced when the Au layer thickness increases. Also the changes in the grain size could be an effect of a different growth dynamics induced by substrate roughness.

Ongoing investigations study in detail the photo-induced changes of metal adhesion, mechanical properties of the polymers or chemical composition. In preliminary results, we see a decrease of the elastic modulus of Au coatings at PET foils with ripples compared to those at pristine PET. This could be a indication for an improved metal-polymer adhesion.

5. Conclusions

We investigated the periodic surface structure formation on PET, generated with linearly polarized F\(_2\) laser irradiation at fluences well below the ablation threshold of the polymer. To our knowledge, the ripples induced at 157 nm laser irradiation are the smallest reported so far. Pristine PET exhibits a value of \( R_a \) of 0.76 ± 0.07 nm. We have shown that irradiation of PET foils at fluences lower than 3.80 mJ/cm\(^2\) induces a polishing of the surface and the value of \( R_a \) decreases slightly. For a fluence range from 3.80 to 4.70 mJ/cm\(^2\), ripples are formed on the polymer surface. The periodicity of these ripples is 130 nm and their height is 10–20 nm. The value of \( R_a \) increased due to the presence of these structures, and at a fluence of 4.7 mJ/cm\(^2\) it reaches a value of 4.0 ± 0.4 nm. For 50 nm thick layers, the roughness of Au coated PET samples with ripples decreases when compared to the uncoated samples. The smoothing effect is probably due to a different growth rate on convex and concave areas. The grain structure of the Au is different for surfaces with different \( R_a \). For considerably thinner Au layers, the ripple pattern is preserved.

The current study on metal coatings on nano-structured polymers may be useful for further applications of these compound systems with nano-patterned metal layers.

Acknowledgements

This work was supported by the GA of the CR under the project KAN400480701, Ministry of Education of the CR under program LC 06041 and the project N102-NAN of the Austria Nano-Initiative.

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