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RBS, XPS, and TEM study of metal and polymer interface modified by plasma treatment

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Abstract

We performed a study of the diffusion of Ag and Au atoms in polyethylenterephtalate (PET). Thin metal layers were deposited using a diode-sputtering technique on polymer foils at room temperature. Simultaneous post-deposition annealing and plasma treatments were used to induce metal–polymer intermixing. Rutherford back-scattering spectrometry and X-ray photoelectron spectroscopy were used to determine the integral amount of metal and chemical structure in the surface layer. After plasma treatment Ag thin films exhibit dramatic changes of chemical composition and an integral amount of metal compared to Au thin films. Transmission Electron Microscopy shows the differences in the size and the depth distribution of metal particles, depending on the annealing temperature at the metal–polymer interface.

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1. Introduction

Metallic films are of a great importance in manufacturing advanced electronic, optical, and mechanical devices ranging from displays to biosensors [1]. The mechanical and electric properties of the metal–polymer interface are influenced by the degree of metal mobility in polymer [2]. Less-reactive metals diffuse deep into the polymer at elevated temperatures, but the aggregation tendency inhibits the atomic diffusion and gives place to a complicated cluster diffusion mechanism [3,4]. In our previous work [5] Ag and Au diffusion coefficients in PET of $10^{-19}$–$10^{-17}$ cm$^2$ s$^{-1}$ were found. The diffusion coefficients of Ag in PET decreased with enhanced temperature and plasma treatment time. Ag films were partially removed by plasma treatment, the source of Ag atoms reduced and the roughness of the surface increased significantly.

2. Experimental

Metal layers were deposited onto 50\textmu m thick PET ($T_m = 260$ °C, $T_g \approx 98$ °C) supplied by Goodfellow Ltd. The Au and Ag were deposited by diode sputtering on a BAL-TEC, SCD 050 device. The typical deposition parameters were: room deposition temperature, deposition time 65 s, total argon pressure about 4 Pa, electrode distance of 50 mm, and current of 20 mA [6]. The estimated metal layer thickness was about 10 nm.

Plasma treatment and annealing were performed simultaneously in the chamber for plasma surface modification of thin film [7]. The RF discharge (13.56 MHz) was applied...
in pure argon or an oxygen/argon mixture (47% O₂ and 53% Ar). The flow rates were adjusted in order to obtain a total mixture pressure of 50–100 Pa, which was the optimum pressure for plasma ignition at an RF power of 35 W. The sample was held on the plasma floating potential during the plasma treatment. The in situ mounted quartz lamp (20 W) was used for indirect heating of the sample holder to temperatures from 80 to 160 °C.

We obtained concentration depth profiles of the metal atoms from the Rutherford back-scattering spectrometry (RBS) spectra. A beam of 2.68 MeV He⁺ ions from a Van de Graaff accelerator was used for the RBS analysis measured at 170° laboratory scattering angle. An Omicron Nanotechnology ESCAProbeP spectrometer was used to measure the X-ray photoelectron spectra (XPS). The X-ray source was monochromated at 1486.7 eV. The exposed and analyzed area had dimensions of 2 × 3 mm². The spectra were measured stepwise with a step in binding energy of 0.05 eV. Specimens for transmission electron microscopy (TEM) were cut from the center of the PET foils with embedded metal nanoparticles and fixed in epoxy resin (Durcupan). Ultrathin cross-sections (ca. 60 nm) were prepared with ultramicrotome Ultracut UCT (Leica), transferred to TEM microscopy grids and sputtered with a thin carbon layer to enhance the resistance of the sample to the electron beam. The specimens were observed in TEM microscope JEM 200 CX at an accelerating voltage of 100 kV.

3. Results and discussion

The data on annealing conditions and plasma treatment are summarized in Table 1. The removal of Ag is faster than that of Au under the same Ar plasma treatment at 80 °C. We observed a significant decrease of the Ag and Au integral amounts with increasing substrate temperature in Ar plasma treatment due to the plasma etching effect [11]. Ar plasma causes a decrease of the metal amount as well, but preferably on the surface (see Table 1). The RBS depth profiles of Ag and Au in PET, the extracted diffusion coefficients, and the AFM morphology study were published in our previous paper [5]. Simultaneous Ar plasma treatment and annealing at elevated temperatures do not increase the diffusion coefficients of Ag in PET compared to the simple annealing treatment. We assume a complicated metal cluster diffusion that cannot be described by simple Fick’s law of diffusion [12].

The creation of intermixed metal–polymer interface was also confirmed by TEM observation, but the number of intermixed metal particles is low. Ag particles are clearly seen near the polymer–metal interface in Figs. 2(a, b). The increasing substrate temperature used during Ar plasma treatment causes a decline of the number of Ag clusters, but the size of the clusters increases. This conclusion was deduced from an evaluation of the whole set of TEM micrographs for each sample. This effect should be connected with the glassy transition temperature of PET, where the amorphous fraction of PET becomes liquid, then the formation and mobility of larger clusters is enhanced. The same plasma treatment was applied to the Au/PET samples. The Au diffusion coefficients increase with the annealing temperature as reported in [5]. From the XPS spectra of Au before and after plasma treatment, it is clear that the characteristic signals for Au⁰ at energies of 83.76

<table>
<thead>
<tr>
<th>Sample with deposited Ag</th>
<th>Integral metal amount from RBS (10¹⁵ atoms/cm²)</th>
<th>Surface fraction of metal from XPS (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag as deposited</td>
<td>38.0 ± 0.5</td>
<td>23.7 ± 0.8</td>
</tr>
<tr>
<td>Ar + O₂ plasma, 10 min, 80 °C</td>
<td>30.3 ± 0.5</td>
<td>*</td>
</tr>
<tr>
<td>Ar + O₂ plasma, 20 min, 80 °C</td>
<td>14.5 ± 0.5</td>
<td>11.2 ± 0.8</td>
</tr>
<tr>
<td>Ar plasma, 20 min, 80 °C</td>
<td>37.8 ± 0.5</td>
<td>20.2 ± 0.8</td>
</tr>
<tr>
<td>Ar plasma, 20 min, 120 °C</td>
<td>33.9 ± 0.5</td>
<td>3.6 ± 0.8</td>
</tr>
<tr>
<td>Ar plasma, 20 min, 160 °C</td>
<td>21.0 ± 0.5</td>
<td>3.5 ± 0.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample with deposited Au</th>
<th>Integral metal amount from RBS (10¹⁵ atoms/cm²)</th>
<th>Surface fraction of metal from XPS (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au as deposited</td>
<td>49.6 ± 0.5</td>
<td>43.9 ± 0.1</td>
</tr>
<tr>
<td>Ar + O₂ plasma, 20 min, 80 °C</td>
<td>37.2 ± 0.5</td>
<td>33.2 ± 0.1</td>
</tr>
<tr>
<td>Ar plasma, 20 min, 80 °C</td>
<td>47.2 ± 0.5</td>
<td>45.7 ± 0.1</td>
</tr>
<tr>
<td>Ar plasma, 20 min, 120 °C</td>
<td>48.0 ± 0.5</td>
<td>29.7 ± 0.1</td>
</tr>
<tr>
<td>Ar plasma, 20 min, 160 °C</td>
<td>39.7 ± 0.5</td>
<td>17.3 ± 0.1</td>
</tr>
</tbody>
</table>

Surface concentration of deposited metals determined using XPS. *XPS spectra of the sample was not measured.
and 87.50 eV stand unchanged. This means that the increasing temperature is the most important factor influencing the mobility of Au atoms, the changes of the integral amount of Au and morphology are not as dramatic compared to Ag. TEM micrographs do not exhibit significant changes of Au/PET interface after plasma treatment.

4. Conclusions

The penetration of Ag and Au atoms from metal layers deposited using a diode-sputtering technique on PET substrate was studied under different plasma treatment conditions and simultaneous substrate heating. RBS and XPS analysis of samples after plasma exposure shows that the integral amount of metals decreases with increasing substrate temperature. The integral amounts of Au and Ag determined by RBS is decreased most significantly by Ar+O₂ plasma due to the plasma-chemical reactions.

The lowest integral amount of Ag as determined by RBS was observed for Ar+O₂ plasma treatment at 80 °C, the lowest surface concentration of Ag determined from the XPS was measured after Ar plasma treatment at 160 °C. The explanation should be as follows: the largest Ag

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Fig. 1. XPS spectra of core levels Ag(3d5/2): (a) as deposited Ag/PET, (b) Ag/PET treated Ar plasma for 20 min at 160 °C. XPS spectra of core levels: (c) C1s and (d) O1s Ag/PET treated Ar plasma for 20 min at 160 °C.
clusters are formed at this temperature, however the entire integral amount is not as low due to the penetration of these clusters into the polymer, the Ag fraction at the surface decreases. Larger Ag cluster formation at an elevating temperature near the polymer–metal interface was confirmed by the TEM. XPS measurement after plasma treatment demonstrates creation of Ag$^+$ in Ag$_2$O, Ag$^0$ and Ag bound on the organic structure.

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References


