Materials Letters 165 (2016) 33–36

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Change of surface properties of gold nano-layers deposited on polyethersulfone film due to annealing

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ARTICLE INFO

Article history:
Received 17 April 2015
Received in revised form
10 November 2015
Accepted 22 November 2015
Available online 23 November 2015

Keywords:
Polymers
Surface characterization
AFM
Sheet resistance
Zeta potential
UV–vis spectra

ABSTRACT

In this paper morphological, electrical and physical properties of polyethersulfone films with deposited gold nanolayers were studied. These samples were examined as-sputtered and annealed to temperature below and above glass transition temperature of polymer. Morphological changes induced by annealing were observed by means of atomic force microscopy. These changes were caused by coalescence of gold layer that was confirmed by change of sheet resistance and shift in UV–vis spectra. Most prominent shifts were observed for samples with 5 nm sputtered gold layer, which exhibited localized surface plasmon resonance after annealing due to semiperiodical structure of gold clusters separated by polymer gaps.

1. Introduction

Analyzing behavior of metal layer on various substrates under heat stress gives us important parameters needed for prediction of point of its electrical failure because of thermal degradation [1,2]. This is essential for preparation of thin film metallic interconnections in modern devices that require higher current densities and clock frequencies than before.

Another important reason for studying annealing of polymer films with metal layer is their ability to self-assemble complex patterns of metal nanostructures [1,3–5]. Self-assembly of such nanostructures on various substrates is currently highly researched field as different patterns offer wide array of unique electric, optical catalytic and biological properties, which can be used in numerous applications ranging from data storage [6], photonics [7] to sensors [5], while maintaining simple preparation procedures and low cost.

One of highly useful properties these structures can exhibit is localized surface plasmon resonance (LSPR) [8]. LSPR is the interaction between noble-metal particle's surface electrons and incident light confined on the nanoparticle surface [9]. For nanoparticles far smaller than the wavelength of the light, the surface electrons collectively oscillate with the light transmission. The plasmon resonance occurs when the oscillation frequency of electrons and photons is matched. [10]. LSPR is used for example in SERS [11], where periodic array of isolated metal nanoparticles is crucial for ultrasensitive SERS realization. Another field of use for patterned polymer substrates is biomedicine, specifically construction of replacements of damaged tissue [12]. Optimization of materials for this purpose requires modification of surface morphology and chemistry, as cells favor certain patterns [13], moderate hydrophilicity [14] and surface electrical conductivity [15].

In this work, morphological, electrical and physical properties of polyethersulfone films with deposited gold nanolayers were studied. These samples were examined as-sputtered and annealed to temperature below and above glass transition temperature of polymer. Morphological changes induced by annealing were observed by means of atomic force microscopy. Changes of surface properties were studied by sheet resistance, UV–vis spectroscopy and electrokinetic analysis.

2. Experimental

2.1. Materials

Polymer polyethersulfone (PES, density 1.37 g cm^{-3}, glass transition temperature T_g=228 °C, thickness 50 μm, Goodfellow, Ltd., UK) was used in the presented experiments.

Gold layers were deposited from Au target (99.999%) by diode sputtering technique (BAL-TEC SCD 050 equipment, Switzerland). Typical sputtering conditions were: room temperature (RT), times

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http://dx.doi.org/10.1016/j.matlet.2015.11.098
0167-577X/

10–300 s, argon pressure of about 5 Pa, electrode distance of 50 mm, electric current of 20 mA. Part of the samples were annealed at 190 °C, 220 °C and 240 °C for 60 min (BINDER thermostat, Germany) and then cooled to RT in air.

2.2. Apparatus and procedures

Surface morphology and roughness of the samples were examined by means of atomic force microscopy (AFM). The AFM images were taken on VEECO CP II setup (Veeco, USA) in a tapping mode. Si probe RTESPA-CP with the spring constant 20–80 N m^{-1} was used. Roughness (R_a) represents the arithmetic average of the deviations from the center plane of the sample. Four areas of each sample were scanned in order to get representative data.

The electrical continuity/discontinuity of the as-sputtered and annealed gold layers was inspected by determination of electrical sheet resistance (R_s). The measurement was carried out with KEITHLEY 487 pico-ammeter by standard Ohm's method. Two Au contacts (thickness about 50 nm) were sputtered on the layer's surface for this measurement.

Electrokinetic analyses (determination of zeta potential) of pristine, sputtered and annealed samples were accomplished on SurPASS Instrument (Anton Paar, Austria). The samples were studied inside an adjustable gap cell in contact with electrolyte (0.001 mol dm^{-3} KCl). Streaming current method was applied and zeta potential was calculated by Helmholtz–Smoluchowski equation [16]. All samples were measured four times at constant pH equal to 6.4 with the relative error of 5%.

Optical properties were studied using Perkin-Elmer Lambda 25 UV–Vis spectrometer. The device was equipped with wire grid polarizer WP25L-UB (250–4000 nm, Thorlabs). The absorption spectra were recorded stepwise with the step in the wavelength of 1 nm and in the wavelength range of 200–800 nm.

The glass transition temperatures (T_g) of the polymer films were determined using a DSC 2920 calorimeter under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

3. Results and discussion

Surface morphology of prepared samples is shown in Fig. 1. Pristine PES surface is very smooth with low surface roughness.

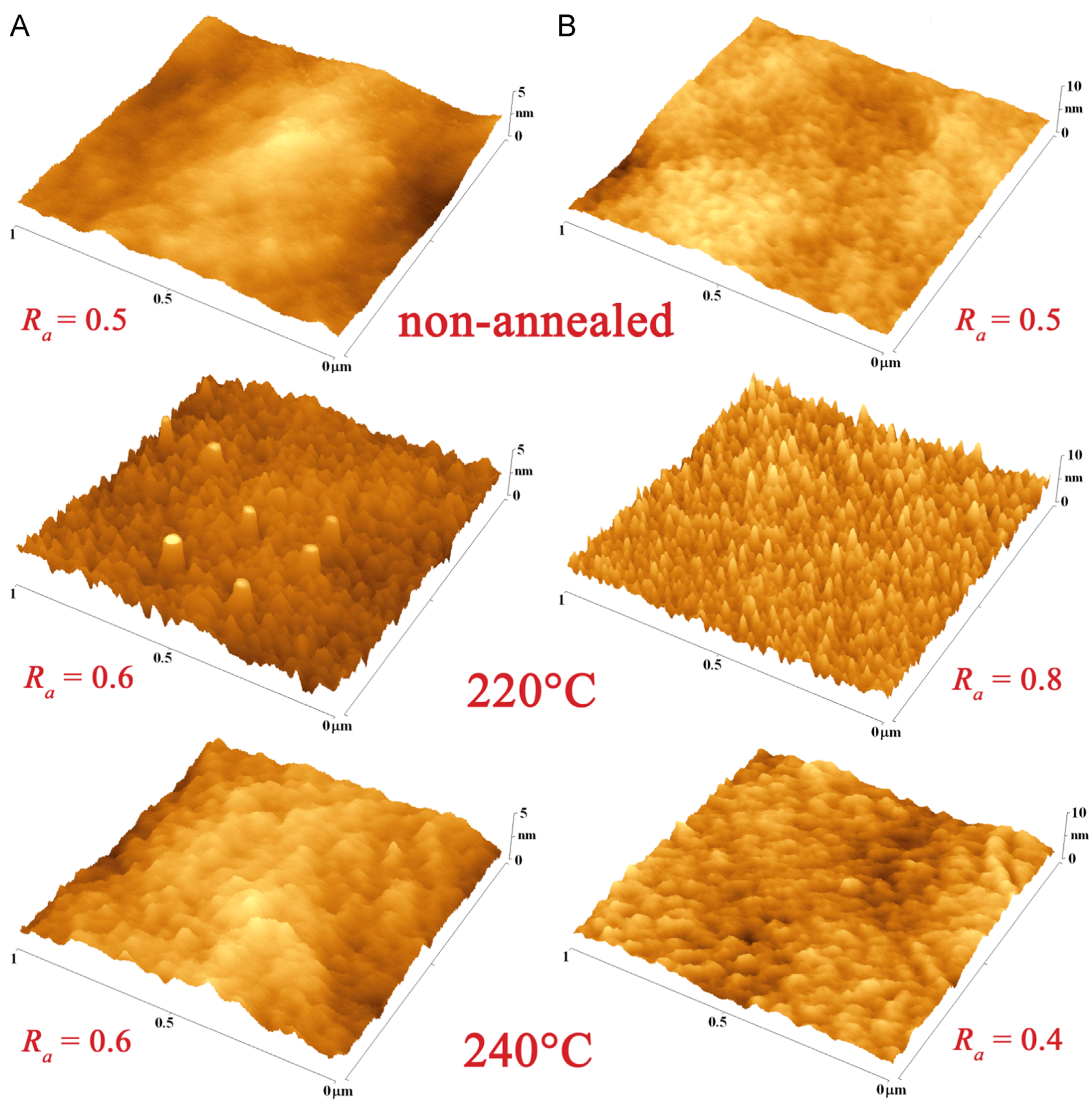

Fig. 1. AFM scans of sample surfaces. Column A shows samples without metal layer, column B shows samples with 5 nm gold layer. In rows the samples non-annealed (1st line) and annealed at temperatures 220 °C (2nd line) and 240 °C (3rd line) are shown. R_a corresponds to surface roughness in nm.