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Laser induced nanostructures created from Au layer on polyhydroxybutyrate

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Abstract. Nanostructures as well as composite materials expand the range of materials properties and allow use of these materials in new and highly specific applications. In this paper, we described laser modification of polyhydroxybutyrate films covered with thin gold layer, which led to the formation of various composite structures. The crucial for the composite structures creation was setting of appropriate laser parameters; 15 mJ cm\textsuperscript{-2} laser fluence and 6 000 pulses were recognized as the best. The morphology of structures was determined by the thickness of the Au layer. The most interesting formations, very porous with the biggest roughness, were observed after treatment of foils covered with 10 nm of Au. The morphology was observed by atomic force microscopy. The influence on roughness and the difference between projected area and surface area was also determined.

1. Introduction

Spontaneous formation of complex structures offers an interesting alternative for the preparation of surfaces with specific properties. The structures formed by self-organization currently have a wide variety of uses, e.g. optical devices [1], the flexible electronics [2] systems for separating particles [3].

One of the self-organizing mechanisms is wrinkling instability. By this bottom-up method it is possible to prepare various surface structures with patterns in a wide range of length scales. Wrinkles are characterized as smooth and shallow surface undulations as a result of the uneven expansion of a surface consisting of materials with different mechanical properties [4]. The wrinkles occur, when the residual stresses exceed a critical value [4], which can be induced by heating [5], solvent swelling [6], mechanical stretching or compression [3] and others. The effect of wrinkling on a thin bi-layer film (polymeric film metalized with a noble metal) was described in the works [7, 8].

Polyhydroxybutyrate (PHB) is an interesting biocompatible and biodegradable polymer, which can be synthesized by bacterial fermentation. PHB is frequently used in medical and pharmaceutical applications as a material for implants, scaffolds or drug delivery systems [9]. To improve processability, PHB is frequently produced in copolymer form with polyhydroxyvalerate (PHV), because the homopolymers of PHB are very fragile and crystalline [10]. Further development of this promising substrate can broaden its applications and eliminate disadvantages of the material.

This paper deals with surface modification of biopolymer foil of polyhydroxybutyrate covered with thin Au layer and treated by excimer laser beam. Observation of such treated samples showed various patterns depending on the Au layer thickness. The surface morphology of these structures was investigated by AFM.
2. Material and Methods

2.1. Materials and modification

For experiments we used biopolymer foils of polyhydroxybutyrate (PHB, with 8% polyhydroxyvalerate) supplied by Goodfellow Ltd., Cambridge, Great Britain (density 1.25 g cm$^{-3}$, 50 µm thick foils).

Gold layers were deposited on the foils from Au target (99.999 %) by diode sputtering technique (BAL-TEC SCD 050 equipment, Switzerland) [11]. Typical sputtering conditions were: room temperature, sputtering times 20, 50, 100 and 280 s to achieve the layers of 5, 10, 20 and 50 nm, argon (purity 99.997 %) pressure of about 5 Pa, electrode distance of 50 mm, and electric current of 20 mA [11].

For modification of the foils covered with Au layer and also the pristine polymer foils we employed a KrF excimer laser (Coherent Compex 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 25×25×25 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. [12-14] We used 6000 pulses with laser fluences in interval 5–30 mJ cm$^{-2}$, but the most interesting laser fluence for experiments was 15 mJ cm$^{-2}$. Figure 1 shows the scheme of modification, where the polymer substrate is first of all sputtered with gold and then the bilayer substrate is modified by excimer laser beam.

2.2. Characterization techniques

As the main method for surface morphology and roughness examination, of the pristine and modified PHB foils, we used atomic force microscopy (AFM) (instrument VEECO CP II in tapping mode and a Si probe RTESPA-CP with the spring constant 20–80 N m$^{-1}$) [12, 13].

The mean roughness values ($R_a$) and ($RMS$) represent the arithmetic and root mean square average of the deviations from the centre plane of the sample. The both roughness values were calculated by software SPMLab.

The mean roughness values ($R_a$) represents the average of the deviations from the centre plane of the sample. The $R_a$ determination is constructed from the matrix 512 × 512 points, the equation is

$$R_a = \frac{\sum_{i=1}^{N} |Z_i - Z_{cp}|}{N}$$  \hspace{1cm} (1)

where $Z_{cp}$ is the value of the central plane, $Z_i$ is the actual $Z$ value, and $N$ is the number of points, where the $Z_i$ is evaluated. The room mean square ($RMS$) is calculated from the formula...
\[ RMS = \left( \frac{\sum_{i=1}^{N} (Z_i - Z_{ave})^2}{N} \right)^{\frac{1}{2}} \]  

where \( Z_{ave} \) is the average value \( Z \) of measured area, \( Z_i \) is the actual \( Z \) value, and \( N \) is the number of points, where the \( Z_i \) is evaluated.

3. Results and discussion

The laser treatment of polymer foils covered by metal layer can have three types of effect: (1) mirror effect or reflection, (2) structures creation and (3) ablation effect. Figure 1. shows the scheme of modification, where the polymer substrate is first of all sputtered with gold and then the bilayer substrate is modified by excimer laser beam. Modification causes the effect mentioned above or their combination, because the combination of these effects is also possible.

The mirror effect occurs if the metal does not absorb laser radiation. In this case the incident beam is reflected from the surface without causing changes of the substrate. We observed the reflection when the applied laser fluence was too low. When the laser fluence is above the ablation threshold of used metal layer, the surface material is sputtered out and the ablation occurs. There is also the possibility that laser beam radiation induces a reaction of metal with polymer and this creates structured composite material. What effects, structures or results are obtained depends not only on the metal composition and the thickness of the layer, but also on the polymer substrate.

The PHB substrates were deposited with Au layer of thicknesses 5, 10, 20 and 50 nm. How the thickness of Au layer affected the composite structure is evident from Figure 2. The pristine PHB obtained from a supplier exhibits specific hilly structure with fibrous surface, which disappear after the Au overlay. Gold surfaces seemed flat and high resolution allowed observing Au clusters. The modification of pristine polymer (without metal layer) by laser treatment led to obliteration of fibrous surface and creation of cracks in the material.

![Figure 2](image-url)
Conversely, the modification of bilayer substrate caused composite structures according to the thickness of the Au layer. The thinnest layer (5 nm) formed in combination with the polymer goblet structures on the surface. With increasing thickness of the Au layer (10 nm), the spongy or lamellar structure was created. Even higher thickening of Au layer (20 nm or more) led to wrinkle-like structure.

At lower laser fluencies, no modification of the surface was observed and the morphology corresponded to the surface morphology before laser treatment. Conversely, at high laser fluencies, the gold layer was ablated without interconnection of materials.

From the Figure 2., it is evident that the structures differ also in roughness, because of that the separate charts of $R_a$ and $RMS$ roughness are included in the Figure 3. As suspected, the trend $RMS$ follows the trend of $R_a$. Without a doubt, the highest value of roughness ($R_a = 149$ nm or $RMS = 180$ nm) belongs to lamellar structure created from Au layer of 10 nm thickness. Other laser modifications significantly differed in morphology, but the roughness remained similar for all other modifications. For laser non-modified samples was roughness quite identical and lower than in case of laser modified substrates. Only sample without gold layer was slightly rougher because sputtered Au caused slight surface leveling.

**Figure 3 (a, b).** The roughness (a) $R_a$ and (b) $RMS$ of PHB covered with different thickness of Au layer for non-treated samples and samples modified by excimer laser (15 mJ cm$^{-2}$ and 6 000 pulses).

**Figure 4.** The surface area of modified PHB (laser treatment: 15 mJ cm$^{-2}$ and 6 000 pulses) depending on the thickness of Au layer. Projected area of each sample was 100 $\mu$m$^2$. 
The surface area documented in Figure 4. naturally corresponded with the trend of roughness. Also in this case the biggest value of surface area was measured and calculated for the lamellar structure (116 $\mu$m$^2$). The surface area was calculated from the projected area 100 $\mu$m$^2$.

4. Conclusion

The laser treatment of polyhydroxybutyrate substrate covered with Au layer of different thickness was confirmed to be a successful tool for production variously structured composite material. The laser treatment of polymer foils covered by metal layer may have in addition to structuring effect also the ablation or reflection effect. The highlights in morphology was achieved by laser modification (by laser fluence 15 mJ cm$^{-2}$ and 6 000 pulses) of PHB covered by 10 nm Au. The gained structure had laminar or spongy character with significant roughness. Also modification with other Au thickness were interesting and caused formation of goblet structure (for 5 nm Au) or wrinkle-like structure (20 nm or more).

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