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Nanowires and nanodots prepared with polarized KrF laser on polyethersulphone

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ABSTRACT

In this paper, we describe laser modification of polyethersulphone films treated with polarized KrF laser under ablation threshold of PES. By this procedure the polymer can be modified under mild conditions and with low laser fluencies. Creation of surface ordered structure was observed already after application of 8 mJ cm^{-2}. Optimal conditions for nanodots and ripples formation were determined. Mechanism of surface ordered structure formation is attributed to enhancement of laser intensity due to propagation of surface waves which interfere with incoming beam. The wettability measurement confirmed increasing trend of surface contact angle with laser fluence. The threshold of laser fluence for morphology collapse was identified to be 20 mJ cm^{-2}. The metal nanolayer of 100 nm consequently deposited of the surface pattern proved to copy and enhance the morphological properties (ripple and dot formation).

1. Introduction

Formation of surface structures with high degree of periodicity has significant technological importance, since it can provide better control of material properties. Regular periodic nanostructures can be constructed by UV radiation caused by excimer lamps, plasma discharge, laser beam radiation, or by ion-beam sputtering [1,2]. The most common periodical nanostructures gained by self-organization are ripples and dots. Nanostructured materials find important place in production of biomedical surfaces [3] or they can be easily metallized, because the pattern has a positive influence on adhesion [4]. These regular patterns find application in electronics for the manufacturing of microchips and memory devices [5], or they are useful in development of biosensors for detection and therapy of various diseases.

An assumption for the creation self-organized periodic structures by laser is use of material with strong absorption coefficient [6]. For generation of periodic structures the laser radiation has to be fully plane-polarized; and the fluence has to be large enough to cause surface melting, but it has to be below the ablation threshold for every particular polymer [7,8]. The periodicity of the surface pattern can be changed by radiation under the different angle [8]. The strong absorption coefficient of polymer allow to prepare the periodic pattern also on other types of polymer, such as polyethyleneterephthalate (PET) [9–11], polyethylenenaphthalate (PEN) [12,13] or polystyrene (PS) [14], which allows also to prepare metal nanowires or other structures on treated surfaces.

The ripple pattern arises from the laser beam interference at the surface and the subsequent surface response [6]. The dot pattern was created by Sendova and Hiraoka on PET substrate by two laser beams which were split with orthogonal polarization planes and the polymer surface was irradiated by the splitted beams at the same time (using same laser setting as for ripples formation) [7]. They explained dot array as a result of the superposition of two separate ripple patterns. It was found out the dots patterns can be created by the sample rotation and the positive effect on formation has a presence of surface impurities [1].

In this paper we present technique which allows to change the polymer surface pattern from ripples to nanodots by simple control of polarized excimer fluence without rotation of sample or source or any additive processing steps. We used polyethersulphone (PES) which is thermally and chemically resistant polymer with dimensional stability. Well known are PES membranes, which are widely used in separation (microfiltration and ultra filtration) [15,16]. They are employed in water purification [17] and as an important tool in biomedicine or for hemodialyses [18] or plasma separation [19].

2. Experimental

Materials and modification: As a substrate we used polymer polyethersulphone (PES, density 1.37 g cm^{-3}, 50 µm thick foils)

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supplied by Goodfellow Ltd., Cambridge, Great Britain. For modification we used a KrF excimer laser (Coherent Complex Pro 50 wavelength of 248 nm, pulse duration of 20–40 ns, repetition rate 10 Hz). The beam of KrF laser was polarized linearly with cube of UV grade fused silica $25 \times 25 \times 25$ mm^3 with active polarization layer. For homogeneous illumination of the samples we used only the central part of the beam by means of an aperture (0.5×1.0 cm^2). The samples were mounted onto a translation stage at perpendicular position of the sample and laser beam. We used 6000 pulses with laser fluences in interval 4–30 mJ cm^{-2}.

Measurement techniques: Surface morphology and roughness of the pristine and modified polymer samples were examined by the atomic force microscopy (AFM) technique using a VEECO CP II device in tapping mode. A Si probe RTESPA-CP with the spring constant 20–80 N m^{-1} was used. The mean roughness values (R_a) and (RMS) represents the arithmetic and root mean square average of the deviations from the centre plane of the sample.

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 FIB–SEM images were taken under an angle of 54.8°.

Contact angle was determined by goniometry with static water drop method. The measurements of water contact angles were performed using distilled water (6 different positions) using the Surface Energy Evaluation System (SEE System, Advex Instruments, Czech Republic).

3. Results and discussion

We studied interaction of PES with KrF laser beam especially from the morphologic point of view for the laser fluences below the ablation threshold of PES for $\lambda = 248$ nm at relatively low laser fluences. Different thickness of PES in comparison to that published previously in [20,21] was used. Non-modified substrate has flat surface without any special structures (Fig. 1A), but excimer laser modification has caused significant changes, which depend especially on used laser fluence. The most interesting part of this work was creation of two different regular patterns, ripples and dots. The most regular ripple formation we have achieved at laser fluence 8 mJ cm^{-2} (Fig. 1B) and dot structure at 16 mJ cm^{-2} (Fig. 1C), while number of pulses (6000) and other settings were identical. In the interval of fluence between 8 and 16 mJ cm^{-2} we observed transition from ripples to dots (gradual "destruction" of ripple pattern). When we decreased the laser fluence (to 4 mJ cm^{-2}), we have received slightly more roughen surface than pristine with random granular structure. By further increasing laser fluence (20 mJ cm^{-2}), the regular pattern of dots has collapsed while the roughness rapidly increased (Fig. 1D). The surface properties changes connected to local surface melting and gradient of surface heat and thus mass flow described in [6] depend also on the polymer foil thickness, which can significantly influence the processes of mass re-distribution. The whole mechanism of pattern formation is complex and different processes have been reported as responsible for ripple formation arising from the beam interference on polymer surface, such as thermal and non-thermal

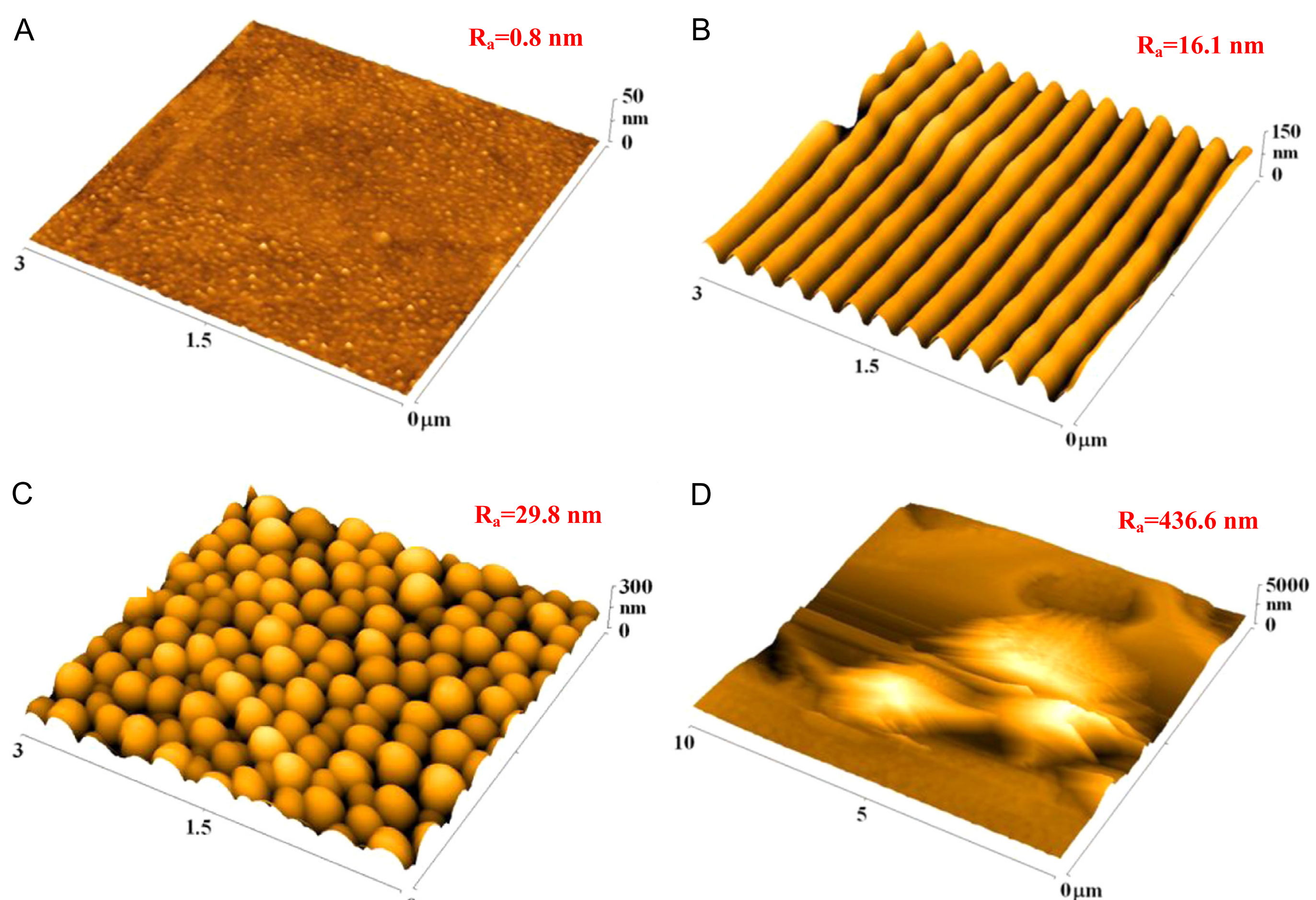

Fig. 1. The surface morphology of PES: pristine (A), and samples treated by KrF laser beam with 6000 pulses and different laser fluence—8 mJ cm^{-2} (B), 16 mJ cm^{-2} (C), and 20 mJ cm^{-2} (D). R_a represents arithmetic mean surface roughness in nm.