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Nanostructured silver coatings on polyimide and their antibacterial response

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ABSTRACT

We report on antibacterial activity of the silver nanostructures prepared by DC sputtering on polyimide foil (Kapton® HN). Sputtered silver nanolayers were transformed into discrete nanoislands by low-temperature post-deposition annealing. The possibility of managing nanostructure size via controlling the thickness of silver nanolayers prior to the annealing is shown. Nanostructure morphology was studied by atomic force microscopy. Atomic concentration of elements in very sample surface was determined by X-ray photoelectron spectroscopy. Integrity of silver coatings was determined by measuring its electrical sheet resistance. Antibacterial properties of the polyimide foils both pristine and silver coated before and after annealing were examined by a drip method using two bacterial strains, *Escherichia coli* and *Staphylococcus epidermidis* frequently involved in infections associated with a biofilm formation.

1. Introduction

Polyimide (PI), more specifically Kapton®, represents a class of engineered materials characterized by high chemical resistance, good patterning capability, and excellent thermal and mechanical properties. Moreover, it is an extremely stable material under conditions of ultraviolet and nuclear radiation exposure. Those properties predetermine this material for medical applications such as catheters or vascular prosthesis [1]. Successful integration of an artificial material into a living body, however, requires effective surface sterilization to eliminate development of postoperative complications caused especially by bacterial contamination and biofilm formation.

In the past two decades, a number of studies have focused on the development of antibacterial surfaces able to inhibit biofilm formation [2–4]. Various approaches have been successfully applied to prevent biofilm proliferation by limiting initial microbial adhesion or by killing of microorganisms as they come into a close contact with the solid surface. The most promising techniques comprise functionalization of materials surface with silver [2] or gold [5], quaternary ammonium group [6], or chitosan [7].

In this work, we report a simple, versatile two-step process enabling production of silver nanostructures homogeneously distributed over the surface of PI foil which acts as a permanent active antimicrobial coating. In principle, this approach enables the formation of antibacterial coatings on a wide spectrum of thermally durable polymeric materials. The two-step preparation process is based on sputtering of an ultrathin silver layer which is then turned into discrete silver nanoislands by mean of low-temperature post-deposition annealing. Composition and chemical structure of the PI surface were investigated by X-ray photoelectron spectroscopy (XPS). Morphology of pristine and silver-coated PI was evaluated by atomic force microscopy (AFM). Transformation of a compact silver layer into discontinuous nanoislands was documented by measuring its electrical sheet resistance. Finally, the antibacterial activity of the newly developed surfaces was assessed by using *Escherichia coli* (*E. coli*) and *Staphylococcus epidermidis* (*S. epidermidis*) as experimental models.

2. Experimental

Materials, apparatus and procedures: Polyimide Kapton HN® foil (thickness 50 μm, density 1.42 g cm^{-3}, upper working temperature $T=310$ °C, supplied by Goodfellow Ltd., UK), was used in this work. The PI samples were coated with silver by diode sputtering system using Balzers SCD 050 device. The metal deposition was accomplished from a silver target (purity 99.999 %, Goodfellow Ltd. UK). The parameters of the deposition were: DC Ar plasma, gas purity 99.995 %, gas flow 0.3 l s^{-1}, pressure 5 Pa, power 20 mA, the inter-electrode distance of 50 mm, sputtering time varied from 10–500 s. The thermal annealing was performed immediately after

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the silver deposition in air at 250 °C for 1 h using a thermostat Binder oven. The annealed samples were then cooled down on air to room temperature.

Analytical methods: Surface morphology and roughness of pristine and silver-coated PI before and after annealing for different deposition times were examined by AFM using VEECO CP II device working in tapping mode. Surface roughness is characterized by the mean roughness value (R_a) which represents the arithmetic average of the deviation from the center plane of the sample.

Effective thickness of the sputtered silver was determined by a scratch method on a glass substrate (coated simultaneously with PI) using AFM VEECO CP II device. Measurements were performed with Bruker Antimony-doped Silicon probe CONT20A-CP (spring constant 0.9 N m^{-1}).

The atomic concentrations of the silver Ag (3d), oxygen O (1 s), carbon C (1 s) and nitrogen N (1 s) in silver-coated (as-sputtered, annealed) PI were determined using XPS method on Omicron Nanotechnology ESCAProbeP spectrometer. The X-ray source was monochromated at 1486.7 eV, the measurement was performed with a step size of 0.05 eV. The spectra evaluation was carried out by CasaXPS software.

Sheet resistance (R_s) of the silver layers before and after annealing was measured by a standard two-point method using KEITHLEY 487 picoampermeter. Two additional silver contacts, defining measured area (about 50 nm thick) on the layer surface were prepared by sputtering.

Antibacterial tests: Antibacterial properties of the PI foils both pristine and silver-coated before and after annealing were examined by the drip method. We have chosen two environmental bacterial strains as model organisms; one Gram-negative bacteria *Escherichia coli* (DBM 3138) and one Gram-positive bacteria *Staphylococcus epidermidis* (DBM 3179). *E. coli* was cultivated in

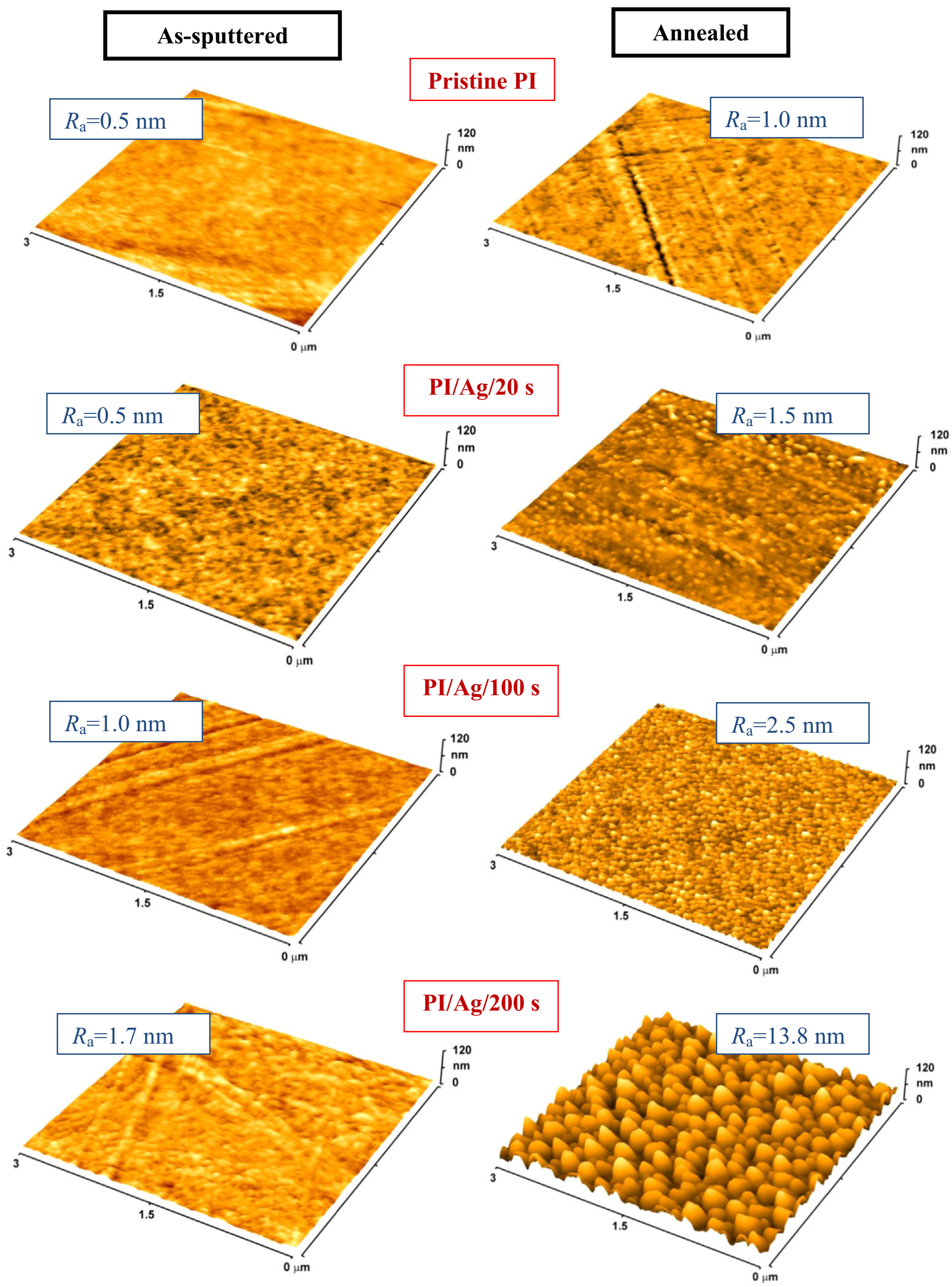

Fig. 1. AFM images of pristine and silver-coated PI samples before (As-sputtered) and after annealing (Annealed) at 250 °C for different deposition times (20, 100, and 200 s). R_a represents average surface roughness in nm.