Modification of conductive polymer PEDOT:PSS layer by SWCNT

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Abstract. In this study, the effect of addition of single-walled carbon nanotubes (SWCNTs) on the morphological properties of poly(3,4-ethylenedioxythiophene/poly(4-styrenesulfonate) (PEDOT:PSS) has been investigated using scanning electron microscope (SEM) as well as the surface roughness evaluation by atomic force microscopy (AFM). The spin-coated films of PEDOT:PSS and PEDOT:PSS with addition of SWNTs (0.5 % by wt.) on glass were compared in our study. Experimental results show that surface roughness of PEDOT:PSS layers increases after addition SWNTs to the solution - from 3.50 nm for the samples without SWNTs to 4.65 nm for the samples with SWNTs. The analysis of SEM images showed that there are some agglomerations of SWNTs on the surface of PEDOT:PSS/SWCNT composite film.

1. Introduction

Water soluble conducting polymer poly(3,4-ethylenedioxy-thiophene)-poly-(styrene sulfonate) (PEDOT:PSS), has been widely used as electrode materials for capacitors, and in printed circuit boards and microactuators. PEDOT:PSS offers many advantages over other conducting polymers because of its ease of processability, commercial availability, high optical transparency in visible light, good mechanical strength, superb thermal stability and excellent atmospheric stability. High quality films can be easily formed on various substrates by conventional solution processing techniques such as spin-coating techniques [1,2,3,4].

PEDOT:PSS is generally used as antistatic coatings and as a hole injection layer in organic devices due to high work function, high hole affinity, and good transparency [2,3,5,6,7]. However, pristine PEDOT:PSS has a low conductivity (generally below 10 S/cm) [6]. Because of this recently, efforts have been focused on improvement of electrical conductivity of PEDOT:PSS films. Electrical conductivity of PEDOT:PSS can be enhanced by adding small amount of solvents such as dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), glycerol, and sorbitol to the PEDOT:PSS aqueous solution [1,3,8].

Another way to improve conductivity of polymer system is adding conductive fillers into this system. Carbon nanotubes (CNTs) have many advantages, above all excellent electrical and mechanical properties and exceptional flexibility. Additionally, CNTs can be dispersed in PEDOT:PSS solutions to obtain highly conductive polymer–CNT hybrid composite films. They are promising anode materials for flexible FOLED applications [9,10,11,12,13]. However, CNTs can change morphology of conductive layers. For OLED application, where layers have nanometers
thickness, a morphological aspect of polymer layers is very important. It has significant effect on performance and lifetime of OLEDs devices.

In the present work, scanning electron microscope (SEM) as well as atomic force microscopy (AFM) are combined to study morphology of spin-coated PEDOT:PSS and PEDOT:PSS/SWCNT films.

2. Experiment details
Commercially available SWCNTs (outer diameter: 0.7-1.1 nm; length: 0.3-2.3 μm) from Sigma Aldrich Company were used in this work. The conducting polymer used was poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) Orgacon Screenprint Ink Transparent EL-P3040 purchased from Agfa (electrical resistance - 680 Ohm/square). The preparation of the PEDOT:PSS/SWCNT solution included two steps. Firstly, the as-received SWCNTs were dispersed in distilled water (concentration of SWCNTs was 1 mg/l) by magnetic stir and sonication. In the next step, the above prepared SWCNT solution was mixed with the PEDOT:PSS solution (in ratio 0.05:1) and mixed for 30 min using an ultrasonic horn.

Two kinds of samples were prepared – the first one with pristine PEDOT:PSS and the second one with a mixture of PEDOT:PSS and SWCNTs (0.5 % by wt.). The analyzed layers were deposited on glass surface (2.5 cm × 2.5 cm squares size) using spin-coating technique (at 7500 rpm). Before layer deposition the glass surfaces were ultrasonically cleaned - washed in an ultrasonic bath of acetone and ethyl alcohol each for 5 min, then dried in a flow of air. After deposition the tested layers were dried on a hot plate for 10 min at 80 °C.

The PEDOT:PSS and PEDOT:PSS/SWCNT surfaces were characterized by AFM with a Digital Instruments Dimension 3100 in the tapping mode. Measurements were conducted at room temperature in the air, using the pyramidal Si₃N₄ tip. Surface roughness of the tested samples was calculated with AFM software.

Morphology of the tested coatings surface was characterized by scanning electron microscopy (SEM) using a JEOL JSM-7600F microscope.

The resistance of tested layers was measured with the four-point probe method using the digital multimeter Agilent 34401A.

3. Results of investigations
The morphology of the spin-coated pristine PEDOT:PSS and mixture of PEDOT:PSS/SWCNT films were investigated using SEM and AFM images.

The SEM micrographs – figures 1 and 2 show that both type of samples have porous and not uniform surface. Additionally, some aggregation was observed in the PEDOT:PSS/SWCNT composite film from the entanglement of SWCNT chains. The results are similar to that received in the works [14,15] where morphology of the spin-coated MWNT/PEDOT:PSS film was investigated. The authors of those work stated that PEDOT:PSS film shows smooth surface morphology without any agglomeration, but the MWNT aggregation was observed in the MWNT/PEDOT:PSS composite film. However, authors of [13] work stated that the PEDOT–CNT composite exhibits a porous morphology which is due to the embedding of CNTs into the polymer.

When CNTs are deposited on a substrate by solution methods, they are randomly tangled together on the surface and normally form an isotropic network. Due to the large aspect ratios of the CNTs, the solution deposition methods tend to form a large amount of voids in the film. This caused that it is very difficult to achieve intimate contact between CNT tube to CNT tube due to physical shape restriction and stiffness of the material. The polymer has filled most voids existed in the CNT network, aligning the surface of CNT film. Conductive polymer helps forming electrical contacts between CNT tubes and increasing the effective electric conductive tube–tube junctions in the CNT network. The composition of the CNT suspension is critical in the fabrication of uniform and reproducible PEDOT–CNT thin films [13,16].
We found that addition of SWCNT to the PEDOT:PSS solution led to the increase of the surface roughness of tested samples. Figures 3 and 4 show the examples of AFM micrographs of the PEDOT:PSS (figure 3) and PEDOT:PSS/SWCNT (figure 4) layers. Additionally, the values of root-mean-square roughness $R_{rms}$, average roughness $R_a$ and peak-to-valley roughness $R_{pv}$ are listed in Table 1.

**Table 1.** The values of surface roughness of pristine PEDOT:PSS and composite of PEDOT:PSS/SWCNT samples.

|                | $R_a$ [nm] | $R_{rms}$ [nm] | $R_{pv}$ [nm] |
|----------------|------------|----------------|---------------|
| PEDOT:PSS      | 3.500      | 11.274         | 15.472        |
| PEDOT:PSS/SWCNT| 4.654      | 15.031         | 22.467        |
The value of $R_a$ roughness increased from 3.5 nm to 4.654 nm and the value of $R_{rms}$ roughness increased from 11.274 nm to the 15.031 nm. The samples with PEDOT:PSS layer had more smooth and homogeneous surface than the samples with PEDOT:PSS/SWCNT layers. That was confirmed during analysis of profiles of the fluctuation of surface roughness for all samples. The higher value of $R_{pv}$ for PEDOT:PSS/SWCNT layer suggests that this layer has more spikes on the surface. This fact was confirmed by analysis of 3D images of the tested samples as well as by view of profiles of the fluctuation of surface roughness.

The results are similar to that received in the works [14,15]. In [14] the effect of CNT oxidation on the film properties of CNT/PEDOT:PSS composite was investigated. The authors of this work stated among other things that surface roughness of PEDOT:PSS film increase from 0.815 nm to 25.4 nm after addition of as-purchased MWCNT (0.980 % by wt.). In addition, in this work it has been concluded that oxidation of CNTs using acid solution leads to decrease in the value of CNT/PEDOT:PSS film roughness (to 10.7 nm). This is connected with formation of functional group and the ring-opening or chain break in the CNT during the oxidation process. This leads to fabrication of CNT suspension with small amount of CNT aggregation and consequently to preparation more uniform CNT/PEDOT:PSS film [14]. However, in [15] the properties of MWCNT/PEDOT:PSS films with various concentration of MWCNT were investigated. There was stated that roughness of MWCNT/PEDOT:PSS film (0.248 % by wt.) is almost ten times higher than for pristine PEDOT:PSS film. In this work it has been also found that roughness of PEDOT:PSS film increases with growth of MWCNT concentration in the solution.

Figure 3. The example of AFM 2D and 3D images as well as profile of the fluctuations of the surface roughness of pristine PEDOT:PSS film.
Figure 4. The example of AFM 2D and 3D images as well as profile of the fluctuations of the surface roughness of PEDOT:PSS with addition of SWCNT (0.5 % by wt.) film.

During analysis of SEM and AFM test results it could be expected that PEDOT:PSS/SWCNT layers will have higher values of sheet resistance than PEDOT:PSS films. The dispersion of SWCNTs in polymer carrier was poor. There were observed some agglomeration of SWCNTs. They caused increase of surface roughness, but they can also contribute to increase of electrical resistivity of the tested layers [11,14]. However, we observed that 0.5 % (by wt.) addition of single walled carbon nanotubes to the PEDOT:PSS solution caused the values of sheet resistance of the tested films to decrease. The sheet resistance of pristine PEDOT:PSS and PEDOT:PSS/SWCNT layers of the same thickness (about 800 nm) were 398 ± 23 Ohm/square and 254 ± 24 Ohm/square, respectively. The results are similar to that obtained in the works [9] and [15]. There was found in the work [9] that sheet resistance of PEDOT:PSS films with 0.5 % (by wt.) SWCNTs is about 70 Ohm/square lower than sheet resistance of pristine PEDOT:PSS films of the same thickness. Also in the work [15] authors found that the resistivity of PEDOT:PSS films decreased with the addition of MWCNTs and for layers of PEDOT: PSS with additive of 0.495 % (by wt.) was twenty times lower than for pristine PEDOT:PSS layers. Our results are also similar to that presented in the work [17] where authors reported that resistivity of PEDOT:PSS/CNTs pastes layers decreases with increasing surface roughness of that layers.

4. Conclusion
The PEDOT:PSS and PEDOT:PSS/SWCNT films on glass substrate by spin-coating method were prepared and morphological properties of those films were studied using AFM and SEM methods. Some aggregation from the entanglement of SWCNT chains in the PEDOT:PSS/SWCNT composite film on the SEM micrographs was observed. Both type of samples had porous and not uniform surface. There was stated from the analysis of AFM micrographs that the PEDOT:PSS/SWCNT composite film had higher surface roughness than the pristine PEDOT:PSS film. The value of $R_d$...
roughness increased from 3.5 nm to 4.654 nm and the value of \( R_{\text{rms}} \) roughness increased from 11.274 nm to the 15.031 nm after addition of SWCNTs to the solution of PEDOT:PSS. There was also observed that 0.5 % (by wt.) addition of single walled carbon nanotubes to the PEDOT:PSS solution caused the values of sheet resistance of the tested films to decrease. The sheet resistance of pristine PEDOT:PSS and PEDOT:PSS/SWCNT layers were 398 ± 23 Ohm/square and 254 ± 24 Ohm/ square, respectively.

The small surface roughness (\( R_{\text{rms}} < 1 \text{ nm} \) [10]) is required for the functional layers in the organic electronic applications. Therefore, high roughness PEDOT:PSS/SWCNT composite film may be a kind of disadvantage in this applications. From the other hand, despite the increase in the surface roughness the sheet resistance of tested layers decrease, after adding CNTs to the polymer carrier. The major advantage of CNT networks is their mechanical flexibility in terms of bending. They are promising anode materials for flexible FOLED applications. There is demonstrated in literature a few ways to improve transparent electrodes based on CNTs such as improving material purity, chemical doping of CNT network or using separated CNTs. The attempts to modify the PEDOT:PSS/SWCNT composite layers in order to reduce their roughness will be a subject of the next article.

5. References
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