PREPARATION OF COMPOSITE PERIODIC METAL-POLYMER NANOSTRUCTURES

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Abstract

This paper investigates the preparation of composite metal-polymer nanostructures formed on the surface of polyethersulfone (PES) by an excimer laser beam. Conditions for laser beam modification varied with the laser fluence of 4-28 mJ·cm^{-2} and number of pulses up to 6000. The samples were further deposited with a layer of metals Ag, Au, Pd and Pt with a thickness of 5-20 nm and their surface morphology was examined by atomic force microscopy (AFM). Electrical properties of layers were also investigated and for optical properties UV-Vis spectroscopy was used. Composites prepared by this approach were studied further for stability under laser modification. Surface morphology measurement revealed creation of laser induced periodic surface structures (LIPSS) in forms of nanoripples after modification with laser fluence value of 8 mJ·cm^{-2} and nanodots after modification with laser fluence value of 16 mJ·cm^{-2}. It has been found that metal layer deposition of the surface leads to formation of isolated clusters. Those metallized with the treatment of laser fluence 8 mJ·cm^{-2}, preferably aggregated on the ridge of the ripples and their electrical continuity was further examined. The nanostructured surfaces may be used as antibacterial material, also with potential to guide the specific types of cells, such are e.g. osteoblasts.

Keywords: Excimer laser, polymer, surface morphology, nanostructure, composite

1. INTRODUCTION

Nanostructuring of the surface brings a number of advantages and new material properties for the material under investigation. The process is based on the preparation of shapes of various patterns in the nanometer scale on a homogeneous surface of functional polymeric materials, which gives to the material modified physical and chemical properties [1]. Such an example of change in properties may be surface treatment associated with increased roughness. That also leads to an increase in reactivity of the material. Surface properties therefore play a significant role in interacting with other substrates, especially in the preparation of the metal-polymer composite material [2].

A suitable alternative for forming nanostructures on the polymer surface is excimer laser exposure. This technique provides the advantage that the morphology of the surface or chemical composition in the surface layer can be altered without changing the properties of the bulk material. Laser-induced Periodic Surface Structure (LIPSS) arises from a surface treatment technique that is governed by laser parameters such as wavelength, fluence, beam intensity, duration, and other radiation conditions [3-5]. The scientific goal of this paper is to introduce a simple method, how to prepare composite material merging both conductive and polymeric properties.

2. EXPERIMENTAL

2.1. Material and modification

For experiments we used polymer foils of polyethersulfone (PES, thickness 50 µm, density 1.37 g cm^{-3}, glass transition temperature T_g 226 °C) supplied by Goodfellow Ltd., Cambridge, Great Britain. The polymer was modified with a 248 nm laser beam using the Compex Pro50 excimer pulse KrF laser with the NovaTube. The value of laser fluence was set at 4-16 mJ·cm^{-2} with an attenuator, and the optical path of the beam was adjusted by dielectric mirrors from SiO_2 for combined reflection 248/633 nm. The modification time was determined by the number of pulses 1000-6000 at a frequency of 10 Hz. For the treatment of the laser beam, a 25x25x25 mm^3 prism polarizer was used with a polarizing layer and a polarizing circular Eksma Optics with a diameter of 25.4 mm. Subsequently, the beam passed through a metal aperture, which bounded the modification area to an area of 0.5 cm^2.

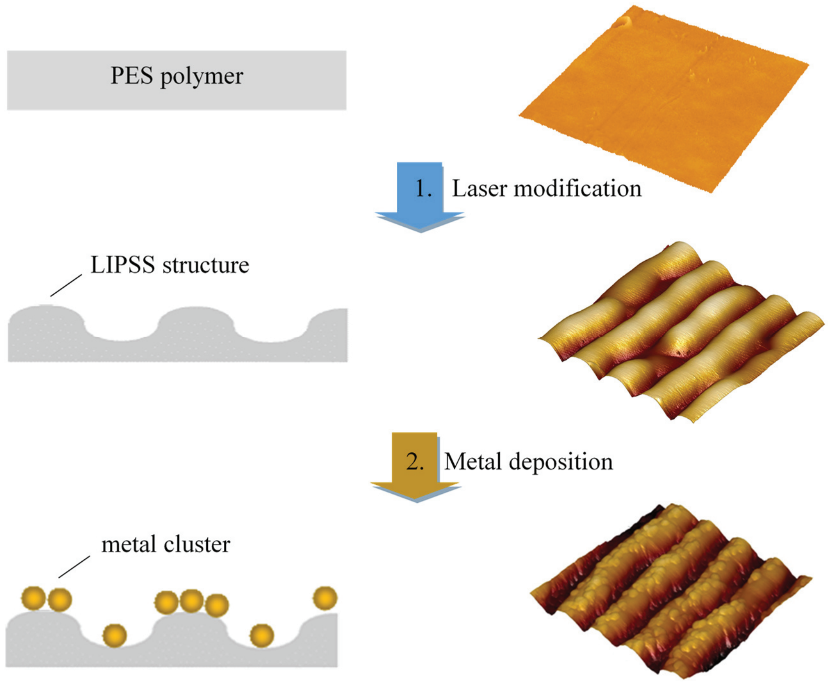

Figure 1 Schema of the preparation of metal-polymer nanostructures

2.2. Characterization techniques

To study morphology, a Dimension ICON (Bruker Corp., US) atomic force microscope was used in ScanAsyst mode. The silicon tip is mounted on a SCANASYST-AIR nitride lever with a spring constant of 0.4 N.m^{-1}. The NanoScope Analysis application was used to process the data, and the average roughness values (Ra) represent the mean of the deviations from the center plane of the sample. The image sizes ranged from 300x300 nm^2 to 10x10 μm^2.

Sheet electrical resistance of the samples was determined by a two-point method using KEITHLEY 487 picoammeter. For this measurement additional Au contacts, about 50 nm thick, were prepared by sputtering. The electrical measurements were performed at a pressure of about 10 Pa in a shielded chamber to minimize influence of atmospheric humidity and stray current. The UV-Vis spectra were measured using a PerkinElmer Lambda 25 spectrometer in the spectral range from 225 to 400 nm. The applicable range is 190-1100 nm with bandwidth of 1 nm (fixed).

3. RESULTS AND DISCUSSION

Substrates after modification with 6000 pulses and the linearly polarized laser beam at laser fluence 8 mJ·cm^{-2} showed the formation of a regular ripple nanostructure. However, the choice of a higher modifying fluence of 16 mJ·cm^{-2} led to formation of the regular nanodots structure and the substrates exhibited a lower surface roughness. After laser modification, samples were deposited with thickness of 5, 10 and 15 nm of Ag layer. The effect of the laser fluence and the thickness of the metal layer on the surface structure was studied.

3.1. Surface morphology and roughness

AFM images of sputtered nanostructures with metal nanolayers showed their similar surface morphology, but the most significant changes in surface roughness were achieved with the silver layers after modification by laser fluence of 8 mJ·cm^{-2}. In all the images, it was evident that metal sputtering did not result in the formation of a layer electrically continuous which would cover the surface of the polymer. The cluster formations of silver atoms, which has predominantly grown on the ridge of the ripples, were formed (**Figures 2A, 2B**). Longer metal deposition time caused cluster to grow, but there was still a significant ripple-like structure typical of the laser fluence value of 8 mJ·cm^{-2} and thus the prevailing influence of polymer on surface morphology. The surface roughness of the sample was 39 nm (**Figure 2A**).

Images of samples irradiated with laser fluence of 16 mJ·cm^{-2} had typical globular structure on the surface (**Figures 2C-D**). Metal sputtering in this case smoothens the surface, as metal clusters preferably fill the deepened formations in the polymer. The 15 nm layer thus appears to be completely planar and also exhibits the lowest surface roughness Ra = 2.5 nm (**Figure 2C**).

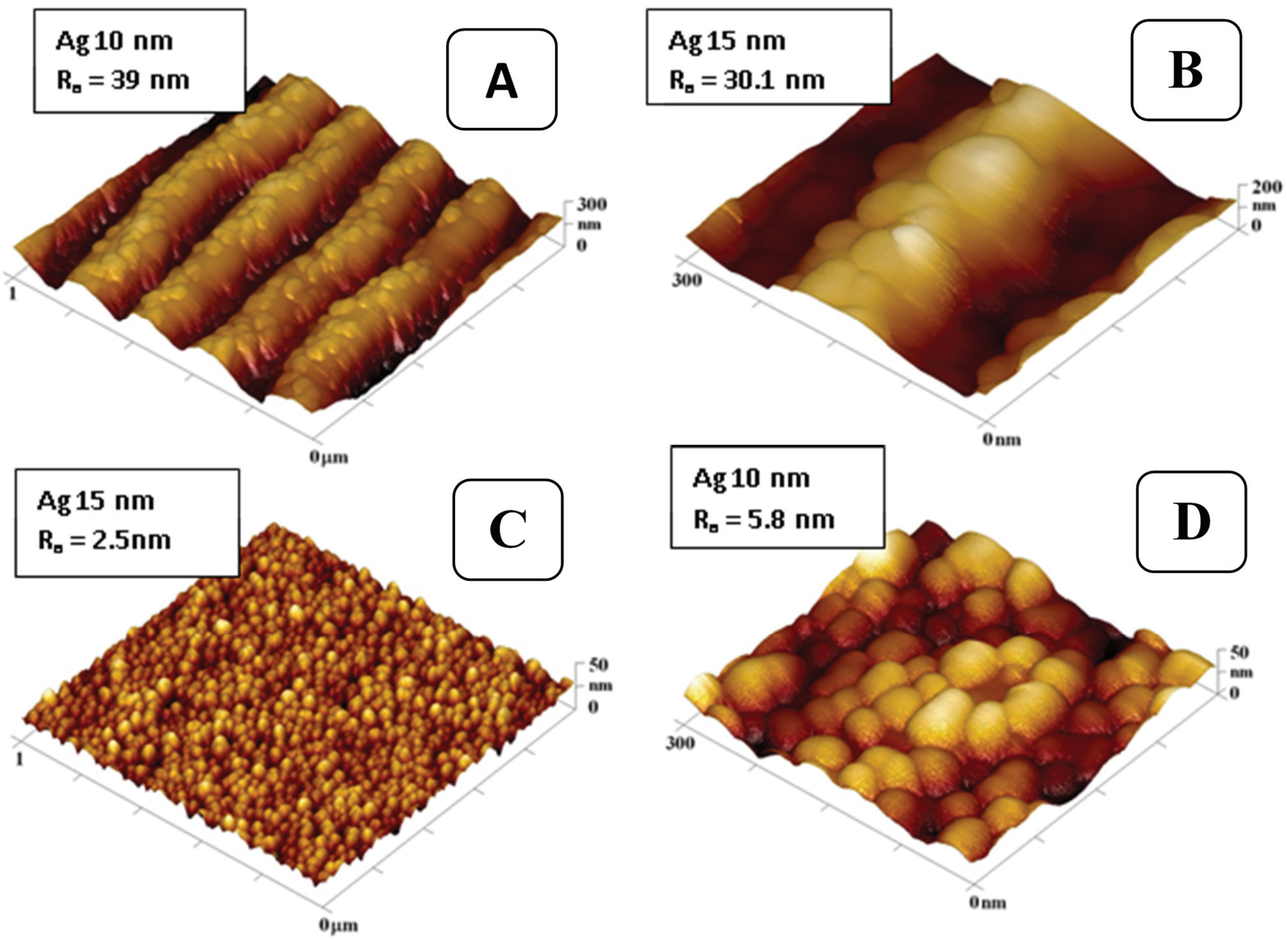

Figure 2 AFM images of samples after irradiation with 6000 pulses of laser fluence 8 mJ·cm^{-2} with a silver layer of 10 nm (A) and 15 nm (B, detailed 300x300 nm^2), and 16 mJ·cm^{-2} with a silver layer of 15 nm (C) and 10 nm (detailed 300x300 nm^2, D).

3.2. Electrical properties

A graph of resistance dependence on effective layer thickness typical for thin metal layers on isolating substrate can be seen (**Figure 3**). The sheet electrical resistance was examined in the direction corresponding to the ripple orientation at a laser fluence value of 8 mJ·cm^{-2}. It is shown that the 5 nm metal layers reach the highest resistances up to MΩ. This resistance values indicate the possible occurrence of conductive joints formed on the surface structure. Higher effective electrical continuity can be observed for metal layers of thickness 10 and 15 nm, where there is no significant decrease in resistance.

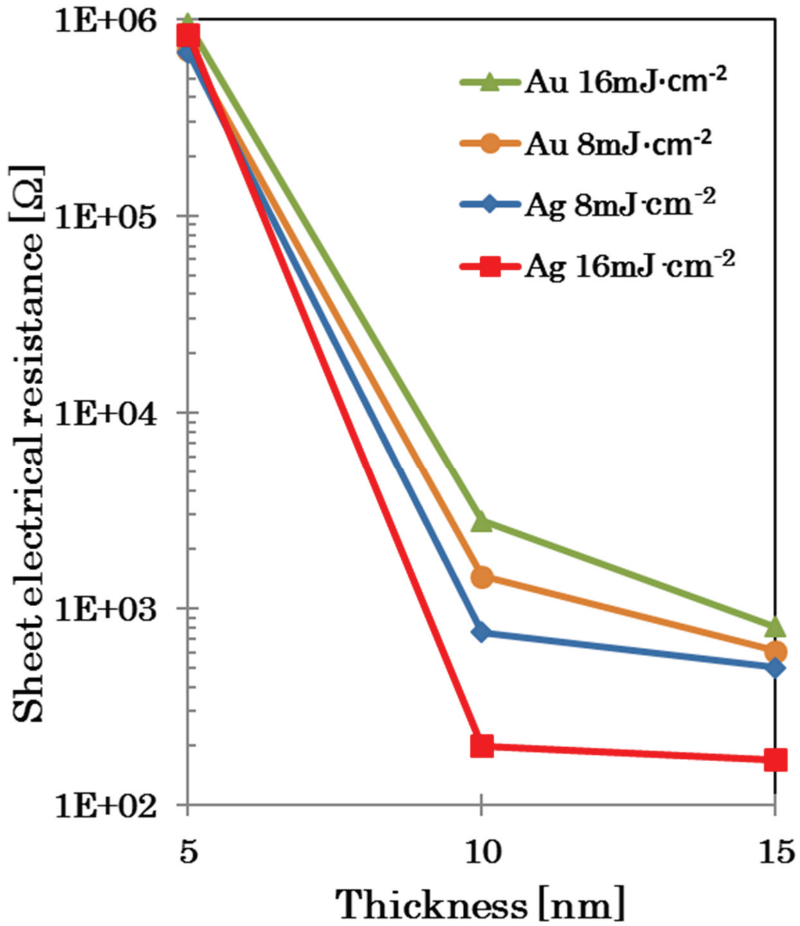

Figure 3 Sheet electrical resistance of thin Ag and Au layers after irradiation with 6000 pulses of laser fluence 8 mJ·cm^{-2} and 16 mJ·cm^{-2}

3.3. Optical properties

The UV-Vis spectroscopy method was subsequently used to characterize the samples. We investigated the absorbance of deposited metal layers in dependence on the wavelength. **Figure (4A)** shows the absorbance of deposited gold layers of 5, 10 and 15 nm thickness after modification of 6000 pulses by laser fluence value of 8 and 16 mJ·cm^{-2}. The graph shows the trend that samples modified by a higher laser fluence value reach higher absorbances across the wavelength range. Similarly, the increasing thickness of the layer resulted in higher absorbance for all wavelengths. Both of these trends were common to other studied samples of Ag, Pt and Pd.

The next **Figure (4B)** examines the effect of modifying pulses on the absorbance of the sample with a thin layer of 5 nm of gold. It is noteworthy that while the pristine PES polymer exhibited the lowest absorbance, the modified samples increased its absorbance with the increasing number of pulses.

A completely different situation occurred after the sample was sputtered with a 20 nm thick layer of metal, as illustrated in **Figure 4C**. Such a strong layer completely suppressed the influence of the substrate and its modification by different pulse counts. Further, the absorbance, unlike all previous cases, showed a stable absorbance value below 0.5 even in the shorter wavelength range.

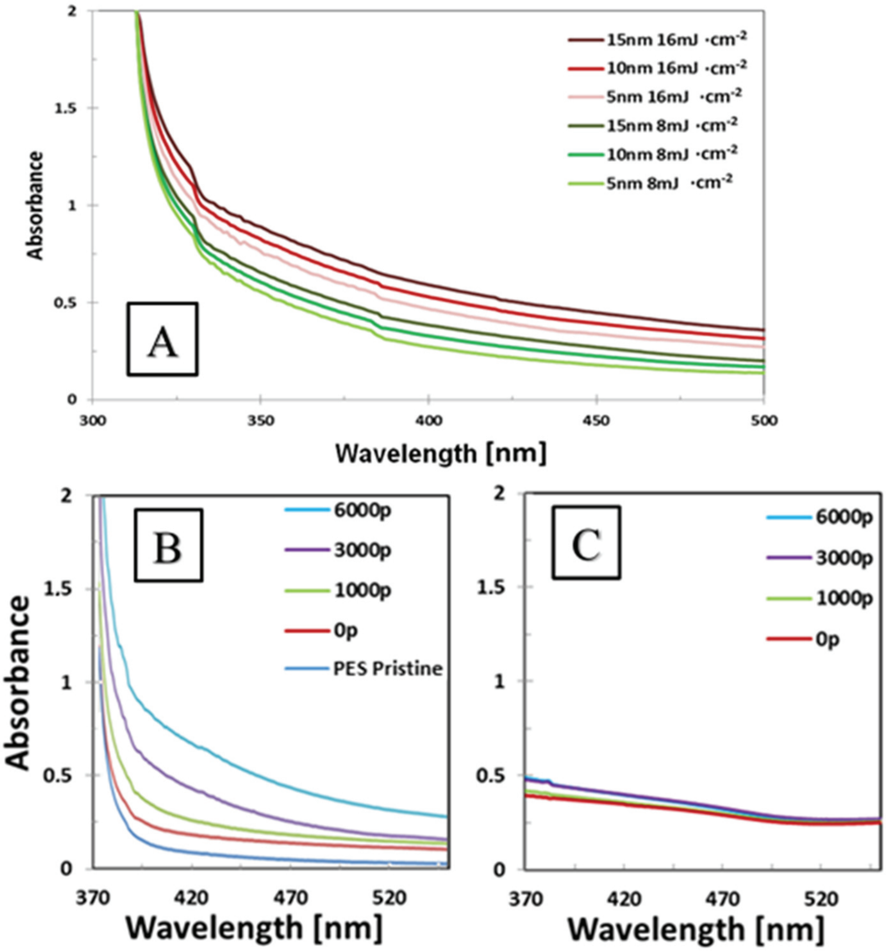

Figure 4 UV-Vis spectra of Au metal layers: 6000 pulses, 8 mJ·cm^{-2} and 16 mJ·cm^{-2}, 5-15 nm of Au (A); 0-6000 pulses, 8 mJ·cm^{-2}, 5 nm of Au (B), 0-6000 pulses, 8 mJ·cm^{-2}, 20 nm of Au (C)

CONCLUSION

This work focuses on the preparation of metal-polymer nanostructures achieved by the excimer laser beam. The PES substrate was modified by a laser beam with a pulse rate of 1000-6000 and a laser fluence in the range of 4 and 16 mJ·cm^{-2}. Modification by a laser fluence of 8 mJ·cm^{-2} led to the formation of nanoripples, whereas the higher value of the laser fluence 16mJ·cm^{-2} led to the formation dot periodic structures. Morphology was investigated on the surface of samples deposited with metal layers. Layer thicknesses of 5-15 nm deposited on the modified surface led to the formation of isolated metal clusters. Surface metallized after the treatment of laser fluence 8 mJ·cm^{-2}, preferably aggregated on the ridge of the ripples. All measurements of UV-Vis spectroscopy revealed that the lowest absorbance showed the original PES substrate, and the effect of increasing the absorbance is caused by the number of modifying pulses, the laser fluence value and the thickness of the layer itself. The rapid increase in absorbance occurred in wavelength ranges of 400 nm or less. If the layer thickness reached 20 nm, the modification of the samples no longer had an effect on the absorbance. Antibacterial properties of these metal layers deposited on nanostructured surface could be used for material supressing the bacteria biofilm formation, surface with regular nanostructures has also potential to guide the specific types of cells, such are e.g. osteoblasts.

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