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Microscopic study of ultra-thin gold layers on polyethyleneterephthalate

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Abstract

Continuous and discontinuous gold layers sputtered on polyethyleneterephthalate (PET) were characterized using atomic force microscopy (AFM), scanning electron microscopy (SEM) and by reflection of microwave radiation. The changes in the surface morphology of the continuous and discontinuous gold layers as a function of the sputtering time were clearly observed by AFM technique. SEM imaging of very thin gold layers was adversely affected by specimen charging. For medium sputtering times, when a continuous gold coverage is already formed, the SEM technique still show the presence of regions with very thin gold coverage which gradually disappear at longer sputtering times. Both, the AFM and SEM techniques confirmed that in the course of the gold deposition the initially small gold clusters grow and finally associate in a continuous layer. It was shown that the sub-microne metallic structures could be modeled by artificial, significantly larger structures prepared on PET by lithographic etching.

Keywords: Polyethyleneterephthalate; Gold; Sputtering; Microscopy (AFM, SEM, optical)

1. Introduction

Metallic films are of great importance in manufacturing of advanced electronic, optical and mechanical devices ranging from displays to biosensors [1–4]. Metallized polymeric films are basic components for fabrication of diodes with negative differential resistance in electronics [5], polymer based light emitting diodes in optoelectronics [6] and food packaging for microwave heating [7]. Metal–polymer systems prepared by metal penetration from thin metallic layers deposited on the polymer surface at increased temperature are intensively studied [8–10]. These structures find applications as components of humidity sensors and optical switches [11]. Irrespective of its technological background, polymer metallization is also interesting from the fundamental point of view because of contrasting properties of polymers and metals. The complex processes during metal deposition, involving metal atom diffusion on polymer surfaces and into the polymer bulk, aggregation and re-emission are far from being understood.

In the investigation of metallic layers thinner than 10 nm a serious problem is the layer characterization. In our previous work [12] it was shown that the continuity of the gold layer on the polymer surface could be determined by combining results from electron

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microscopy, layer resistance measurements and measurements of microwave reflection. In the same report the thickness of the gold layer was determined using UV–VIS and atomic absorption spectroscopy.

This work is a continuation of our previous study [12] and it is focused mainly on atomic force microscopy (AFM) and scanning electron microscopy (SEM) characterization of continuous and discontinuous gold layers deposited on polyethyleneterephthalate (PET). The deposition of gold layers on PET was recently studied by others e.g. in [13,14] but under different experimental conditions. The observed gold layer growth is discussed in the frame of microscopic nucleation theory [15–18] with the use of the results from microwave reflection. In this study we use mainly AFM and SEM, which allow for a detailed study of the time-dependent deposit of the gold layer on the polymer surface. Despite the fact that AFM is a relatively new technique, it became very popular in many important fields. Therefore we focus on the recent relevant AFM studies of surfaces coated by metal (Au, Ag) nanoparticles [19–22].

2. Experimental

2.1. Materials and methods

Gold layers were deposited onto 50 μm thick polyethyleneterephthalate (PET, $T_m = 260$ °C, $T_g \approx 80$ °C), supplied by Goodfellow Ltd., using a diode sputtering technique (Balzers Instrument). The sputtering was performed in argon atmosphere under the pressure of 4×10^{-2} mbar. The electrode distance was 50 mm and with 20 mA current the sputtering rate was 0.2 nm/s (for more details see also [12]). The sputtering time was varied from 0 to 80 s. According to [12] the 50 s sputtering time is sufficient for creation of a continuous gold layer with homogeneous thickness.

The model of discontinuous gold coverage on the PET surface was prepared by the following procedure. Continuous, homogeneous gold layers produced by 65 s sputtering [12] on PET surface was lithographically etched in water solution of iodine + potassium iodine through the masks with long, linear openings. The samples with lower coverage were produced in a subsequent step when the mask was turned by 90° and the etching was repeated. In such a way a discontinuous gold layer was prepared with regularly distributed gold islands, the size of which may be controlled by the etching time. Under the present experimental conditions PET samples with 0–100% gold coverage were prepared. The Au coverage was controlled by optical microscopy in transmitted polarized light on JENAPOL microscope equipped with image analyzing system LUCIA (see Fig. 4).

2.2. Microscopy and analytical methods

The surface morphology of pristine and metallized PET was examined using AFM measurements (contact mode technique), performed under ambient conditions on a commercial MultiMode Digital Instruments NanoScope™ Dimension IIIa set-up. Olympus oxide-sharpened silicon nitride probes OMCL TR with the spring constant 0.02 N/m were chosen. The normal force of the tip on the sample surface was reduced to the lamest possible level and it did not exceed 10 nN. It was certified by repeated measurements of the same region that the surface morphology did not change after five consecutive scans of imaging.

A scanning electron microscope HITACHI S 4700 (resolution 1.5 nm at 5 kV voltage, 5×10^5 maximum magnification) was used for the detection of sputtered Au particles on the sample surface by registration of secondary and scattered electrons and X-ray gold mapping. While with scattered electrons and X-ray mapping the lateral resolution was insufficient for resolving the details of the surface morphology, the registration of secondary electrons at 5 kV voltage results in best images of the surface morphology.

Reflection of electromagnetic waves was used for the characterization of continuous and discontinuous gold layers on the PET surface. The technique was described earlier in Ref. [12]. The frequency of the wave incident perpendicularly on the gold layer was 8.2 GHz. In the present experimental arrangement reflection dominates over absorption which is of marginal importance. From the voltage standing waves ratio (VSWR) it is possible to estimate continuity and homogeneity of the deposited gold layer and especially to detect transition to continuous and homogeneous gold coverage (see [12]). Generally $1 < \mathrm{VSWR} < \infty$ and $\mathrm{VSWR} \to \infty$ indicates an ideally conductive metallic layer. The VSWR of linearly etched lattice was measured in the cross-polar direction (electric field is perpendicular to the conductive strips). For double etched samples with discrete gold islands (see above), the 1/VSWR value did not exhibit any dependence on the sample orientation.

3. Results and discussion

In our previous study [12] it was proved experimentally that the gold layers sputtered for less than 28 s are discontinuous while for longer sputtering times the layers are continuous under the specific experimental conditions used. The surface morphologies of pristine and metallized PET obtained using AFM in contact mode are shown in Fig. 1. Only a few representative images are shown for illustration. Sputtering for 10 s and less does not result in any observable changes in the surface morphology in comparison with pristine PET. For

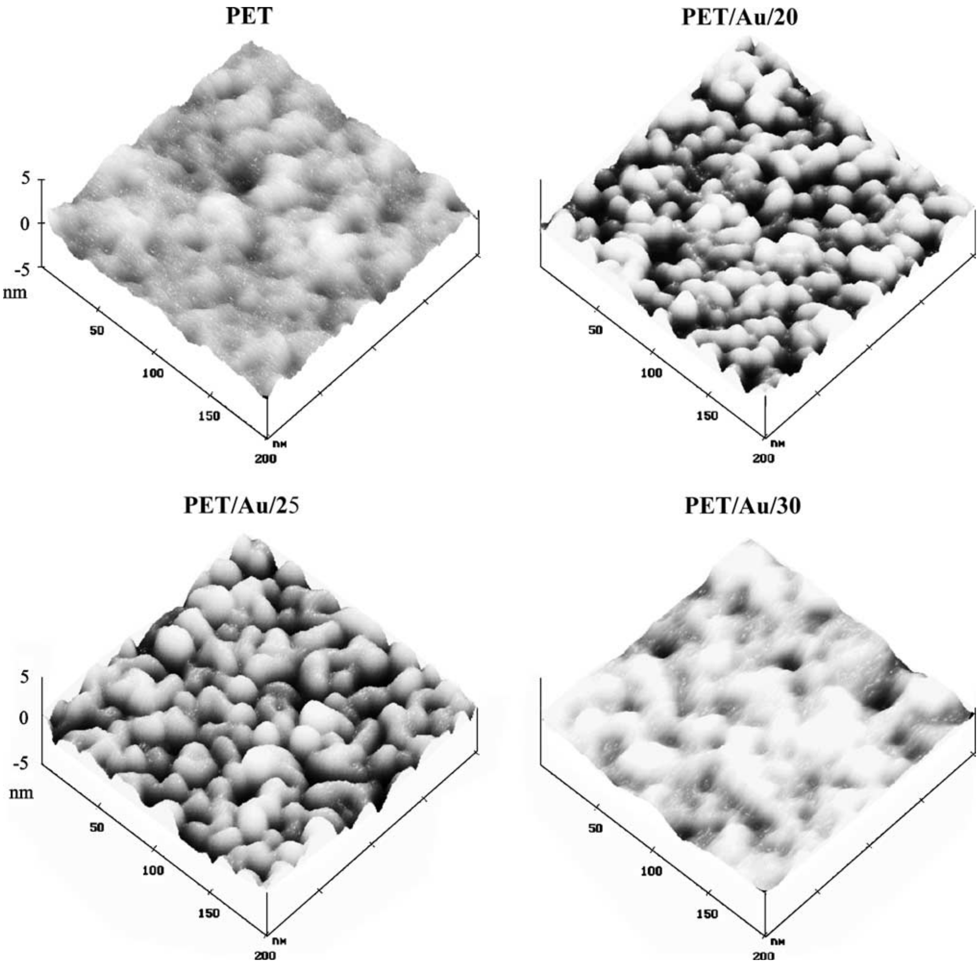

Fig. 1. Contact mode AFM height images of pristine PET and PET with sputtered gold layers. The full length of the positive vertical axis z is 10 nm. The numbers correspond the sputtering times in seconds.

longer sputtering times a discontinuous Au coverage is gradually built up with a rather dramatic morphology change occurring between 20 and 25 s sputtering time. At 25 s sputtering time the Au domains become much larger and more rounded off in comparison with shorter sputtering time. For still longer sputtering times the Au coverage becomes continuous and more homogeneous and above 30 s sputtering time no further morphological changes are observed by AFM.

The dependence of the average vertical distance on the sputtering time is shown in Fig. 2. This vertical distance (with max. error ±15%) was obtained from the section analysis as a mean of average vertical distances measured on several 500 nm long sections (in different positions of the sample) in two perpendicular directions. It is seen that the samples sputtered for less than 10 s and for 30 s and more exhibit approximately the same, low vertical distance, while the samples sputtered for 20 and 25 s exhibit significantly larger vertical distances. This result is in accordance with the images shown in Fig. 1 and with previous results reported in Ref. [12]. The presence of the pronounced maximum on the curve in Fig. 2 indicates that in the medium deposition stage the gold grows as three-dimensional clusters. This finding is in agreement with recent observations on polymers with evaporated metal layers [16,17]. Generally, the cluster density and size is expected to depend on the deposition technique and on the particular metal–polymer combination. It may be concluded that in the initial phase of the sputtering, the gold forms nanoparticles on the PET surface. With progressive sputtering the particles enlarge and finally for sputtering times above 30 s they associate and form a continuous gold layer (see also Fig. 1). Initially the layer mean thickness is very low (about 5 nm [12]) and the layer copies the substrate surface relief. This finding is consistent with basic

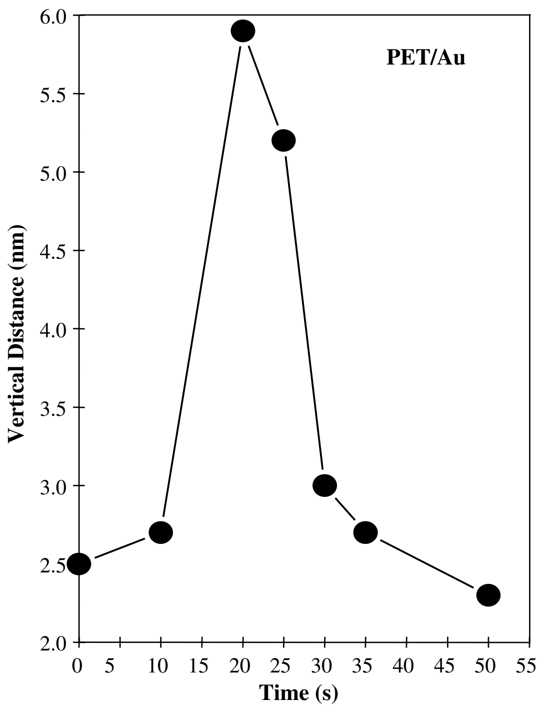

Fig. 2. Dependence of the average vertical distance, obtained from AFM section analysis, on the sputtering time (details in the text).

knowledge from the electron microscopy of isolators, namely that the thin but already continuous gold layer, deposited in order to avoid specimen charging, copies the underlying specimen relief.

Typical SEM images of pristine and gold covered PET samples for different sputtering times are shown in Fig. 3. The SEM imaging of the samples sputtered for less than 20 s was precluded by sample charging. Much weaker but still significant charging was observed even on the samples sputtered for 20–25 s, indicating a discontinuity of the deposited gold layer [12]. The charging adversely affects the quality of the first two SEM images which should be viewed cautiously. No charging was observed on the samples sputtered for 30–65 s, when the deposited gold layers are continuous but lateral fluctuations of the thickness values are still significant (see also [12]). The average thickness of these layers change from 4 to 10 nm. The thickness fluctuation manifest itself by the presence of worm-like, dark regions on the SEM images which likely correspond to the regions with very thin gold coverage. The dark regions essentially disappear for the 80 s sputtering time. It should be noted that according to our previous measurements of gold layer electrical conductivity [12] the layers produced by sputtering for 30 s and more are continuous in the sense of a good electrical conductivity. It is seen from Fig. 3 that with increasing sputtering time (above 30 s), gradual association of gold clusters takes place and for the sputtering times above 80 s a homogeneous gold layer is formed.

Our AFM and SEM observations proved, in accordance with known nucleation theory of metallic layer deposition [15], that in the course of sputtering the gold layer grows from small gold clusters. The theory assumes that the deposition starts from creation of metallic clusters at the atomic level on the substrate surface, which gradually enlarge at later deposition stages. Thus at the beginning of the deposition process the gold layer must be discontinuous and partially transparent for electromagnetic waves [12]. The transparency was examined in next experiment performed on the samples with discontinuous gold layers prepared by sputtering and on the reference samples prepared by lithographic etching (see above). By the etching it was possible to prepare the samples with μm gold strips or islands corresponding to (15–100%) gold coverage. Optical images of typical reference samples with different gold coverage, prepared by one or two etching steps, are presented in Fig. 4.

The dependence of the measured 1/VSWR ratio on the sample coverage for the samples prepared by lithographic etching and by sputtering is shown in Fig. 5. The measured 1/VSWR ratio is the same for the structures prepared by one- and two-step etching. As expected, the measured values of 1/VSWR indicate that the layers prepared by lithographic etching are discontinuous. For the samples prepared by sputtering for 0–25 s in average, constant values of $1/\mathrm{VSWR} = 0.301 \pm 0.002$ were measured, which are also shown in Fig. 5 by open circles. It is seen that the samples with sputtered, discontinuous gold layers exhibit similar values of 1/VSWR as the reference samples prepared by the lithography. From comparison of the SEM observations (Fig. 2) with the results of microwave reflection measurement it may be concluded that the microwave technique is insensitive to the details of the gold layer morphology if the layer is discontinuous, or continuous but still heterogeneous with the regions of very thin gold coverage. The rapid decrease of the 1/VSRW value takes place at the moment when the gold coverage becomes sufficiently thick and homogeneous. Thus, it may be concluded that the microwave reflectivity of sub-μm, discontinuous gold layers can be simulated by artificial μm structures prepared by common lithography and that the microwave technique may be an useful instrument for investigation of metal coverage of polymers.

4. Conclusion

The results of this study can be summarized as follows:

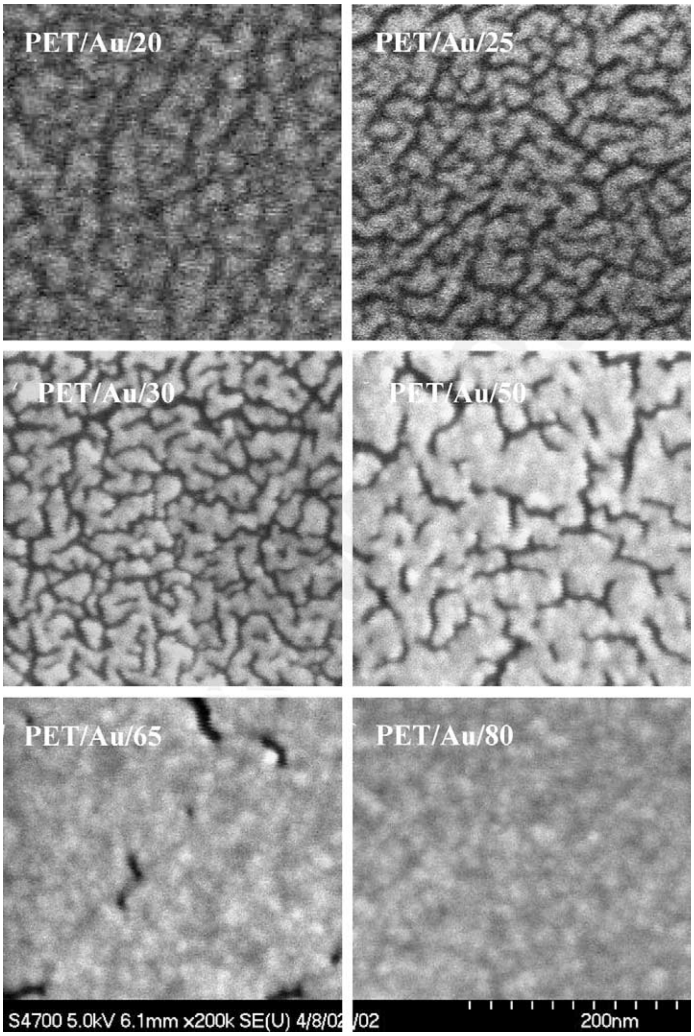

Fig. 3. SEM images of PET with gold layers sputtered for 20, 25, 30, 50, 65 and 80 s. Weak but still significant charging was observed on the samples sputtered for 20–25 s, which adversely affects the quality of the first two SEM images which should be viewed cautiously.

- The surface morphology of the sputtered gold layer observed by AFM technique differs significantly for discontinuous and continuous gold coverage. It was shown by AFM that the gold layer growth starts from small gold clusters, which later associate and form a continuous coverage. The surface morphology of pristine PET substrate and the PET covered with very thin gold layer (sputtering times below 10 s) does not differ significantly on AFM images.
- By SEM imaging it is possible to follow the grow of the gold coverage as a function of the sputtering time too. At medium sputtering times from 30 to 65 s, for which the conductivity measurements prove continuous gold coverage, the SEM images still show the presence of the regions with very thin gold coverage.
- Both, AFM and SEM observations confirm the layer growth from small gold clusters which later associate and form larger aggregates. This finding is consistent with known nucleation theory of metal layer formation on substrates.
- The measured VSWR depends on the gold coverage and it is similar for sputtered samples and control samples prepared by lithographic etching. It may therefore be concluded that the microwave reflectivity of sputtered, discontinuous gold layers can be simulated by much larger structures prepared by lithographic etching. The microwave technique appears to be useful instrument for the examination of thin

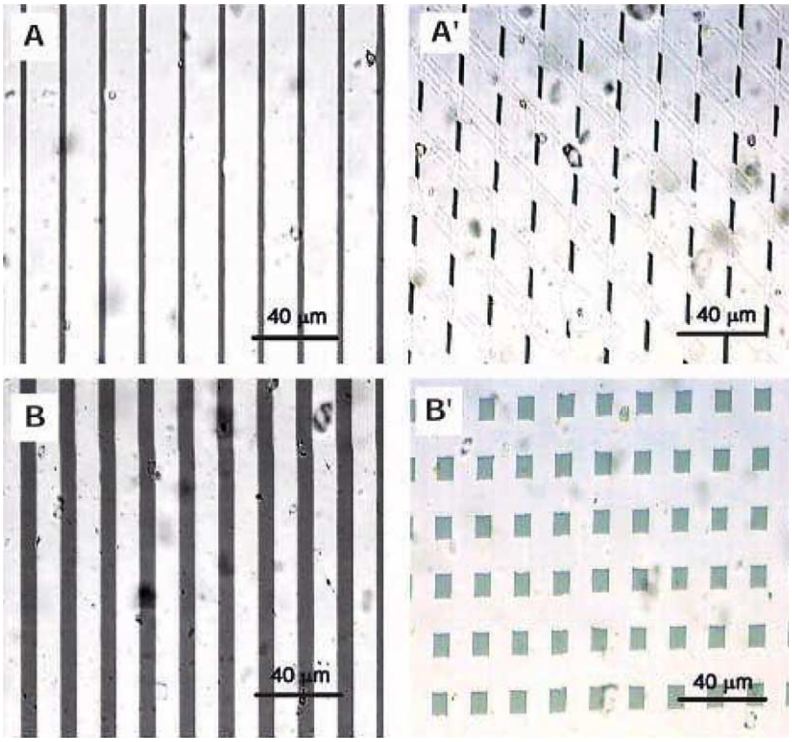

Fig. 4. Optical microscopy images of control samples prepared by lithographic etching of sputtered gold layer on PET. The samples with gold strips and mean gold coverage of 15% and 40% prepared in one etching step are shown in (A) and (B) respectively. The samples with gold islands prepared by additional etching through the mask turned by 90° with 6% and 16% mean coverage are shown in (A′) and (B′) respectively.

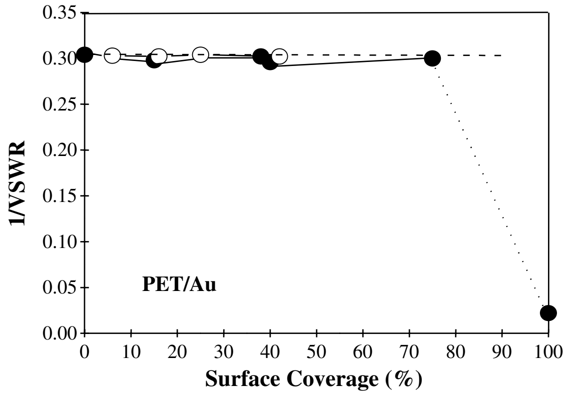

Fig. 5. The dependence of the 1/VSWR on the mean gold coverage measured on the samples prepared by the lithographic etching. Solid circles: the samples after first etching measured in cross-polar direction (see Figs. 4A and B). Open circles: the same after additional etching (see Figs. 4A′ and B′). The average 1/VSWR value for the samples sputtered for 0–25 s is shown by dashed line.

metal coverage on polymers and especially for the determination of the transition point to homogeneous, continuous coverage.

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