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Biopolymer nanostructures induced by plasma irradiation and metal sputtering

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ABSTRACT

Modification based on polymer surface exposure to plasma treatment exhibits an easy and cheap technique for polymer surface nanostructuring. The influence of argon plasma treatment on biopolymer poly(L-lactide acid (PLLA) will be presented in this paper. The combination of Ar^+ ion irradiation, consequent sputter metallization (platinum) and thermal annealing of polymer surface will be summarized. The surface morphology was studied using atomic force microscopy. The Rutherford Backscattering Spectroscopy and X-ray Photoelectron Spectroscopy were used as analytical methods. The combination of plasma treatment with consequent thermal annealing and/or metal sputtering led to the change of surface morphology and its elemental ratio. The surface roughness and composition has been strongly influenced by the modification parameters and metal layer thickness. By plasma treatment of polymer surface combined with consequent annealing or metal deposition can be prepared materials applicable both in tissue engineering as cell carriers, but also in integrated circuit manufacturing.

1. Introduction

Polymeric materials gathered their importance due to wide possibilities of mechanical, chemical and biological modification. The micro-channels shaped for cell interaction and cell incorporation for optimal sets of antigen exposure lead to new results in diagnostic testing [1]. The strong application of nanostructured materials analysis can be found in the family of ion beam analysis methods, e.g. Rutherford Backscattering Spectroscopy [2]. Nanostructured polymers also allow to stimulate the natural environment of the cell or to study the cell responses for specific stimulus [3].

The lithographic procedures, which are used mostly in semiconductor technology are based on the exposure of photo resist with appropriate electromagnetic/ion beam. During the process the high purity of resist is required [4]. The lithographic procedure [5] can be very easily applied to polymer substrates. The surface polymer layer can be treated with UV-light using a mask for the pattern construction. Such structures are widely used for isolation of island cell formations [6]. Instead of UV-light the electron beam can be also applied for polymer scissoring [7]. The laser exposure can lead to direct removal of polymer material (ablation), which is very fast method often used for construction of gaps of defined dimensions [8–13]. During the wrinkling process the lacquer covering the polymer is exposed to uniaxial pressure, which leads to the creation of linear structures on the surface [14]. Better results were observed when the pressure was realized by the movement of silicon wafer edge on the polymer surface covered with thin metal layer [15,16]. Thermal annealing of thin metal layer on polymer surface led to the coalescence of metal layer and creation of submicron clusters and nanostructures [17–19].

This paper describes a simple and cheap method for biopolymer surface nanostructuring by metal nanostructure deposition and subsequent thermal annealing. The parameters of pattern were controlled by the plasma pre-treatment and most of all by the layer thickness. The surface elemental composition, surface morphology and depth profile of ripple pattern are introduced.

2. Materials and methods

2.1. Materials and treatment

Biopolymer poly(L-lactic acid) foils (PLLA, density 1.25 g cm^{-3}, glass transition temperature T_g = 60 °C, crystallinity 60–70%, 50 μm thick foils, supplied by Goodfellow, Ltd., UK) were used

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for the present experiments. The platinum layers on PLLA substrate were deposited from a Pt target (99.999%) by means of diode sputtering technique (BAL-TEC SCD 050). Typical sputtering conditions were: room temperature, time 5–500 s, total argon pressure of about 5 Pa, electrode distance of 50 mm and current of 20 mA. For the Rutherford Backscattering Spectroscopy(RBS) and X-ray photoelectron spectroscopy (XPS) analysis the sample with average thickness 30 nm (measured with AFM) was chosen. Thermal annealing of the polymers was accomplished in thermostat BINDER. The samples were heated for 30 min at 60 °C and then they were cooled down to room temperature.

2.2. Measurement techniques

The surface morphology was examined using an Atomic Force Microscopy (AFM). The AFM images were taken under ambient conditions on a Digital Instruments CP II set-up. R_a represents the arithmetic average of the deviations from the center plane of the sample.

RBS analyses were performed on Tandetron 4130MC accelerator using 1.7 MeV ^{4}He ions. The measurements were performed in Cornell geometry with incident angle 0°, and laboratory scattering angle of 170°. The typical energy resolution of the spectrometer was FWHM = 15 keV. The RBS spectra were evaluated using SIMNRA [20] and GISA [21] software using cross-section data from IBANDL [22].

The presence of oxygen, carbon and platinum in PLLA surface layer was analyzed by ARXPS (Angle Resolved XPS). The spectra were measured at different positions of the detector axis with respect to the sample normal. An Omicron Nanotechnology ESCAProbeP spectrometer was used. The exposed and analyzed area had a dimension of 2 × 3 mm^2. The X-ray source was monochromated

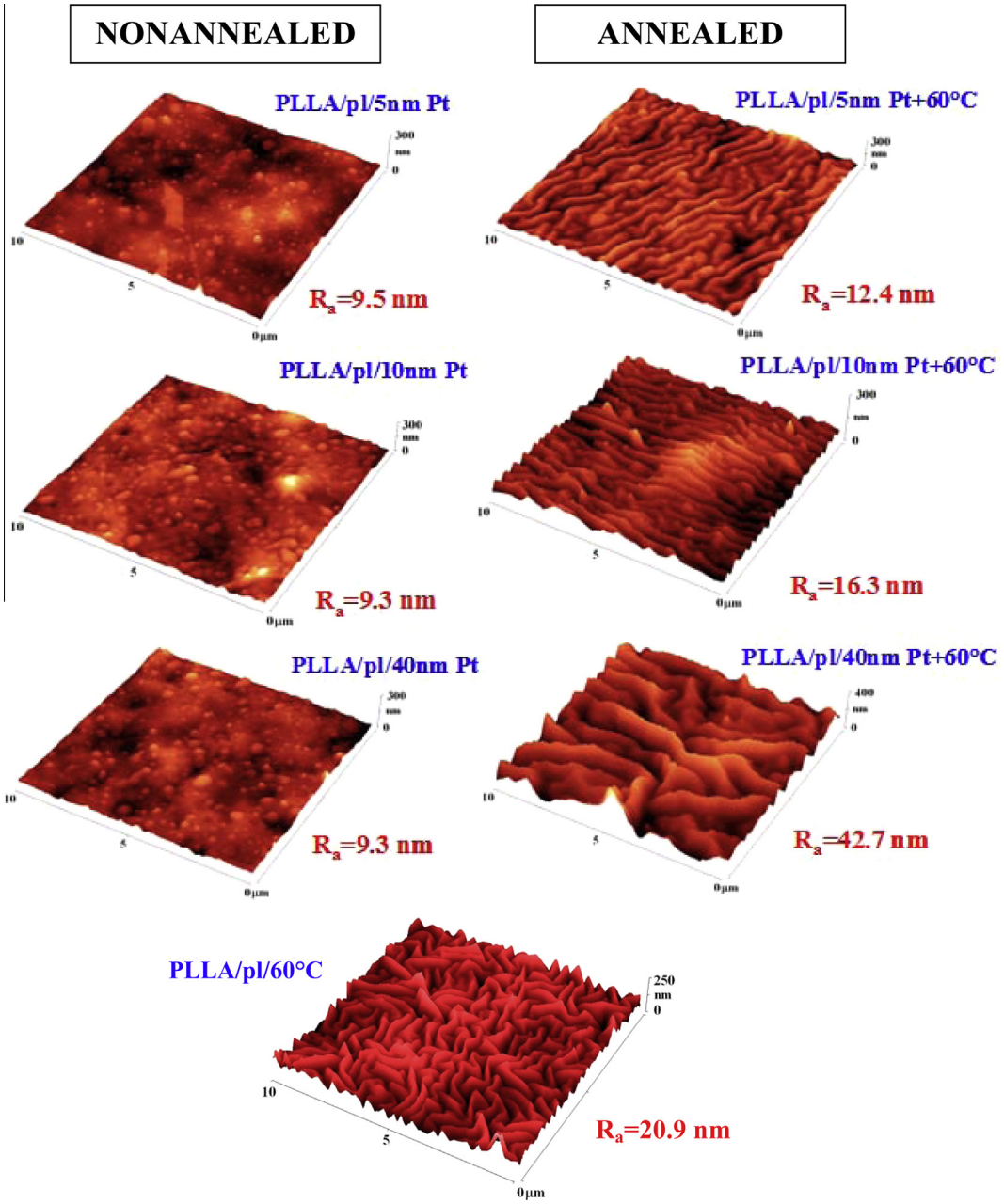

Fig. 1. AFM images of plasma treated (10 W and 240 s) PLLA with 5, 10 and 40 nm of sputtered Pt (left column – nonannealed) and the same samples consequently annealed by 60 °C (right column). The PLLA sample treated with 10 W and 240 s and annealed to 60 °C (PLLA/pl/60 °C) is introduced for comparison. R_a is the average surface roughness in nm.

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