Preparation of Thin Metal Layers on Polymers

J. Siegel, V. Kotál

Continuous gold layers of increasing thickness were prepared by the vacuum deposition method on pristine and plasma modified sheets of PE, PET and PTFE. Various surface profiles were obtained. The surface morphology was studied using atomic force microscopy (AFM). The continuity of the metal layer on the polymer surface was validated by measuring its electrical resistance. Changes in the wettability of the plasma treated polymers were evaluated by measuring the aging curves. These were obtained as the dependence of contact angle on ageing time.

Keywords: polymer, metal, vacuum deposition, atomic force microscopy, contact angle, plasma etching.

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1 Introduction

Metallized polymer films are widely used in industries ranging from food packaging to biosensors [1–4]. Interesting studies have been made on various aspects of metal/polymer interface formation [5]. Polymeric films metallized from both sides are basic structures for constructing diodes with negative differential resistance.

A crucial role in preparing metal layers on polymers is played by the interface properties between substrate and deposited metal. This attribute can benefit from plasma treatment of the polymeric surface. Plasma processing of polymer materials is routinely used to control the properties. Just by varying the plasma treatment conditions it is possible either to increase or to decrease the wettability of the given polymeric surface. In order to understand the changes made to the surfaces during plasma treatment, we need analytical techniques that can accurately characterize the surface before and after modification. The most important characteristic factor that affects interfacial interactions, such as adsorption, wetting and adhesion, is surface energy. The surface energy of plasma treated polymers can easily be examined by measuring the contact angles.

Metal deposition on polymers can be carried out by sputtering, vacuum deposition, and also by various electrochemical procedures [4,6,7]. The thicknesses of the prepared layers proceed in an interval ranging from a few nanometres to hundreds of nanometers. The structure of the metal layer is mainly influenced by nucleation processes [8,9]. One of the main problems when a metal layer is formed on a polymer is its adhesion to the substrate. Adhesion of the metal layer to the polymer can be increased by various methods, including chemical changes, plasma charge, laser and ion beam irradiation [10]. Plasma treatment is probably the most versatile surface modification technique, and it has become an important process for altering the chemical and physical properties of surfaces [11].

This work studies modification of polymers (PE, PET, PTFE) and also the formation of metal layers on polymers. Surface profiles of pristine and modified PE and PET and images of the Au film were obtained by the AFM technique. The continuity of the metal layer on the polymer surface was validated by measuring its electrical resistance.

2 Experimental

PE (HDPE, thickness 25 μm, density 0.965 gcm^{-3}), PET (thickness 50 μm, density 1.370–1.395 gcm^{-3}) and PTFE (thickness 25 μm) sheets with dimensions of 3×3 cm were prepared. Gold layers were deposited on these pristine and modified polymeric sheets. Plasma etching proceeded in an argon atmosphere of pressure 10 Pa at room temperature. The etching times were held at constant levels for each type of polymer. The times were 180 s, 180 s, 240 s for PET, PTFE and PE, respectively. These times had been found to be the most effective in terms of improving wettability (according to our earlier investigation [13]). The power of the plasma discharge was constant at a level of 8.6 W. The contact angle of the pristine polymers and of the polymeric sheets directly after plasma treatment, and also of the future development of surface wettability was determined using the Surface Energy Evaluation System device. To determine the sheet resistance we used a multimeter UNI-T, type UT83. The surface morphology of the pristine and modified PET and PE films and also the deposited gold layers was examined using AFM (contact mode, microscope Digital Instruments NanoScope TM Dimension III engine). Olympus oxide – OMCL TR sharpened silicon nitride probes with spring constant 0.02 N/m – was chosen. The normal force of the tip on the sample did not exceed 10 nN.

3 Results and Discussion

The surface morphology of pristine and plasma-treated PE and PET is shown in Fig.1, Fig. 2, Fig. 3, and Fig. 4. These images clearly demonstrate the changes in surface roughness when plasma treatment is applied.

Further investigation of gold layers and their morphologies provided a large number of AFM images. Two of them have been chosen as representative, and are shown in Fig. 5 and Fig. 6. The changes in surface roughness after gold deposition on polymers are obvious.

The last two pictures above demonstrate that increasing the thickness of the gold layer goes hand in hand with increasing the roughness of the surface of the samples.

A rapid decrease in surface wettability for the samples immediately after plasma treatment is obvious from the measurements of the dependence of the contact angle on time

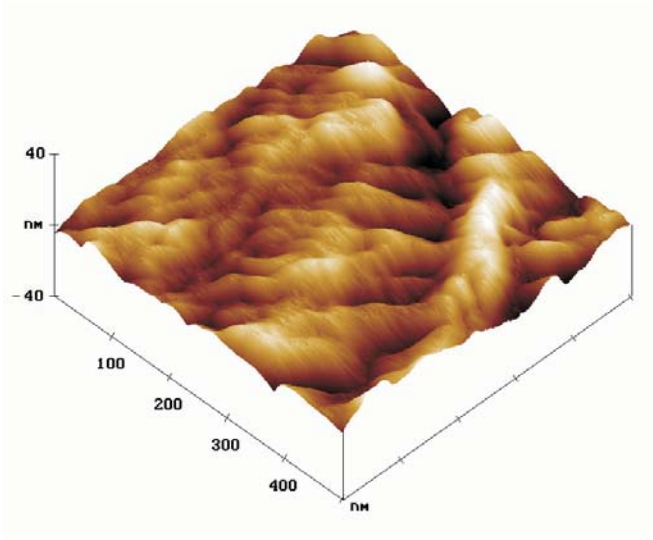

Fig. 1: AFM image of pristine PE

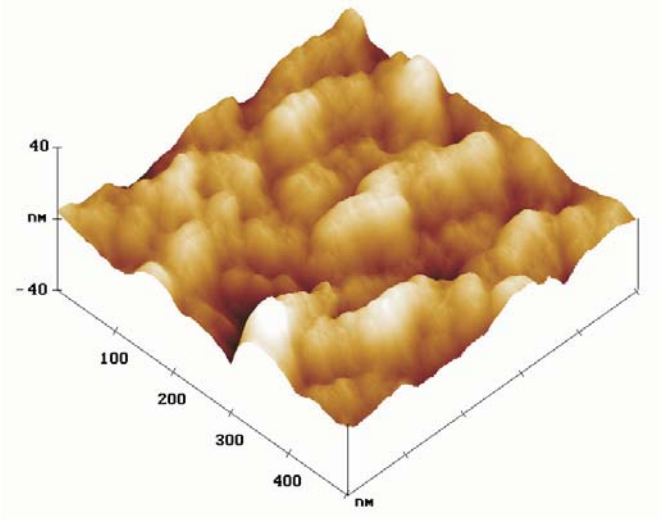

Fig. 2: AFM image of 240 seconds plasma treated PE

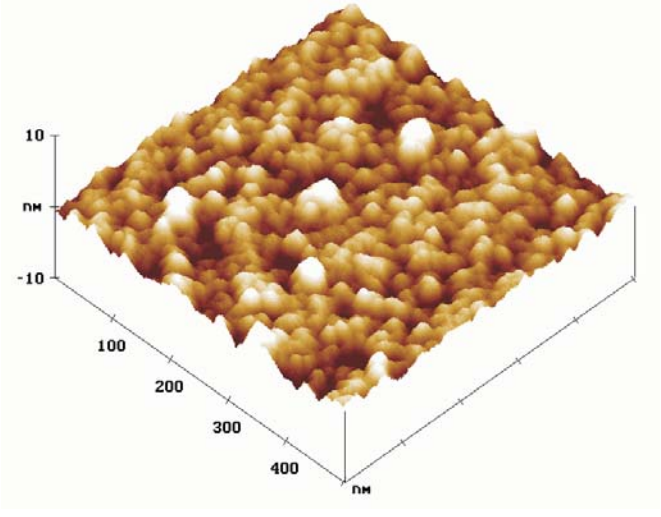

Fig. 3: AFM image of pristine PET

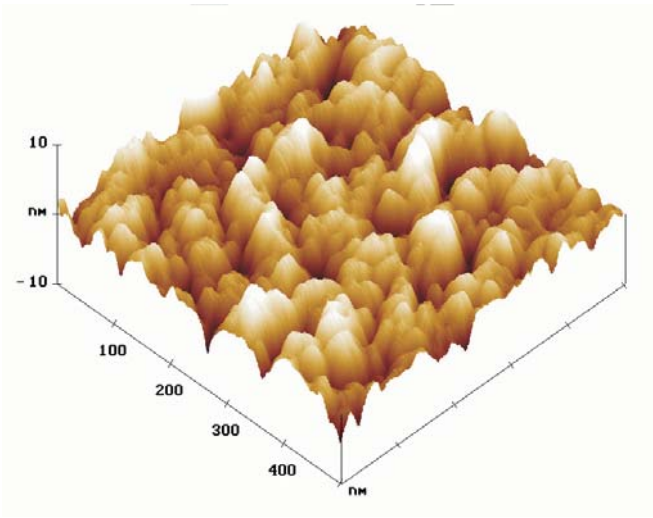

Fig. 4: AFM image of 180 seconds plasma treated PET

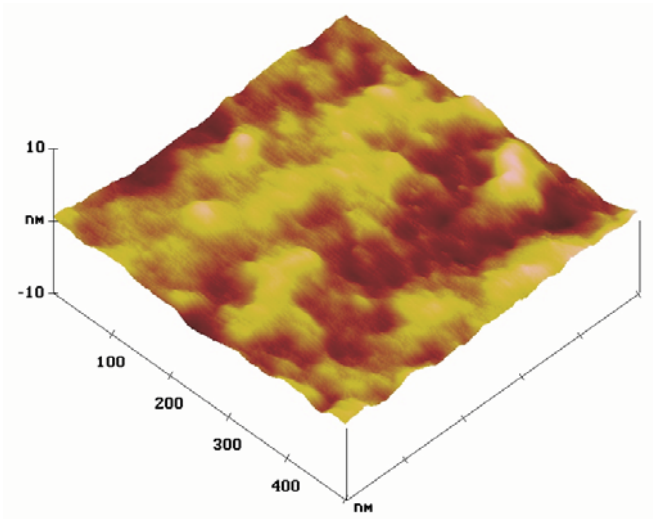

Fig. 5: AFM image of pristine PET/Au 20nm

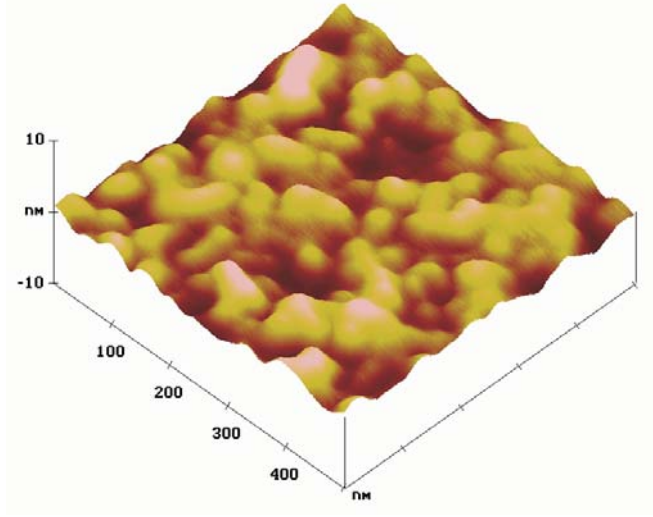

Fig. 6: AFM image of pristine PET/Au 100nm

after deposition (see Fig. 7). The value of the contact angle reached its lowest level immediately after exposure to radiation in the case of all investigated samples. When focused on PET and PE sheets, it is evident that after approximately 48 hours the contact angle increases to the level of about 20 degrees above that of the pristine samples. It then remains con-

stant. This corresponds to values of 100° or 125° for PET and PE, respectively (see Fig. 7). A different dependence was obtained in the case of PTFE. It is evident that the increase in the contact angle is more gradual than in the case of PE and PET. However, subsequent measurement of the PTFE contact angle showed that the final value stabilized at a level near to that of pristine PTFE (about 115°, time 260 hours). It is also evident that immediately after exposure to radiation the value

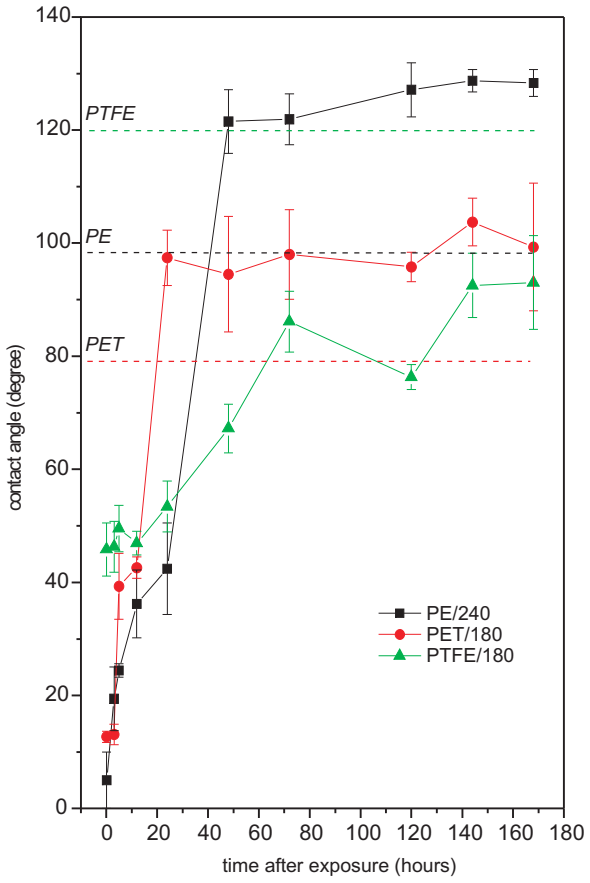

Fig. 7: Dependence of the contact angle of the studied polymers on time after exposure to Ar plasma. The numbers in the legend represent treatment times in seconds

of the contact angle is higher in the case of PTFE (about 45) than in PE and PET (see Fig. 7).

4 Conclusions

The results of this work can be summarised as folows:

- plasma treatment of polymers increases the surface roughness for PE, PET and PTFE,
- the surface morphology of deposited Au layers depends on the type of polymeric substrate,
- the value of the contact angle reached its lowest level immediately after exposure to radiation, in the case of all investigated samples,
- the surface roughness of vacuum evaporated Au layers studied by the AFM technique is an increasing function of deposition time (thickness of the layer),
- the ageing curves of PTFE differ from those obtained for PE and PET.

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