Deposition of gold nano-particles and nano-layers on polyethylene modified by plasma discharge and chemical treatment

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Abstract

Polyethylene (PE) was treated in Ar plasma discharge and then grafted from methanol solution of 1,2-ethanediethiol to enhance adhesion of gold nano-particles or sputtered gold layers. The modified PE samples were either immersed into freshly prepared colloid solution of Au nano-particles or covered by sputtered, 50 nm thick gold nano-layer. Properties of the plasma modified, dithiol grafted and gold coated PE were studied using XPS, UV–VIS, AFM, EPR, RBS methods and nanoindentation. It was shown that the plasma treatment results in degradation of polymer chain, creation of excessive free radicals and conjugated double bonds. After grafting with 1,2-ethanediethiol the concentration of free radicals declined but the concentration of double bonds remained unchanged. Plasma treatment changes PE surface morphology and increases surface roughness too. Another significant change in the surface morphology and roughness was observed after deposition of Au nano-particles. The presence of Au on the sample surface after the coating with Au nano-particles was proved by XPS and RBS methods. Nanoindentation measurements shown that the grafting of plasma activated PE surface with dithiol increases significantly adhesion of sputtered Au nano-layer.

1. Introduction

Metal–polymer composites are attractive for many applications, especially in microelectronics [1]. Mutual interaction between metal and polymers is generally very weak but it can be increased if the polymer surface is modified prior to metal deposition. Several modification techniques, physical, chemical or their combination, have been suggested for enhancing metal adhesion [2,3]. Gold nano-particles, due to their unique electrical, optical and photophysical properties, are expected to provide variety of potential applications in electronic and sensor materials [4–7]. The well known stability, non-reactivity and bioinertness of gold is used with advantage in medical diagnostics [8], Raman spectroscopy [9], biological imaging [10] and biosensors [11]. Gold nano-particles are promising structures for biomedical applications, structures combining gold nano-particles with polymers [12–14]. Since gold is the most inert metal the adhesion between gold particles and polymers is expected to be very poor. However, gold can easily react with thiol (–SH) groups, which can be fixed on the polymer surface modified beforehand in a proper manner. The polymer surface can efficiently be modified by irradiation with plasma, ultraviolet light from an excimer lamp or by ion irradiation [15–17].

In this work the polyethylene (PE) surface was modified by plasma discharge and subsequently grafted with 1,2-ethanedithiol to introduce thiol (–SH) groups. Short dithiol is expected to be fixed via one of –SH groups to radicals created by the preceding plasma treatment. Next, the free –SH group are allowed to interact either with gold nano-particles or with gold atoms from sputtered Au nano-layer. The main goal of this study is to examine the effect of the plasma treatment and dithiol grafting on the binding of gold nano-particles and on the adhesion of sputtered gold layer on the PE surface.

2. Experimental

2.1. Materials, plasma modification, grafting and sputtering

Oriented, high density polyethylene (PE, ρ = 0.952 g cm⁻³) in the form of 40 μm thick foils (supplied by Granitol Ltd., Czech Republic) was used in the present experiments. The samples were modified in diode plasma discharge on Balzers SCD 050 device for
240 s. DC Ar plasma was obtained under following conditions: Ar gas purity 99.997%, discharge power of 8.6 W, Ar flow ~0.3 l s\(^{-1}\), working pressure of 10 Pa, distance between the electrode (48 cm\(^2\) in area) and the sample of 50 nm, chamber volume about 1000 cm\(^3\) and plasma volume of 240 cm\(^3\).

The plasma modified PE surface was coated either with Au nano-particles or with sputtered Au layer. For coating with Au nano-particles the plasma modified PE was first grafted for 12 h from methanol solution of 1,2-ethanediethiol (HS–(CH\(_2\))\(_2\)–SH) to about 15 nm in diameter (citrate reduction according to Řezanka et al. [18]). Excess of Au colloid was removed by immersion of the sample into fresh water for 12 h. In another experiment pristine, plasma modified and dithiol grafted PE samples were coated with 50 nm thick, sputtered Au layer. The sputtering was performed on the same Balzers SCD 050 device. Different phases of the PE modification are schematically shown in Fig. 1.

2.2. Material characterization

Properties of the PE samples modified by plasma treatment, by grafting with dithiol and coated either with Au nano-particles or covered with sputtered Au layer were studied using various analytical methods. Presence of O, Au and S in the PE surface layer was determined non-destructively with the typical depth resolution of about 10 nm. The RBS spectra were evaluated with the GISA3.99 standard experimental arrangement. Elemental depth profiles were obtained on Omicron Nanotechnology ESCAProbeP spectrometer. Exposed and analyzed area had dimension 2 \times 3 \text{ mm}^2. X-ray source was monochromated at 1486.7 eV with step size 0.05 eV, the take off angle was 0° according to surface normal. Characteristic O1s, C1s, S2p and Au4f peaks were searched. The spectra evaluation was carried out by CasaXPS programme.

RBS analysis was performed with 2.72 MeV He\(^+\) ions in a standard experimental arrangement. Elemental depth profiles were determined non-destructively with the typical depth resolution of about 10 nm. The RBS spectra were evaluated by the GISA3.99 code [19]. Typical RBS detection limits vary from 1 at.% for C and O to 0.1 at.% for Au.

The concentration and length of conjugated double bonds before and after the PE plasma treatment and dithiol grafting were determined from UV–VIS spectra in 200–700 nm wavelength interval. The spectra were measured with Perkin–Elmer device [20].

The concentration of free radicals was determined with a relative error of 10% using an electron paramagnetic resonance spectroscopy (EPR) with an x-band spectrometer Elexys E-540, Bruker-Biospin. The samples were placed in a quartz tube and measured at RT. The typical experimental conditions were: the magnetic field range of 600 mT, sweep time of 180 s, magnetic modulation of 0.4 mT and field modulation of 100 kHz. The standards Mn/ZnS and Cr/MgO were used for the calibration of the g-factor and for quantitative evaluation of the spectra. Identification and determination of signals were performed by comparison with the standards.

Surface morphology and roughness of pristine and modified PE samples were examined by AFM technique using VEECO CP II device. The measurement in tapping mode was accomplished with Si probe RTESPA-CP (spring constant of 0.9 N/m). By repeated measurements of the same region (1 \times 1 \text{ mm}) it was proved that the surface morphology did not change after five consecutive scans. The mean roughness value (R\(_a\)) represents the arithmetic average of the deviations from the centre plane of the sample.

Measurements of the mechanical properties (hardness, elastic modulus) were carried out using a Nanindenter XP MTS instrument with a CSM additional module at loadings up to 20 mN and displacement into the surface up to 2 mm. The results were obtained as the mean of 20 different indentations (4 rows each with 5 points at the distance of 100 mm). Scratch tests were performed over a distance of 500 mm with the tip being gradually loaded from 0 to 20 mN.

3. Results and discussion

Radical concentration (R), determined from EPR measurement on the plasma modified PE (PE/plasma) and plasma modified and dithiol grafted PE (PE/plasma/SH), is shown in Table 1 as a function of the time from the plasma treatment. Plasma treatment results in scission of C–H and C–C bonds and production of free radicals (unpaired electrons). As could be expected, the radical concentration declines with increasing time from the treatment due to radical recombination [21]. Grafting of plasma treated PE with dithiol leads to significant decrease of the radical concentration. The decrease indicates that the dithiol is chemically bound to the PE surface enriched with free radicals.

Plasma treatment leads to creation of conjugated double bonds on PE molecular chains [22]. The concentration and conjugation length of the double bonds was examined by UV–VIS method [20] and the typical spectra for plasma modified and plasma modified–dithiol grafted PE are shown in Fig. 2. Plasma treatment leads to an absorbance increase indicating creation of excessive double bonds. It is known that the plasma treatment results also in ablation of the PE surface layer [23] and that a part of the plasma modified material becomes soluble in methanol [24]. For that reason the spectra from the PE samples, plasma treated (PE/plasma) and plasma treated and grafted from methanol solution of 1,2-ethanediethiol (PE/plasma/SH) are compared in Fig. 2. It is seen that no significant change in the UV–VIS spectra takes place after the dithiol grafting. It can therefore be concluded that the dithiol probably does not interact with double bonds created by plasma treatment.

Plasma treatment is important industrial process for modifying polymer surfaces [25,26]. The surface morphology of PE was examined by AFM method (see Fig. 3). Obviously, the exposition to plasma discharge leads to dramatic morphology change. After plasma

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time after plasma treatment (h)</th>
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<tbody>
<tr>
<td>PE/plasma</td>
<td>2</td>
</tr>
<tr>
<td>PE/plasma/SH</td>
<td>1.98</td>
</tr>
<tr>
<td></td>
<td>1.47</td>
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treatment the PE surface roughness, characterized by the mean roughness value ($R_a$), increases significantly. As a result of the ablation [5,23], a lamellar structure on the PE surface appears [23]. It can be concluded, in accord with the data reported earlier [27], that amorphous phase of PE is ablated faster than the crystalline one. After subsequent dithiol grafting, $R_a$ declines and the surface morphology changes dramatically again, due to a surface etching [21]. In analogy with earlier reports [28,29], obtained on different, plasma modified polymers, we conclude that the observed changes may indicate removal of low-molecular, oxidized segments. It is also seen from Fig. 3 that the coating with gold nano-particles results in a mild increase of the surface roughness and minor changes in the surface morphology.

The surface composition of the PE samples modified by plasma discharge, dithiol grafted and coated with Au nano-particles was investigated using XPS and RBS methods. By both methods the presence of chemically bound gold nano-particles is clearly proved. Also oxygen, adsorbed on the PE surface and sulfur from dithiol are observed. Typical XPS spectrum is shown in Fig. 4. Oxygen appears as a result of unintentional oxidation during plasma treatment. Earlier it was shown that by the oxidation carbonyl, carboxyl and ester groups are created on the PE surface [3,22,26]. From XPS measurements the following concentrations were determined: C-79.43, O-19.43, Au-0.50 and S-0.82 (in at.%).

Depth concentration profiles of O, S and Au were determined from RBS spectra. Typical results for the plasma treated, plasma treated and water etched PE samples are shown in Fig. 5 together with those obtained from the plasma treated, dithiol grafted and
gold nano-particle coated PE sample. It is seen that the elements are present not only on the very surface, accessible to XPS, but also they exhibit measurable depth profiles extending to the depth of about 250–300 nm. The concentrations of all elements decrease monotonously with increasing depth. After water etching of the plasma treated PE the concentration of oxygen decreases rapidly, the decrease being due to a removal of the plasma modified PE surface layer [24,30]. Minor difference between the depth profiles of Au and S may indicate that the smaller, sulfur containing dithiol molecules diffuse deeper than gold nano-particles (15 nm in diameter). Both XPS and RBS measurements shown higher concentration of sulfur comparing to gold. Earlier, it was shown by sheet resistance measurements that the gold nano-particles, deposited by the present method, do not form a continuous layer [22].

Main goal of this work was to verify whether the pretreatment by the plasma discharge and by subsequent grafting with diithiol may affect adhesion of Au layer deposited onto PE by sputtering. For that purpose the mechanical properties of gold layers sputtered on pristine, plasma treated and plasma treated and diithiol grafted PE were examined using nanointender. The surface elastic modulus and hardness were determined and scratch tests were performed. The surface elastic modulus as a function of tip displacement is shown in Fig. 6(A). It is seen that the elastic modulus decreases rapidly from the surface up to the depth of 50 nm, which is the thickness of the sputtered gold layer. Plasma pretreatment results in a dramatic decrease of the elastic modulus and another decrease is observed after the diithiol grafting. From the measured dependence of the hardness on the tip displacement (Fig. 6(B)) it is seen that the plasma treatment results in a dramatic hardness decline. Subsequent deposition of Au, however, leads only to minor change in the hardness vs. displacement dependence.

The results of scratch tests are illustrated in Fig. 7. The scratch path in the sputtered gold layer for the pristine PE and plasma treated PE is qualitatively different (Figs. 7(A and B)). In several recent studies [2,3] no significant effects of plasma treatment on the adhesion of sputtered gold layer has been observed. Dramatic changes in the shape and the character of the scratch path are observed on the diithiol grafted PE (see Fig. 7(C)). It is seen from Figs. 7(A–C) that under the same indenter load (about 10 mN) most pronounced adhesive destruction of the gold layer takes place on the pristine PE, where underlying substrate appears. Lower adhesive destruction is observed on the gold layer deposited on the plasma treated PE (see Fig. 7(B)). On the diithiol grafted PE (Fig. 7(C)) adhesive destruction is much smaller and cohesive destruction becomes dominant. The cohesive destruction is demonstrated by radial
spreading of scratches in the Au layer. It may therefore be concluded that the adhesion of the sputtered gold layer may greatly be enhanced by the dithiol grafting. The higher adhesion is probably due to chemical binding of the sputtered Au atoms to –SH groups present on the plasma treated and dithiol grafted PE.

4. Conclusion

It was shown that the plasma treatment results in degradation of the PE macromolecular chain, creation of free radicals and conjugated double bonds. After grafting from methanol solution of 1,2-ethanediethiol the concentration of free radicals declines but the concentration of double bonds remains unchanged. This finding shows that most of the grafted dithiol molecules are bound onto the surface. Nanoindentation measurements show that the surface morphology is observed together with a decline in the surface roughness. After coating with Au nano-particles another significant change in the surface morphology is observed together with a decline in the surface roughness. Nanoindentation measurements show that the grafting with dithiol increases adhesion of sputtered Au layer significantly, thanks to interaction of sputtered Au atoms with –SH groups introduced by the dithiol grafting.

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References