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Effect of deep UV laser treatment on electroless silver precipitation in supported poly-3,4-ethylenedioxythiophene layers[♣]

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Poly-3,4-ethylenedioxytiophene (PEDOT) polymer layers are electrodeposited on Pt substrates and irradiated with deep ultraviolet light. The 248.6 nm line of a UV Cu^+ laser is used. UV-treated and non-treated PEDOT samples are used for electroless silver precipitation carried out in a Ag-EDTA plating solution. The electroless metal deposition is studied as a function of the initial oxidation state of the polymer layers. A massive precipitation of metallic silver nanoparticles (10-40 nm) is observed in the case of reduced PEDOT. A larger amount of silver and a highly homogeneous distribution over the entire visible surface are found on the UV laser treated samples. The electroless precipitation in non-treated, oxidised PEDOT is sluggish and results in a non-uniform precipitation of Ag agglomerates (100-200 nm). The use of UV laser treated PEDOT layers in the oxidised state provokes a marked increase in the number of deposited Ag agglomerates and a uniform distribution over the polymer surface.

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1. Introduction

Poly-3,4-ethylenedioxytiophene is one of the most studied electronically conducting polymers provoking interest from both fundamental and practical points of view. PEDOT is investigated as a component of hybrid inorganic/organic materials in view of applications in microelectronic, photovoltaic, sensing and catalytic devices [1]. A frequently used approach for the preparation of supported metal/polymer composite materials is the electrochemical crystallization of metal particles in the already deposited polymer layers. An alternative to this approach is electroless metal precipitation in conducting polymers [2-5]. The basic advantage of the electroless over the electrodriven deposition method is the opportunity to coat the upper polymer surface by metal particles irrespective of defects and inhomogeneities in the polymer coverage of the underlying surface. The key to improving the characteristics (number, size and surface distribution) of the electroless precipitated metal is the development of suitable treatments providing homogeneity in the surface chemical state of the polymer layer. In previous investigations [6, 7] we have shown that UV-treatment of PEDOT results in a mild modification of the external polymer surface without affecting the bulk properties of the polymer. It was established that the UV irradiation activates significantly the process of copper electrodeposition on PEDOT.

The subject of this work is to investigate the effect of the deep UV laser surface treatment of PEDOT for silver electroless precipitation.

2. Experimental

For the polymer irradiation an UV Cu^+ laser excited by a Ne-CuBr nanosecond pulse longitudinal discharge is used [8]. The laser operates at five Cu^+ lines – 248.6 nm, 252.9 nm, 259.7 nm, 260.0 nm and 270.3 nm. PEDOT layers are treated with the laser line of 248.6 nm which corresponds to the HOMO energy level (5 eV) of doped

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PEDOT [9]. The experimental details for the laser set-up and laser irradiation of the polymer layers are given in [6].

PEDOT layers are electrodeposited on platinum plate substrates at constant anodic potential using an aqueous microemulsion [6]. The thickness of the electrodeposited PEDOT layers is about 2 μm. After electrodeposition, the PEDOT layer surface is partially shaded and irradiated for less than 5 min at an exposition dose of 40 J.cm^{-2}. This provides the opportunity for a direct comparison between non-irradiated and irradiated parts of each PEDOT sample.

Two types of PEDOT layer – reduced (Red-PEDOT) and oxidised (Ox-PEDOT) are used in our investigations. Red-PEDOT layers are subjected to electrochemical reduction in a supporting electrolyte (H_2SO_4) before the onset of silver deposition. Ox-PEDOT layers are dipped directly in silver plating solution without electrochemical pre-treatment.

Silver electroless precipitation is carried out in a 10 mM solution of silver and ethylenediamine-tetraacetic acid solution (Ag-EDTA) at pH 4.1 [3].

The samples are characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) analysis by means of a computer driven Field Emission Scanning Microscope JSM - 7500F and Quantax 200 EDXS system.

X-ray Photoelectron Spectroscopy (XPS) for surface chemical analysis is performed using an OMICRON EA 125 energy analyser and an OMICRON DAR 400 source.

3. Results and discussion

Electroless precipitation of metal particles in a conducting polymer takes place due to the specific properties of these types of polymer material and namely the possible coupling of polymer oxidation and metal ion reduction. The process depends on various factors such as the initial oxidation state of the polymer, the intrinsic oxidation charge, Q_{ox}, the concentration and type of the metal ions plating solution, etc. [2-3]. In this investigation Red-PEDOT and Ox-PEDOT layers with a constant initial oxidation charge are studied for electroless silver precipitation.

3.1 Silver electroless precipitation in reduced PEDOT (Red – PEDOT) layers

Figs. 1-5 show SEM images and EDX spectra of Red-PEDOT layers after silver electroless precipitation. A massive precipitation of densely packed silver nanoparticles (with sizes ranging between 10 and 40 nm) is observed on both non-irradiated (Fig. 1) and irradiated (Figs. 3 and 4) parts of the sample. As shown by EDX analysis, a larger amount of silver is characteristic for the laser treated Red- PEDOT layer. Moreover, a very uniform distribution of Ag nanoparticles, covering the entire visible polymer surface is observed. This means that the UV-treatment provokes a homogenisation of the surface with respect to its oxidation properties and favours a uniform initiation of the process occurring subsequently through the bulk of the polymer layer. Bearing in mind that a destruction of the surface bonds was found to occur as a result of the UV irradiation of PEDOT [6], this finding should mean that additional surface states, emerging as a result of the irradiation, favour the metal ion reduction. This surface effect does seemingly not disturb the conjugation of the underlying polymer chains and thus the redox coupling which is at the origin of the electroless metal precipitation.

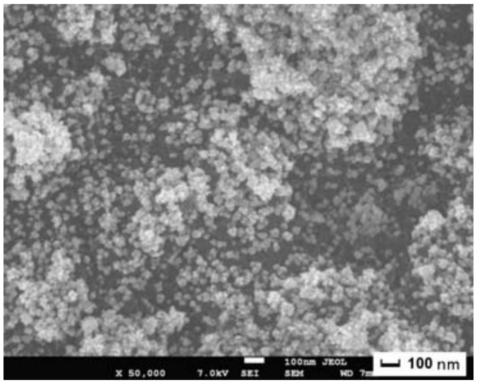

Fig. 1. SEM I mage of the non-irradiated part of a Ag – (Red - PEDOT) layer, d (PEDOT)=1.8 μm. The Ag particles are the small structures with bright contrast. Magnification 50 000 x.

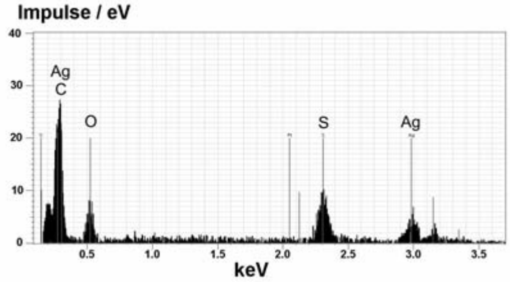

Fig. 2. EDX spectrum of the non-irradiated part of the Ag – (Red - PEDOT) layer.

The chemical state of the deposited silver was investigated by XPS analysis (Fig. 6) and shows on both non-treated and UV-treated parts of the polymer layer the presence of metallic silver alone. The higher intensity of the Ag-peaks, registered on the irradiated parts of the layer, indicates again a higher silver content.

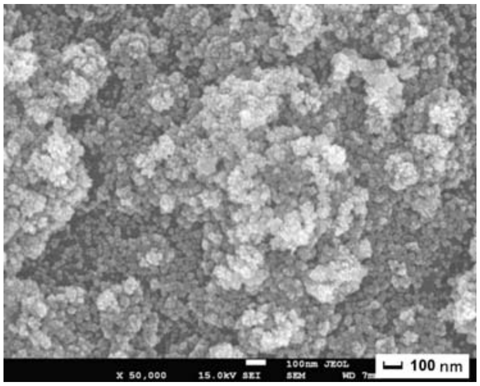

Fig.3. SEM image of the irradiated part of a Ag – (Red - PEDOT)layer, Magnification 50 000 x.

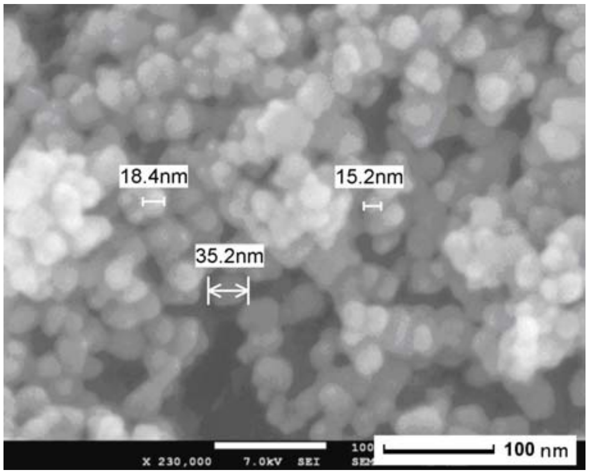

Fig.4. SEM image of the irradiated part of the Ag - (Red - PEDOT) layer, Magnification 230 000 x.

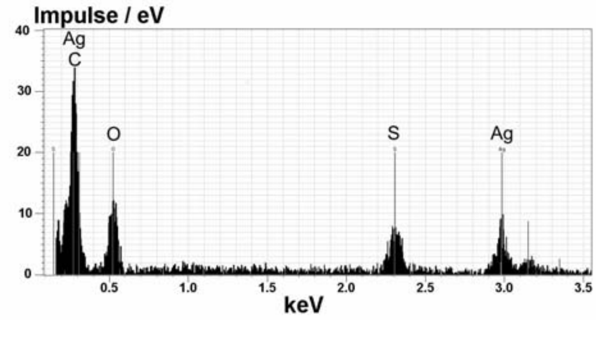

Fig. 5. EDX spectrum of the irradiated part of the Ag – (Red – PEDOT) layer.

It is known [3] that the amount of electroless deposited metal depends on the polymer oxidation charge. The latter is controlled through the number of redox centers and is proportional to the polymer mass. Having one and the same mass and at least initially one and the same number density of redox centers on both the non-treated and UV-treated parts of the polymer layer, no significant difference in the amount of precipitated metal should be expected.

The observed marked increase in the amount of silver on the UV-treated PEDOT should be related to an increase in the number of centers active for metal reduction, but also to a more effective oxidation process. In fact, it was shown [3] that the transformation of the intrinsic oxidation charge Q_{ox} of the polymer layer into a reduction charge of the metal ions Q_{Me} is not complete, i.e. $Q_{Me}/Q_{ox}<1$ and the charge transformation ratio drops with increasing polymer amount and layer thickness. Thus it could be suggested that the initiation of the oxidation process at an increased number of sites covering the complete external surface, as in the case of the UV-treated PEDOT surface, provides more effective oxidation paths through the bulk of the polymer layer and thus an increase in the charge transformation ratio.

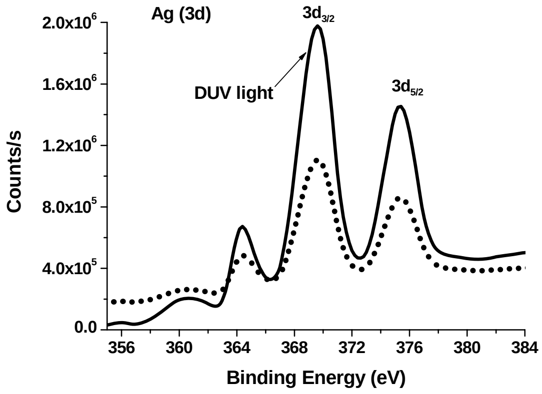

Fig. 6. Ag (3d) core level spectra of the non-irradiated (doted line) and irradiated (solid line) parts of Ag - (Red – PEDOT) layer.

3.2 Silver electroless precipitation in an oxidized PEDOT (Ox – PEDOT) layer

Figs. 7-9 present SEM images of the non-irradiated and irradiated parts of an Ox-PEDOT sample after Ag electroless precipitation. A non-uniform deposition of a rather small number of silver crystals (Figs. 7 and 9 a) or no crystals at all are found on the non-irradiated part of the PEDOT. A uniform distribution of a larger number of silver agglomerates (Figs. 8 and 9b) is observed on the irradiated part of the sample. These observations are in support of the already established UV-induced homogenisation of the polymer surface and the emergence of new oxidation paths for the electroless precipitation process.

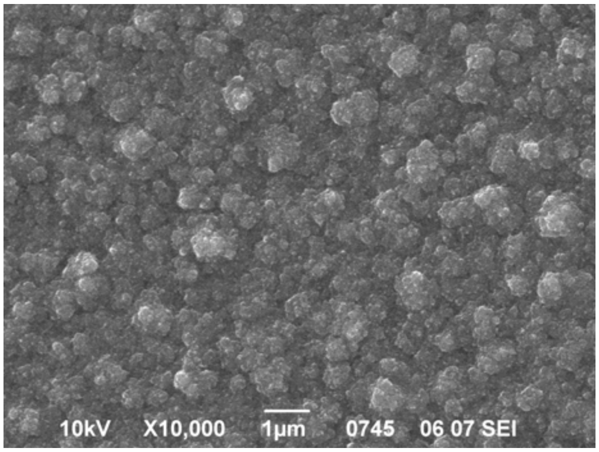

Fig. 7. SEM image of the non-irradiated part of a Ag - (Ox - PEDOT) layer.

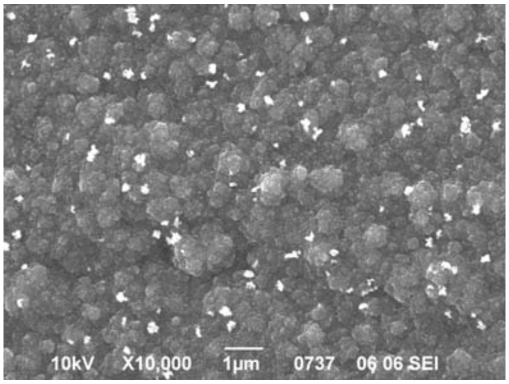

Fig. 8. SEM image of the irradiated part of a Ag - (Ox - PEDOT) layer.

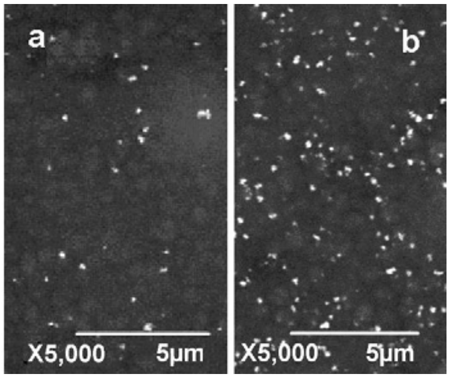

Fig. 9. SEM images in back scattered electron mode of non-irradiated (a) and irradiated (b) parts of a Ag - (Ox - PEDOT) layer. The Ag structures are those with bright contrast.

4. Conclusions

The investigations presented in this work demonstrate the effect of the deep UV laser treatment of PEDOT layers for the microscopic characteristics (amount, size and location) of electroless precipitated silver particles. The UV irradiation provokes a homogenisation of the polymer surface with respect to its oxidation properties and, as a consequence, a more effective coupling of polymer oxidation and metal ions reduction. Thus a complete coverage of the external polymer surface by closely packed Ag nanoparticles becomes possible.

The demonstrated approach has prospects for application in metallization of conducting polymer layers and for producing metal/conducting polymer catalytic materials with a large metallic content.

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