Characterization of Evaporated and Sputtered Thin Au Layers on Poly(ethylene terephtalate)

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ABSTRACT: Gold layers were prepared on poly(ethylene terephtalate) substrate by diode sputtering and vacuum evaporation. The mean layer thickness was determined by atomic absorption spectroscopy. Sheet electrical resistance and reflection of electromagnetic waves were used for the characterization of layers. Surface morphology of the layers was determined using atomic force and scanning electron microscopy. While the sputtering was found to proceed with two different rates, the vacuum evaporation proceeds at a constant rate. Rapid decrease of the sheet resistance was observed during sputtering, depending on the layer thickness, in contrast to vacuum evaporation. This can be due to different mechanisms of the Au deposition. According to the measured reflection of electromagnetic waves, the layers prepared by both techniques, *i.e.*, sputtering and vacuum evaporation, are discontinuous for thicknesses below 4 nm, continuous but heterogeneous for thickness from 4 to 10 nm, and continuous and homogeneous for thickness above 10 nm. The morphology of the layers prepared by vacuum evaporation does not depend on the layer thickness. Rounded clusters are observed on the surface of the evaporated layers. The layers prepared by sputtering exhibit significantly different morphology with much smaller, pointed clusters. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1698–1704, 2006

Key words: poly(ethylene terephtalate); gold; thin layer; sputtering; evaporation; surface and layer characterization

INTRODUCTION

Metallized polymer films (from one or both sides) are widely used in industry for different purposes, ranging from food and microelectronics packaging to biosensors.[1–5] Structure of the metal coverage is mainly influenced by the nucleation, growth, and adhesion of metal films on polymers.[5,6] For example, in microelectronics, this metallized films form basic structures for construction of diodes (with negative differential resistance)[7] and light-emitting polymer-based diodes in optoelectronics.[8] Metal layer can be prepared on the polymer surface by sputtering, vacuum evaporation, or by electrochemical procedures.[4,7,9]

Microscopic theory of nucleation processes for sputtering and vacuum evaporation was suggested by Walton[10] and for polymer–metal systems by Faupel et al.[5] Two nucleation mechanisms are usually considered. In so-called preferred nucleation, metal atoms are trapped at preferred sites while, in random nucleation, nuclei are formed by metal atom encounters. Both processes have been observed in polymer metallization.[5,11]

Metals and polymers are extremely dissimilar materials. While metals are densely packed crystalline solids with a high cohesive energy, polymers are made up of large covalently bonded macromolecules held together by very weak Van der Waals interactions in an open structure. Practically, no intermixing should occur when a piece of metal of low reactivity (*e.g.*, Au, Ag, Pt, and Pd) is brought into close contact with a polymer surface.[5] Nucleation takes place at special surface sites, the nature of which is not known yet. One can, for example, think of terminal groups of the polymer chains, impurities, or attractive local arrangements of the chains. The number of these surface defects can be strongly increased by a polymer surface treatment.[5]

In this work, gold layers of different thickness, prepared by sputtering and vacuum evaporation on poly(ethylene terephtalate) (PET), are characterized by measuring of sheet electrical resistance, reflection of electromagnetic waves and by atomic force (AFM) and

scanning electron microscopy (SEM). The mean layer thickness is determined by atomic absorption spectroscopy (AAS).

EXPERIMENTAL

Oriented PET (Goodfellow Ltd., Cambridge, UK; density, 1.4 g cm^{-3}; T_m = 260°C; T_g = 80°C;) in the form of 50-μm thick foils was used in the present experiments. The gold layers were prepared from Au target (99.999%) by two deposition methods:

i. diode sputtering on BAL-TEC, SCD 050 device. Typical deposition parameters were room deposition temperature, deposition times from 0 to 130 s, total argon pressure about 4 Pa, electrode distance of 50 mm, and current of 20 mA.
ii. vacuum evaporation on LEYBOLD-Heraeus, Univex 450 device with typical parameters, such as room deposition temperature, deposition times from 0 to 180 s, total pressure of about 10^{-5} Pa, and molybdenum nef with current 4.8 A.

The thickness of deposited Au layers was determined by means of AAS on a Varian AA 880 device. For this to be done, the Au deposited on a 4 × 4 cm^2 sample area was dissolved in a HCl/HNO$_3$ (3:1) mixture, and the Au concentration in the solution was determined by AAS using flame-atomization technique at 242.8 nm wavelength. From Au concentration, the mean layer thickness was determined with a typical uncertainty of ±5%.

Reflection of electromagnetic waves was used for the characterization of continuous and discontinuous gold layers on the PET surface. The technique was described earlier.[4] The frequency of the wave, incident perpendicularly on the Au 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 homogenous Au coverage. [4] Generally, vswr→ ∞ indicates an ideally conductive metallic layer. The continuity and homogeneity of the layers were further examined (by measuring of layer sheet resistance) using two point technique with a picoammeter KEITHLEY 487. The measurements were performed at a pressure of about 10 kPa.

The surface morphology of pristine and metallized PET was examined using AFM (contact mode technique), performed under ambient conditions, on a commercial MultiMode Digital Instruments NanoScope™ Dimension IIIa device. Olympus oxide-sharpened silicon nitride probes OMCL TR with a spring constant of 0.02 N m^{-1} were chosen. The normal force

of the tip on the sample surface was reduced to the lowest possible level and it did not exceed 10 nN. It was certified by repeated measurements of the same region, so that the surface morphology did not change after five consecutive AFM scans.

A SEM HITACHI S 4700 (resolution, 1.5 nm; maximum magnification, 5 × 10^5) was used for the detection of deposited 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 10 kV voltage results in best images of the surface morphology.

RESULTS AND DISCUSSION

The continuity, homogeneity, and surface morphology of Au layers prepared by sputtering on polymer surface were studied earlier.[4,12] In this work, Au layers prepared by sputtering and vacuum evaporation on PET substrate are characterized and their parameters compared. In Figure 1, the dependence of the layer thickness on the deposition time is shown for both deposition techniques. The layer thickness, determined from AAS analysis of Au amount detached from the sample surface, represents the average layer thickness. Because of limited sensitivity of the AAS method, it was impossible to measure the layer thickness for very thin layers prepared by sputtering for times below 10 s and by vacuum evaporation for times below 20 s. It is obvious that the sputtering proceeds with two different deposition rates (tangent a and a' in Fig. 1) expressed as a slope of layer thickness *versus* deposition time dependence. It proceeds slower for deposition times 10–25 s (a = 0.09) and much faster for longer deposition times (a' = 0.18). The deposition using vacuum evaporation proceeds with a constant deposition rate. To facilitate the comparison of both deposition techniques in transient region between continuous and discontinuous layers, the deposition rate of vacuum evaporation was adjusted to be close to that of sputtering for short deposition times (b = 0.08, see Fig. 1) typical for preparation of discontinuous layers.[4] Properties of the layers prepared by different deposition techniques are compared in dependence on their real thickness.

The measured sheet resistance R_s (A) and 1/vswr values (B) as a function of the layer thickness are shown in Figure 2. Both complementary quantities well characterize the transition from discontinuous to continuous, homogenous metal coverage.[4] The sputtering (Fig. 2(A)) leads to a very rapid decrease of R_s at the moment when the layer becomes suddenly continuous. For vacuum evaporation much slower decrease of R_s is observed and continuity is achieved for larger
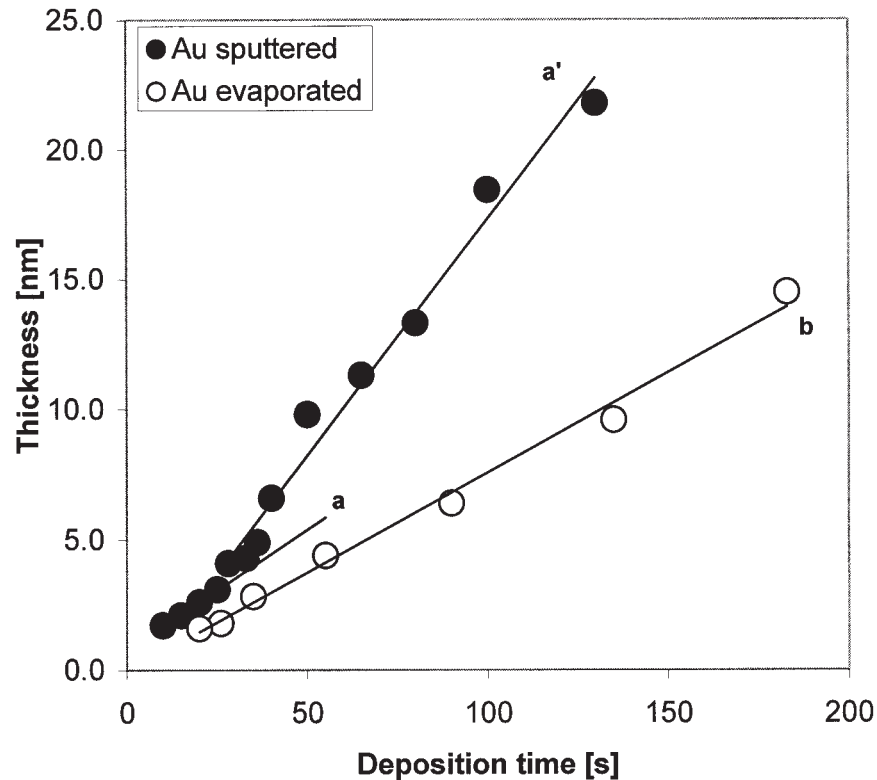
Figure 1 Dependence of the Au layer thickness deposited on PET substrate on deposition time for sputtered (*a*, *a'*) and evaporated (*b*) Au layers.

layer thickness. The difference can be explained by different mechanisms of Au deposition, deposition of separated atoms by sputtering and larger atomic clusters by vacuum evaporation. The deposition of separated atoms facilitates creation of continuous layer. The observed difference between the layer R_s and the resistivity[13] of bulk Au $R_{Au} = 2.5 \times 10^{-6}$ Ω cm can be explained by extremely low thickness of the layers and their lower compactness in comparison with bulk Au produced by common metallurgical processes.

From comparison of Figures 2(A) and 2(B) it is obvious that the quantity 1/vswr, characterizing reflection of electromagnetic waves, is less sensitive to the layer continuity in comparison with sheet resistance R_s. This can be explained by the fact that the electromagnetic wave reflection depends not only on the layer continuity but also on its homogeneity. According to the sheet resistance measurement, the layer continuity is achieved at lower layer thickness for sputtered layers in comparison with evaporated ones. However, there is no principle difference, within experimental errors, between electromagnetic wave reflection from the continuous layers prepared by both methods. According to the measured 1/vswr values, both sputtered and evaporated layers are discontinuous for thickness below 4 nm, continuous but heterogeneous for thickness from 4 to 10 nm, and continuous and homogenous for thickness above 10 nm.

Surface morphology of deposited Au layers was characterized by AFM (Fig. 3) and SEM (Fig. 4) techniques. The differences in the surface morphology of layers with similar thickness prepared by sputtering and vacuum evaporation are obvious. Discontinuous as well as continuous homogenous layers were prepared [see also Fig. 2(B)]. It is seen from Figure 3 that oriented PET film exhibits homogenous surface, the roughness of which was about 1 nm according to AFM measurement.[14] As expected, the Au deposition leads to changes in the surface morphology and roughness in comparison with pristine PET. On the layers prepared by vacuum evaporation no significant changes in the surface morphology are observed in dependence on the layer thickness (Fig. 3). Rounded Au clusters appears on the sample surface. Most pronounced roughness along the *z*-coordinate was observed on the 4.9-nm thick Au layer. Quite another surface morphology was observed on the layers prepared by sputtering. Au in discontinuous layers creates much smaller, pointed, and higher clusters. With increasing layer thickness, the clusters enlarge and at the same time the surface roughness increases. The differences in the surface morphology can be explained by different mechanisms of Au deposition, single atoms in sputtering and atomic clusters in vacuum evaporation. Needle-like surface of sputtered, discontinuous layers may be due to the mechanism of
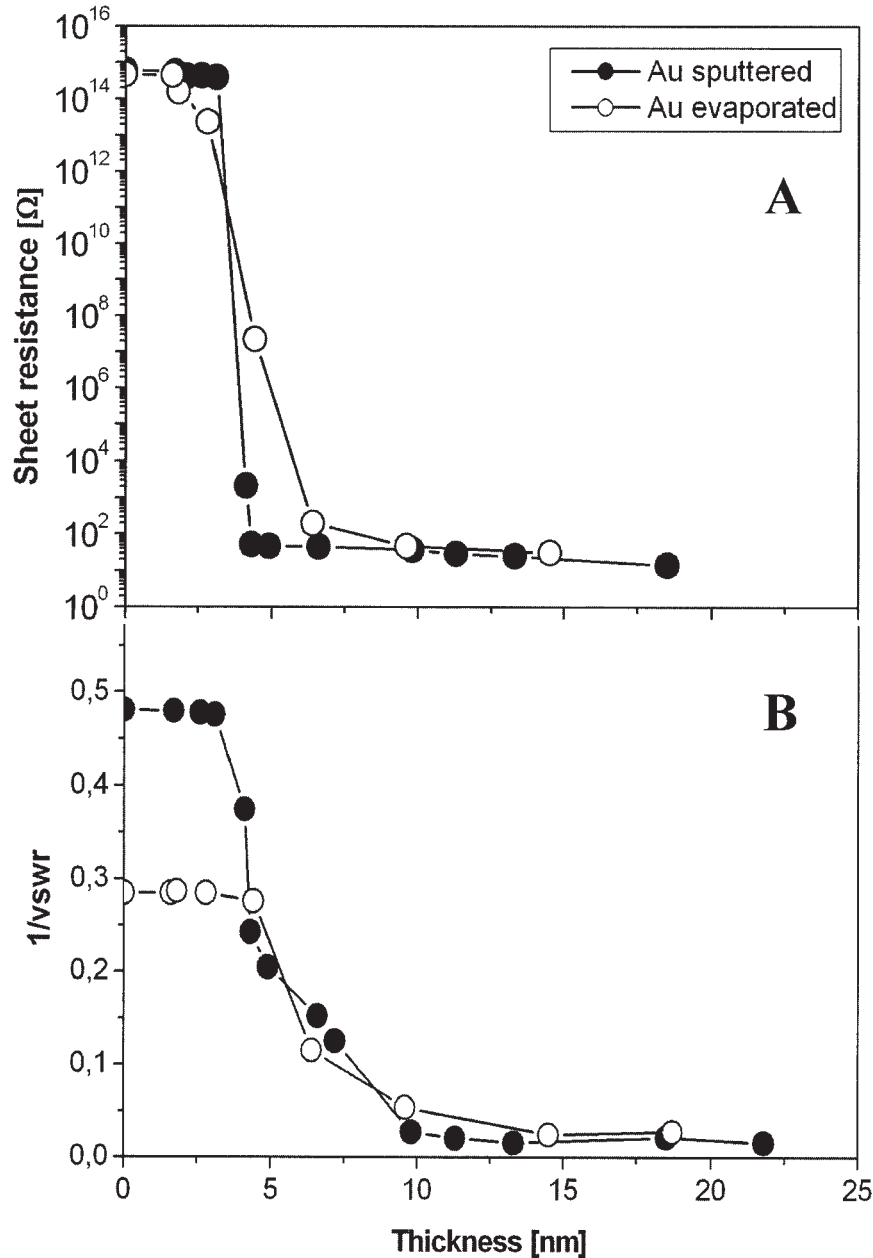
Figure 2   Dependence of the sheet resistance (A) and value 1/vswr (B) on layer thickness for sputtered and evaporated Au layers on PET substrate.

Au deposition, in which the initial metal islands serves as preferential nucleation centers for further Au atoms than do dissimilar polar substrates.[5]

The SEM images of the same samples as in Figure 3 are presented in Figure 4. SEM imaging of pristine PET is impossible because of sample charging. This effect is also observed on discontinuous layers (thickness about 3 nm) prepared by both techniques and partly on the evaporated layer 4.9-nm thick. As to continuity of the deposited layers, the results of SEM imaging are in accord with those obtained in the measurement of sheet resistance and reflection of electromagnetic waves (Fig. 2). By comparison

with Figure 2, it is obvious that for thickness above 5 nm the layer is continuous, but in SEM imaging an island-like structure is still observed. In contrast to AFM results, in the SEM imaging, no significant differences are observed in worm-like structure of layers prepared by sputtering and vacuum evaporation. With increasing layer thickness, the surface regions in which the Au presence is not detected by SEM (because of too low thickness of Au coverage) diminish. The present results confirm the well-known fact that for the SEM imaging of insulators the Au coverage of samples by vacuum evaporation is more suitable than by sputtering, since the former
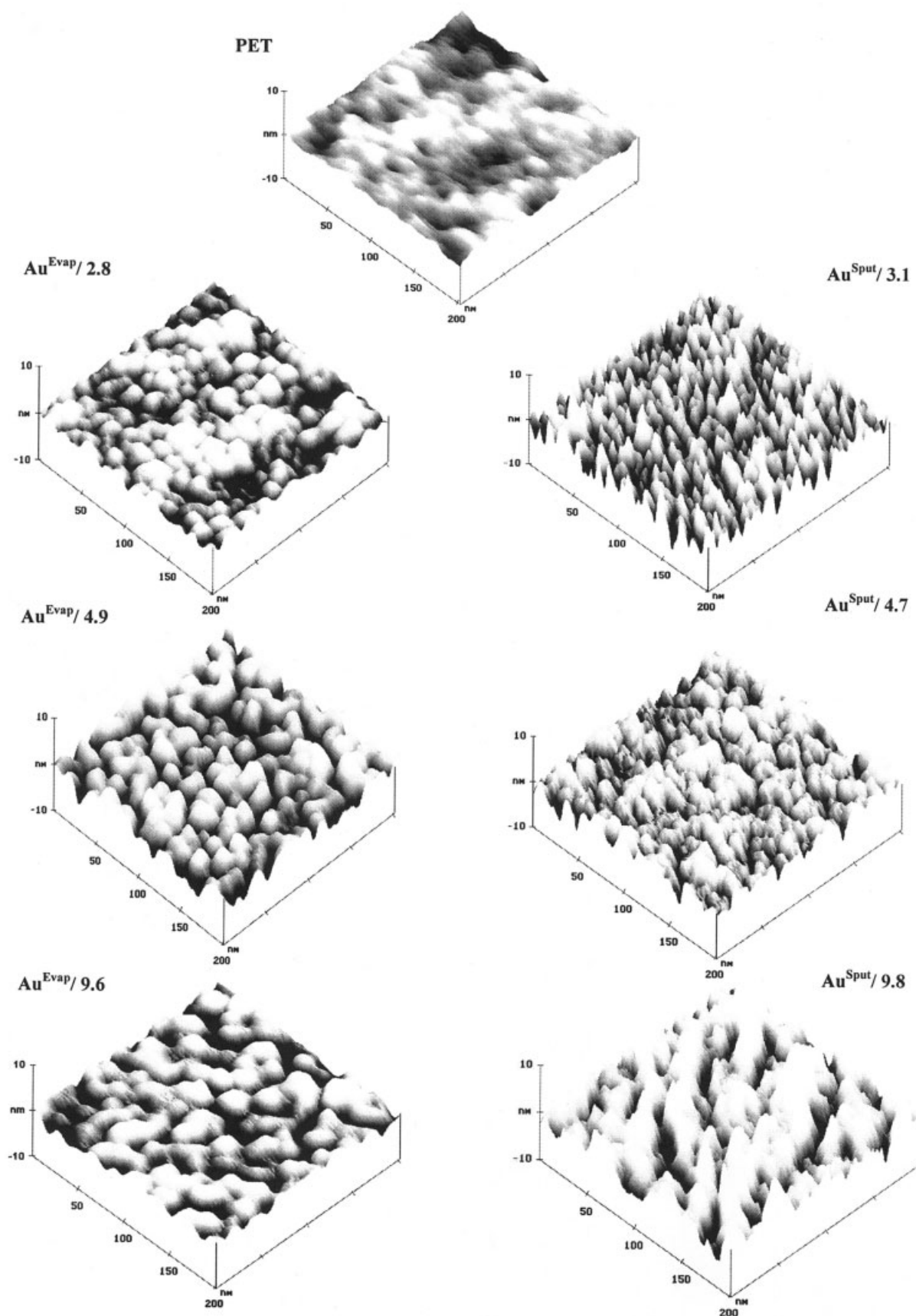
Figure 3 AFM images of PET and evaporated (Evap) and sputtered (Sput) Au layers on PET. The numbers denote layer thickness of deposited Au layers in nanometers.
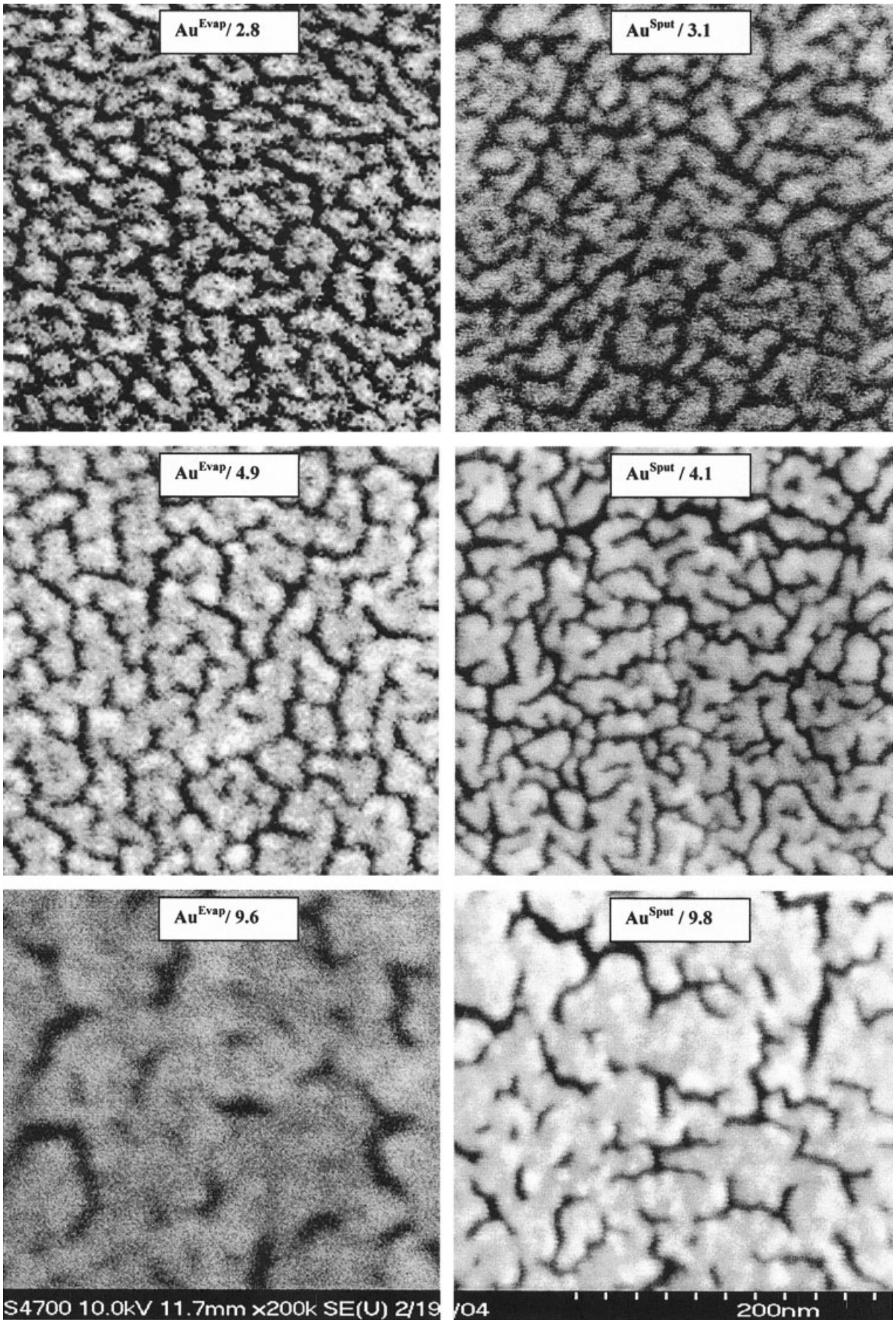
Figure 4 SEM images of evaporated (Evap) and sputtered (Sput) gold layers on PET. The numbers denote layer thickness of deposited Au layers in nanometers.

technique leads to smaller deformation of the sample surface. The ultrathin silicon oxide coatings on PET substrate does not influence the surface morphology (study with SEM method) of evaporated thin Au (45 and 90 nm) layers.[15]

CONCLUSIONS

The results of the present study can be summarized as follows:

- The sputtering of Au layers proceeds with two different deposition rates, depending on the sputtering time, and the vacuum evaporation proceeds with a constant deposition rate.
- The sputtering leads to a very rapid decrease of sheet resistance R_s at the moment when the layer becomes suddenly continuous. For vacuum evaporation, much slower decrease of R_s is observed and the continuity is achieved for larger layer thickness. The difference can be explained by different mechanisms of Au deposition, deposition of separated atoms by sputtering, and larger atomic clusters by vacuum evaporation.
- According to 1/vswr value, characterizing the reflection of electromagnetic waves, both sputtered and evaporated layers are discontinuous for thickness below 4 nm, continuous but heterogeneous for thickness from 4 to 10 nm, and continuous and homogenous for thickness above 10 nm.
- On the layers prepared by vacuum evaporation no significant changes in the surface morphology are observed in dependence on the layer thickness. Rounded Au clusters appears o the sample surface. Quite another surface morphology was observed on the layers prepared by sputtering. Au in discontinuous layers creates much smaller, pointed, and higher clusters. With increasing layer thickness, the clusters enlarge and at the same time the surface roughness increases. The differences in the surface morphology can be ex-

plained by different mechanisms of the Au deposition, single atoms in sputtering and atomic clusters in vacuum evaporation.
- As to continuity of the deposited layers, the results of SEM imaging are in accord with those obtained in the measurement of sheet resistance and reflection of electromagnetic waves.
- The present results confirm the well-known fact that for the SEM imaging of insulators the Au coverage of samples by vacuum evaporation is more suitable than by sputtering, since the former technique leads to smaller deformation of the sample surface.

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