

Correlation between Structure and Stress–Strain Characteristics of Metallic Coatings Deposited onto a Polymer by the Method of Ionic Plasma Sputtering¹

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Received April 8, 2010;

Revised Manuscript Received October 18, 2010

Abstract—Data on the strength of coatings based on noble metals (Pt, Au) deposited onto PET films by the method of ionic plasma sputtering are analyzed. In addition to precipitation of the metal, this mode of deposition is accompanied by modification of the surface polymer layer due to its interaction with plasma. As a result, a complex three-layered structure near the polymer surface forms. A new method for estimating the strength of coatings deposited onto polymer supports is advanced. This method makes it possible to analyze stress–strain characteristics of the three-layered systems that emerge owing to deposition of nanoscale layers of noble metals on polymer films via ionic plasma sputtering. The proposed relationships are in fair agreement with the experimental data.

DOI: 10.1134/S0965545X11030047

INTRODUCTION

Metallized or metal-coated polymeric films are widely used in different areas: from food packaging to microelectronics and biosensors [1–3]. The structure of metallic coatings depends on metallic films' nucleation, growth, and adhesion to polymers. Metallic layers can be deposited onto the surface of polymers by ionic plasma or vacuum sputtering or an electrochemical procedure [4].

The procedure of depositing metallic layers onto polymers can exert a marked effect on the polymers' structure and, hence, characteristics. In particular, as was shown in [5], the deposition of a gold coating onto the surface of PET by the method of thermal evaporation of a metal in vacuum or by ionic plasma sputtering can lead to the preparation of systems with different structures of metallic layers and different characters of their interaction with the supporting polymer. It was shown in [6, 7] that the ionic plasma deposition of noble metals onto polymers involves not only condensation of metal on the surface but also interaction between plasma and the polymer surface. As a result, there forms a complex polymer–metal system that contains not only a cold-plasma modified surface layer

of the polymer but also a supporting polymer and a metallic layer.

The objective of this study is to estimate the contribution from each component of the above complex system to the strength characteristics of layers produced via the deposition of noble metals onto the surface of PET by the ionic plasma method.

EXPERIMENTAL

In this study, we investigated commercial films of amorphous unoriented PET with a thickness of 100 μm . Dumbbell-shaped specimens were cut from films; their gage size was 6 mm \times 22 mm. The cut samples were decorated with gold and platinum layers of different thicknesses by the method of ionic plasma sputtering on an Eiko IB-3 unit. To measure the thickness of the coating, the following procedure was applied. Under similar conditions, a glass plate was decorated with a thin film of the material under study; then, the coating was scratched with a thin wooden stick that did not disturb the integrity of the support, and the depth of the scratch was measured with an atomic force microscope. These measurements allowed construction of calibration plots illustrating the thickness of the coating versus the time of deposition of the metal onto the glass support. The coating thickness was controlled by the duration of deposition.

¹ This work was supported by the State Program for Support of Leading Scientific Schools (NSh 2467.2008.3) and State Contract no. 02.740.11.0143.

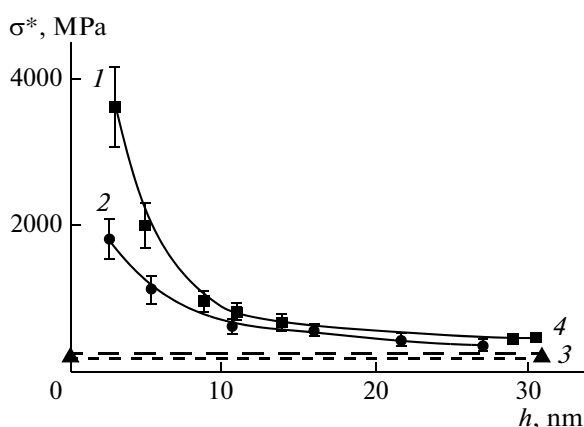


Fig. 1. Strengths of (1) platinum and (2) gold coatings deposited onto a supporting PET film by ionic plasma sputtering versus their thicknesses, calculation according to Eq. (1) at 20°C [10]; (3, 4) the strengths of bulk platinum and gold [11].

The metal-coated PET samples were stretched on an Instron 1122 universal tensile machine at a constant crosshead speed of 100 mm/min at 20°C. Microscopic observations were performed on a Hitachi S-520 scanning electron microscope and on a Nanoscope IIIa atomic force microscope (Digital Instruments, Santa Barbara, United States) in the contact scanning mode.

The strength of the deposited coatings was estimated through the relationship

$$\sigma^* = L\sigma_0/3h, \quad (1)$$

where h is the thickness of the coating, σ^* is its strength, and σ_0 is the stress on the support. Details of the calculation procedure were described in [8–10].

RESULTS AND DISCUSSION

Figure 1 presents the dependence of the strengths of the platinum and gold coatings deposited onto the supporting PET film by the method of ionic plasma deposition as calculated through Eq. (1) on the thicknesses of the coatings [9, 10]. It is well seen that the strengths of both metals are nearly independent of their thicknesses in the interval from 30 to ~15 nm. In this interval, the strengths of metals vary from 180 to 220 MPa for gold and from 250 to 300 MPa for platinum. These values quantitatively agree with the known values of strength for bulk polymers (176–250 MPa for gold and 240–350 MPa for platinum) [11]. At the same time, as follows from Fig. 1, starting with a thickness of ~15 nm, both of metals show dramatic increases in strength with a decrease in the thickness of the deposited coating. The strength reaches 1800 MPa for platinum and 3700 MPa for gold. The strength of the metal in nanolayers exceeds the strength of the bulk material by at least one order of magnitude. Note

that the strength of a coating strongly depends on the deformation temperature of the supporting film. As follows from Fig. 1, this effect occurs only at low thicknesses (less than ~10 nm). When the thickness of the coating is greater, the strength of the coating becomes independent of the deformation temperature and the strength approach the strength of the bulk metals. Evidently, in this narrow temperature interval, it is unlikely that there will be any marked changes in the strength of the bulk noble metals with very high melting temperatures ($T_m(\text{Au}) = 1063^\circ\text{C}$; $T_m(\text{Pt}) = 1769^\circ\text{C}$). A question arises about the validity of the high values of strength of the metallic coatings in the interval of low thicknesses because Eq. (1) used here for estimation of the strength of the coatings gives adequate estimates of strength only for the bilayer-polymer-metallic-coating system, which in [12–15] was called a “soft coating on a rigid substratum” system. In this case, the key parameter in estimating the strength is the size of the fracture fragments of the coating, L , that form during tensile drawing of the supporting polymer.

At the same time, numerous studies [16–18] show that deposition of the metallic coating on the polymer supports via ionic plasma or thermal sputtering does not immediately provide a continuous layer. Usually, the first portions of the deposited metal condense on the polymer surface as individual islands. In other words, at the early stages of sputtering, the polymer surface is covered by a formed system of discrete nanoclusters whose dimensions, size distribution, and mutual arrangement on the support are controlled by the sputtering rate, by the temperature on the polymer support, by the reactivity of metallic atoms, etc. In this context, the very concept of “thickness of the coating” becomes vague at short times of deposition and at low rates of sputtering of the metal onto the polymer surface. In this case, it helps to use the effective or nominal thickness of the coating [19, 20], because, in fact, at the early stages of metal sputtering, no continuous coating on the polymer surface forms. This circumstance leads to evident difficulties in the estimation of the mechanical characteristics of the coatings at low thicknesses because thickness h is involved in Eq. (1).

Evidently, this mechanism of formation of coatings strongly affects characteristics of the polymer-metal system on the whole. Figure 2 presents the surface electrical resistance plotted against the thickness of the metallic (Au) coating [5] deposited by ionic plasma and thermal sputtering. It is well seen that, in both cases, electrical resistance is independent of the thickness of the gold coating when the thickness exceeds approximately 5–7 nm. With a decrease in the nominal thickness, resistance critically increases (by more than 12 orders of magnitude). Obviously, this dramatic increase in the electrical resistance is related to the disturbed integrity of the metallic layer; perco-

lation of the metallic clusters on the polymer surface is violated, and, as a consequence, electrical conductivity decreases.

Therefore, at the early stages of the deposition (sputtering) of the noble metals onto the polymer surface, no continuous coating forms, but fragmentation of the surface polymer layer occurs, a circumstance that allows the use of Eq. (1) to estimate the strength. A question arises about which units are involved in fragmentation on the polymer surface in the absence of any continuous metallic coating. This problem was discussed in detail in [21]. It was found that the ionic plasma deposition of coatings based on noble metals onto the polymers is accompanied by the precipitation and modification of the polymer surface by cold plasma. It is well known that the action of cold plasma on polymers includes chemical modification of their surface. This phenomenon has been well studied and is widely used in practice [22, 23]. Plasma treatment of the polymer surface is primarily used to modify contact characteristics (wetting, adhesion to metallic thin layers, glueability, controlled adhesion of print inks, etc.). Nowadays, it is known that modified nanolayers form on the surface of polymers subjected to plasma treatment and that these nanolayers have specific chemical compositions and unique physicochemical, electrical, and other characteristics.

Evidently, the stress–strain characteristic of plasma-modified nanolayers in the polymers too should be different from the corresponding characteristics of the unmodified virgin polymer. Indeed, as was shown in [6, 7, 21], the cold-plasma treatment of polymers leads to development of a rigid surface layer on their surface and they acquire the characteristics of “a rigid coating on a soft substratum” system. Because of further deformation of the supporting polymer, the plasma-modified layer undergoes fragmentation, a phenomenon that makes it possible to estimate the stress–strain characteristics of the above layers according to the approach advanced in [8–10, 12–15].

It was shown in [6, 21] that the fragmentation of the plasma-modified layer is appreciably different from the earlier studied processes of fragmentation of metallic coatings. From the scatter of the experimental data, it may be concluded that fractured-fragment size L is almost independent of the duration of plasma treatment of PET. This circumstance implies that the chemically modified layer forms in the polymers at the earliest stages of plasma treatment. Further plasma treatment is not accompanied by any marked increase in the thickness of the modified layer, which remains almost unchanged. At the same time, this result agrees with other surface characteristics of the polymer [24], which indicate that both the contact angle and the surface charge density change only within the several first tens of seconds of plasma treatment; after, these char-

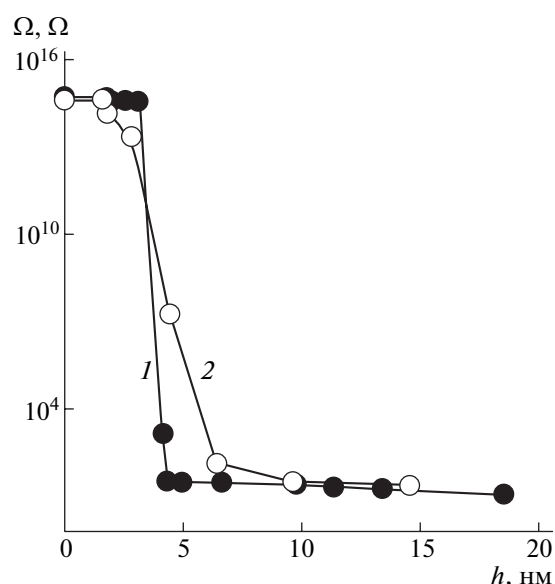


Fig. 2. Electrical resistance Ω of thin gold-based layers plotted against thickness h . Metal is deposited onto the polymer via (1) ionic plasma sputtering and (2) thermal sputtering [5].

acteristics remain unchanged. Note that the thickness of the plasma-modified surface layer (according to microscopic data [6, 21] and experimental data obtained by other methods [25–27]) is approximately 50–150 nm. In particular, for PET, this parameter approaches ~ 80 nm and is practically independent of the duration of plasma treatment of the polymers. Under the assumption that the thickness of the modified layer is $h = 80$ nm, the stress–strain characteristics of the above layers were estimated through Eq. (1) in [21]. It was shown that the strength of the coating is ~ 33.3 MPa when the supporting polymer is stretched at 20°C and ~ 3.7 MPa when the supporting polymer is stretched at 90°C . The above data show that, depending on temperature, the strength of the modified layer markedly changes. Even though, in this layer, the polymer is crosslinked [23], it remains sensitive to transition from the glassy state to the rubbery state.

Therefore, the dependence of metallic-coating strength on metallic-coating thickness shown in Fig. 1 does not reflect the actual physical nature of this phenomenon and does not allow the use of the above data for estimation of the stress–strain characteristics of metallic coatings deposited onto metals by the methods of ionic plasma sputtering. This dependence can be used only at the thickness of the coating at which a continuous metallic layer forms on the polymer surface. According to the data obtained from electron microscopic observations [28] and via other methods [5], a continuous metallic coating forms on the polymer surface when the nominal thickness is greater than 7–10 nm.

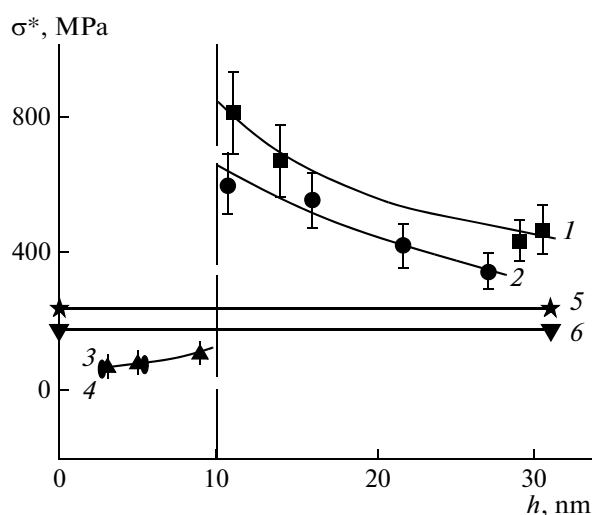


Fig. 3. Strengths σ^* of (1) gold and (2) platinum coatings plotted against thicknesses of the deposited coatings at 20°C and $h > 10$ nm, calculation according to Eq. (1); (3, 4) below 10 nm, calculation according to Eq. (1) with allowance for the thicknesses of the plasma-modified layer (80 nm) for (3) gold and (4) platinum; (5, 6) the strengths of bulk gold and platinum.

In this context, the data shown in Fig. 1 can be conditionally divided into two parts. Some values of this dependence characterize the strength of the metallic coating; this situation corresponds to a nominal thickness of 10–30 nm, when a continuous metallic coating forms [5, 28]. Other data correspond to a nominal thickness below 10 nm; i.e., they can be related to the strength of the plasma-modified surface polymer layer. As was mentioned above, the thickness of this layer is practically constant for all durations of plasma treatment: ~80 nm. If, in Fig. 1, for the values of the coating thickness below 10 nm, the value of 80 nm is substituted, the resultant dependence is critically different (Fig. 3). Of course, the data shown in Fig. 3 are conditional, but they reflect the three-layered structure of the system under study. At the same time, as was mentioned above, Eq. (1) for the estimation of strength, in its physical meaning, makes it possible to estimate the strength of only bilayered “rigid coating on a soft substratum” systems.

Therefore, it is necessary to gain quantitative relationships for the analysis of the stress–strain characteristics of the three-layered polymer–coating systems that can be prepared via ionic plasma sputtering of noble metals onto polymers. Let us try to advance a quantitative approach for the analysis of such three-layered systems comprising a surface polymer layer, a polymer, and a support. Figure 4 presents the schematic pattern of this system.

One of the key features of the above system is the assumption that the plasma-modified sublayer generated at the early instants of ionic plasma sputtering of

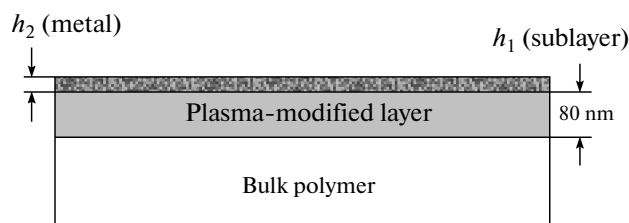


Fig. 4. Schematic presentation of a polymer film with a deposited coating based on a noble metal deposited by the method of ionic plasma sputtering.

metals has a fixed thickness and that, during further sputtering, only the thickness of the pure metallic layer localized on the sublayer changes.

To analyze the real situation, let us consider a thin coating composed of two layers (Fig. 4). Let the strength of layer 1 (the so-called sublayer) with thickness h_1 be equal to σ_1 and the strength of layer 2 (the layer of pure metal resting on the sublayer) with thickness h_2 be σ_2 . Then, after fracture of the coating, it would bear the stress

$$F = \sigma_1 h_1 w + \sigma_2 h_2 w,$$

where w is the width of the coating (the sample). In this case, the effective strength of the coating is calculated by means of dividing the total applied force, F , by the cross section of the coating, $w(h_1 + h_2)$:

$$\sigma_c = \frac{\sigma_1 h_1 + \sigma_2 h_2}{h_1 + h_2}$$

Here, σ_c is the overall strength of the coating, which is estimated through Eq. (1). Figure 1 presents its dependence on the overall thickness of the coating. This dependence can be rewritten as

$$\sigma_c (h_1 + h_2) = \sigma_1 h_1 + \sigma_2 h_2 \quad (2)$$

The strength of the coating calculated through Eq. (1) multiplied by the overall coating thickness, $\sigma_c (h_1 + h_2)$, is plotted against the thickness of the metallic coating, h_2 . This dependence makes it possible to estimate the strength of the bulk metal from its slope, and the interval intersected on the ordinate axis stands for the product of the strength of the sublayer, σ_1 , and its thickness, h_1 . Evidently, it is necessary to consider only the case when $h_2 > 10$ nm, because, at smaller thicknesses, no continuous metallic coating on the polymer surface forms [5, 28]. If the assumption concerning the bilayered structure of the coating is valid, this dependence should be straightened in the coordinates of Eq. (2).

Figure 5 presents the results of treating experimental data that were earlier analyzed according to the bilayered model in [8–10]. First, note the fair straightening of the experimental data in the coordinates of Eq. (2). This result suggests that the assumptions on the bilayered structure of the coating have real experimental justification. The strength estimated from the

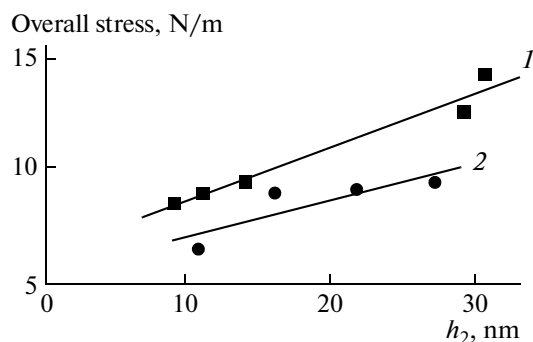


Fig. 5. Strength of the bilayered coating multiplied by its overall thickness, $\sigma_c(h_1 + h_2)$, plotted against the thickness of the metallic coating, h_2 , for (1) platinum and (2) gold coatings deposited onto the PET support by the method of ionic plasma sputtering.

slopes of curves 1 and 2 in Fig. 5 is 243 MPa for platinum and 168 MPa for gold. These values quantitatively correspond to the well-known values of strength for bulk metals (240–350 MPa for platinum and 176–250 MPa for gold) [11]. The fragments intersected by curves 1 and 2 on the ordinate axis make it possible to estimate $\sigma_1 h_1$. If it is assumed that the thickness of the plasma-modified layer (the sublayer) is 80 nm, then strength σ_1 is ~ 77 and ~ 66 MPa for the gold and platinum coatings deposited by ionic plasma sputtering, respectively. It is seen that, in both cases, the strength of the sublayer is practically the same because, in both cases, the regime of ionic plasma deposition was nearly the same (only the kind of metal changed).

In [21], the strength of the plasma-modified layer was estimated through Eq. (1) for the plasma-treated PET samples without any deposition of the metal. In this case, we deal with the bilayered system based on a rigid coating resting on a soft substratum; hence, the use of Eq. (1) to estimate the strength seems quite correct. In this case, the strength of the sublayer is ~ 33.3 MPa. In both cases, the strength of the plasma-modified PET layer with a thickness of 80 m is several megapascals. Our estimates agree well, thereby justifying our assumptions adopted in the derivation of Eq. (2) and, above all, assumptions about the three-layered structure of the systems produced by ionic plasma sputtering of noble metals onto PET.

The two-fold difference between the estimated strength values can have the two following causes. First, the joint action of plasma and atoms (clusters) of noble metals on the polymer is accompanied by the development of a sublayer that contains some traces of the metal in its structure. Evidently, when a polymer is treated with pure plasma, this structure does not form. It is possible that this incorporation of metallic atoms (clusters) into the plasma-modified layer at the early stages of sputtering leads to its strengthening. Second, it is necessary to the fact that estimation of the thick-

ness of the plasma-modified layer (the sublayer) is far from correct. Moreover, this layer likely has no sharp boundary; in this context, its schematic presentation in Fig. 4 is idealized. These phenomena are apparently responsible for the different strength values of the plasma-modified layer obtained through Eqs. (1) and (2).

Hence, in this paper, we have proposed a new approach to estimating the strength of coatings deposited onto polymer supports. This approach makes it possible to analyze the stress–strain characteristics of the three-layered systems that are produced via the deposition of nanoscale layers of noble metals onto polymeric films by the method of ionic plasma sputtering.

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