Construction and Properties of Ripples on Polymers for Sensor Applications

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Surface modification of polystyrene and polyethylene naphthalate by a KrF pulse excimer UV laser under the angles of incidence of the laser beam in the range of 0 to 60° with a step of 7.5° was studied in this paper. The influence of the angle of incidence on the period of the resulting surface structures and the modified refractive index of the substrates was determined with all the other parameters of the laser radiation held constant. All data was acquired on the basis of surface analysis. Atomic force microscopy was used to study the morphological changes in the laser treated samples and to determine the period of the ripple-like surface structures, from which the modified refractive index was subsequently calculated. Selected samples were metallized with gold with aim to determine the influence of patterned substrate on consequently formed nanolayer. These information may be useful for consequently constructed SERS system based on ripple-metal system.

Keywords: Polystyrene, Polyethylene naphthalate, Laser treatment, Microscopy, Polymer, Periodic nanostructures

1 Introduction

Interactions between solid substances were determined by chemistry and morphology of their respective surfaces, both of which can be altered using a multitude of methods, such as chemical, plasma or laser treatment [1-3]. In applications where it's desirable to modify the properties of a substance's surface while leaving the bulk intact, excimer laser can be utilized as it affects only the top layers of the material due to its low penetration depth [4]. Such excimer laser surface treatment is used for microprocessing of various substrates (organic and inorganic) [5,6] and facilitating the metallization [7] of polymers as well as improving the adhesion of living cells to their surface [8], thus allowing for a wide range of applications in medical engineering [9,10].

Laser-induced periodic surface structures (LIPSS) can be divided into two categories, depending on the relation between their period and the wavelength of the laser beam. Low spatial frequency LIPSS (LSFL) [11] have a period comparable with the wavelength of the laser beam and are, in the form of ripples oriented along the main axis of polarization of the laser beam [12], most commonly found in laser treated polymer substrates, while high spatial frequency LIPSS (HSFL) [13] have a period noticeably smaller than the wavelength of the laser beam. Assuming the conditions for the formations of the low spatial frequency ripples are met on a polymer substrate, their period is a function of wavelength λ, modified refractive index n and the angle of incidence θ according to equation (eq. 1):

$$\Lambda = \frac{\lambda}{n - \sin\theta} \tag{1}$$

which was the first used to qualitatively describe the dimensions of ripples formed on PET [14]. The laser-induced LSFL have been created on a variety of polymers, including, but not limited to polyethylene terephthalate (PET), polyethylene naphthalate (PEN) or polystyrene (PS) [15] and have shown promising possibilities in various technological applications.

Periodic surface pattern on polymers with/without metal nanostructures or nanolayer can be used for various types of sensor construction. The development of new fast analytical methods able to detect the disease or infection markers represents one of the more actual issues in the field of tissue engineering and medicine, the applications of periodic nanowires not limited only to polymer substrate [16-23]. Interesting new strategies of construction of sensing devices that can perform the analytical procedure in a label free manner were introduced recently [24] This problematics is very important in the medical field, and also actual in the food safety, where the standard procedures rely on chromatographic approaches which are extremely sensitive [25]. Raman spectroscopy can be considered as technique which provides detailed information on the chemical composition of biomolecules, cells and moreover, tissue, at the molecular level, thus considered very promising clinical and outdoor tool for medical diagnostics [26]. However, the Raman effect is particularly weak, significant enhancements of some Raman scattering process can be realized through the implementation of so-called surface-enhanced Raman scattering (SERS) [7]. The physical background of SERS excitation can be described by photon-plasmon conversion phenomena, which leads to the high focused of light energy near the surface of noble metal nanostructures, metal nanostructures which are actually employed both for diagnostic and treatment purposes [27]. One of the most advantages of SERS based sensor is its very high sensitivity, which enables to detect extremely low levels of analyte [28]. Polymer foils treated with an excimer laser also allows the construction of simple sensor arrays based on immobilization of biotin on the surface [29], which can be further developed into optical affinity-based bioanalytical microsystem, with capability to construct the micropattern functional biosensing layers on the surface of

PEN foil in a fast and easy way and thus brings all necessary aspects for continuous roll-to-roll fabrication of low-cost optical bioanalytical devices [30].

In this work, polystyrene and polyethylene naphthalate foils were treated under the angles of incidence of 0 - 60°, with a step of 7.5°, by KrF excimer laser for the duration of 6000 pulses with laser fluence 10 mJ·cm^{-2}. Surface morphology of the laser treated samples was examined by atomic force microscopy. On the basis of the collected data, the modified refractive indexes of polymer foils were calculated. Selected samples were metallized with gold nanolayers and their morphologies were studied.

2 Materials and methods

Biaxially oriented foils of PS (1.05 g·cm^{-3}, thickness of 0.05 mm, T_m ~ 240°C, T_g ~ 100°C) and biaxially oriented foils of PEN (1.36 g·cm^{-3}, thickness of 0.05 mm, T_m ~ 250-290°C, T_g ~ 120°C), both supplied by Goodfellow Ltd., UK, were used.

Samples were treated by a KrF excimer pulse UV laser (Lambda Physik Complex Pro 50, wavelength of 248 nm, frequency of 10 Hz) for the duration of 6000 pulses under the angles of incidence of 0 - 60°, with a step of 7.5°, with laser fluence of 10 mJ·cm^{-2}.

Surface roughness and the dimensions of the ripple-like structures were measured by atomic force microscopy (AFM) in a tapping mode. The AFM images were taken under ambient conditions on a Digital Instruments CP II set-up.

The gold layers on pristine and excimer laser treated PEN were deposited from a gold target (99.999 %) by means of diode sputtering technique (BAL-TEC SCD 050 equipment). Typical sputtering conditions were: room temperature, time 300 s, total argon pressure of about 5 Pa, electrode distance of 50 mm, current of 40 mA. For the measurement of the layer thickness gold layer was deposited under the same conditions on a Si substrate. The gold layer thickness was determined from scratches measured with AFM. Typically 5 measurements on 3 scratches each was accomplished on each sample. The thickness of the gold layer sputtered under above this conditions was about 100 nm.

SEM images and FIB (focused ion beam) cuts were prepared with an adapted scanning electron microscope (FIB-SEM, LYRA3 GMU, Tescan, Czech Republic). The FIB cuts were made with a Ga ion beam. The polishing procedure was performed to clean and flatten the investigated surfaces. The FIB-SEM images were taken under an angle of 54.8°.

3 Results and discussion

Laser treatment of appropriate polymer substrates under optimal conditions leads to the formation of periodic surface structures in the form of ripples. The period of these ripples increases with an increasing angle of incidence of the laser beam, according to equation (1). For equation (1) to give satisfying results at all angles of incidence, however, the modified refractive index n itself has to be a function of the angle of incidence. This is entirely possible since the modified refractive index has been argued to be dependent on both the refractive index of the polymer and the refractive index of the surrounding atmosphere. The refractive index of polymer is a material property and depends on its physical-chemical properties, which change during the laser treatment.

In this paper, we modified two polymer substrates, PEN and PS, under a wide range of angles of incidence, and, using the equation obtained from eq. 1, calculated the modified refractive index as a function of the angle of incidence from experimentally obtained periods of the laser induced surface structures.

$$\boldsymbol{n} = \frac{\boldsymbol{\lambda}}{\Lambda} + \mathbf{sin}\boldsymbol{\theta} \qquad (2)$$

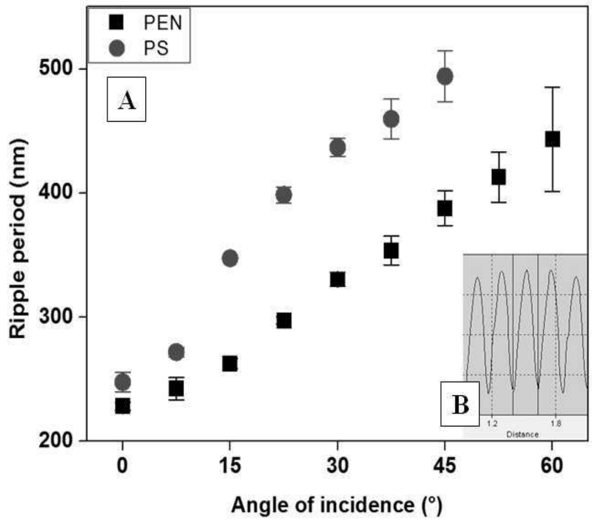

Fig. 1 *A dependence of the ripple period of PEN and PS on the angle of incidence of the KrF laser beam (A) and cutout from a screenshot of the SPMLabs program, depicting the process of the ripple period measurement (B).*

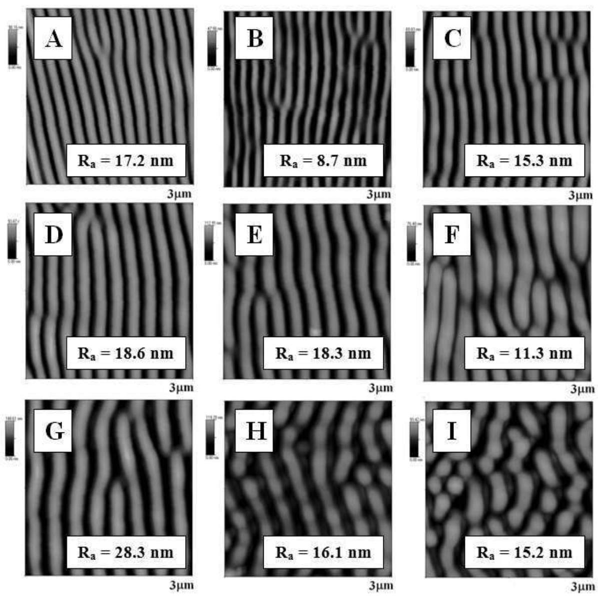

Fig. 2 *Surface scans of PEN treated by laser fluence of 10 mJ.cm^{-2} for the duration of 6000 pulses under the angles of incidence: 0° (A), 7.5° (B), 15° (C), 22.5° (D), 30° (E), 37.5° (F), 45° (G), 52.5° (H) and 60° (I).*

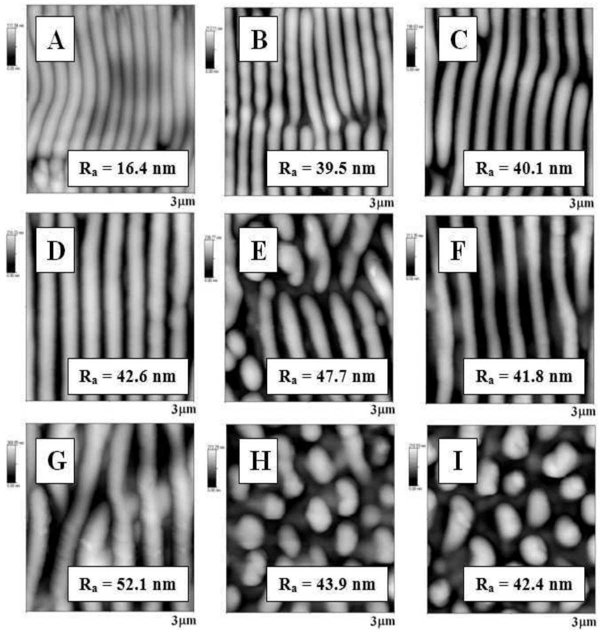

Fig. 3 *Surface scans of PS treated by laser fluence of 10 mJ.cm^{-2} for the duration of 6000 pulses under the angles of incidence: 0° (A), 7.5° (B), 15° (C), 22.5° (D), 30° (E), 37.5° (F), 45° (G), 52.5° (H) and 60° (I).*

Scans of laser-treated samples obtained by AFM show that not only does the period of ripples (Fig. 1) increase with an increasing angle of incidence as expected; their homogeneity suffers as a result as well. While the disintegration of a homogenous ripple pattern becomes prominent at the two highest angles (52.5 and 60°) for both PEN (Fig. 2) and PS (Fig. 3), the ripple pattern formed on PEN doesn't crumble completely, allowing the period measurement to take place even on these samples with low homogeneity. The ripple pattern on PS, unfortunately, disintegrates completely at the highest angles, and proper measurements of the ripple period cannot be obtained from these two samples.

Experimental data shows that both polymers exhibit a dependence of the ripple period on the angle of incidence that is linear in nature (PEN more so than PS), while a constant n in eq. 1 would result in an exponential one. The standard deviation of the period increases greatly for samples treated under higher angles of incidence due to the above mentioned disintegration of the homogenous ripple pattern.

The dependence of the modified refractive index on the angle of incidence calculated according to eq. 2 is shown in Fig. 4. The modified refractive index increases with increasing angle of incidence for both PEN and PS. While the modified refractive index of PEN exhibits a linear dependence on the angle of incidence, the modified refractive index of PS exhibits a polynomial one, due to ripples with unexpectedly large period being formed in the 15 - 30° range of the angles of incidence. Unfortunately, since the ripple structure disintegrates at the highest angles of incidence on PS samples, no period measurements were made and thus no modified refractive index could be calculated for these angles.

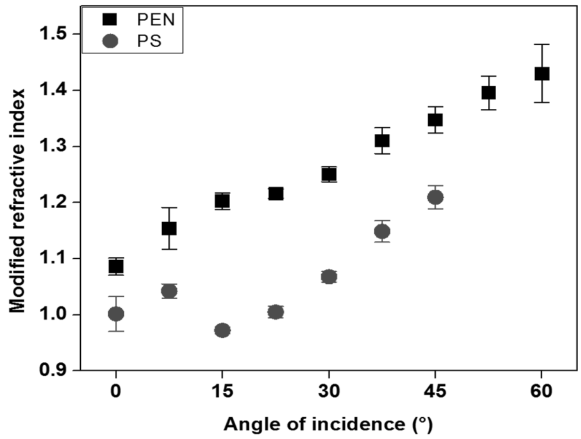

Fig. 4 *A dependence of the modified refractive index of PEN and PS on the angle of incidence of the KrF laser beam.*

The difference in surface morphology for the same laser fluence, but different number of laser pulses is well documented in Figs. 5A, B. If we analyze the influence of number of laser pulses, we can conclude that at 1000 pulses the periodic structures did not appear on PEN surface (Fig. 5A). With an increasing number of laser pulses the periodic ripple pattern appears, maximum periodicity of ripple pattern was achieved at 6000 pulses (Fig. 5B). These results were used as an input parameter for construction of gold nanolayers on treated PEN substrates. PEN foils with the most pronounced changes in surface pattern parameters (height of ripples and surface roughness) modified with 10 mJ·cm^{-2} and 6000 pulses were consequently sputtered with 100 nm Au layer and this sample with nanopatterned PEN surface was evaluated by FIB-SEM analysis (Figs. 5C, D). It was found, that the sputtering leads to the formation of wires on the patterned surface, which are electrically connected, and are similar to that pattern prepared with laser treatment.

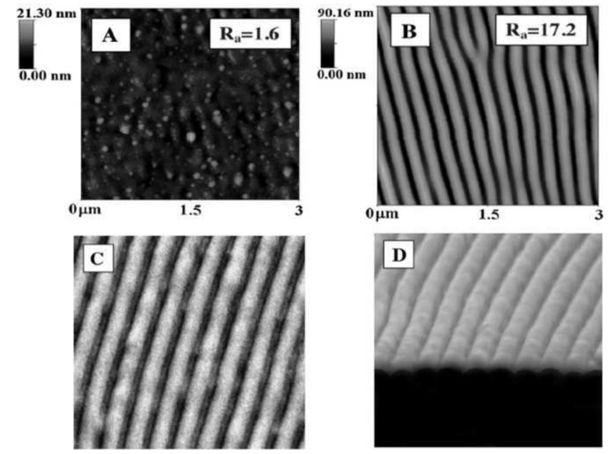

Fig. 5 *Detail of surface morphology (2D, 3x3 μm^2) of PEN treated with 10 mJ cm^{-2} and number of pulses 1000 (A) and 6000 (B). R_a represents average surface roughness in nm. 2D SEM image detail of PEN treated with 10 mJ·cm^{-2} and 6000 pulses metallized with 100 nm Au (C, 2x2 μm^2) and the detailed FIB-CUT of this sample (D, 2x2 μm^2).*

4 Conclusions

We assume that eq. 1 holds true for all polymer materials and all angles of incidence when nanopatterning a surface by UV excimer laser. Experimental data then suggests that increasing the angle of incidence of the laser beam increases not only the period of the resulting surface structures, but must also necessarily increase the modified refractive index of the polymer substrate. While the period of the surface structures exhibits a linear increase with an increasing angle of incidence (more so in the case of PEN than PS), the modified refractive index increases in a linear fashion for PEN and in a polynomial one for PS, due large period of ripples measured on PS samples treated under the angles of incidence of 15, 22.5 and 30°. The homogeneity of the ripple pattern generally suffers with an increasing angle of incidence, and at the highest angles of incidence (52.5 and 60°), the ripple pattern starts becoming fragmented on PEN and deteriorates completely on PS. We have also found that the sputtering onto PEN substrate with periodic pattern leads to the formation of nanowires, which are electrically connected, and are excellently similar to the substrate pattern prepared with an excimer laser. We believe that the major impact of this paper is in the detailed calculation of the modified refractive index from empirically obtained data, which could be of great benefit for all those involved in laser induced periodic surface structure preparation (LIPSS) and so far has never been realized, to our best knowledge.

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