Influence of PEDOT:PSS morphology on performance of bulk heterojunction solar cells

S M Loganchuk¹, A N Yatsenko¹, A V Varnavskaya¹, L G Miroshnichenko¹, S N Chebotarev¹, V A Irkha¹
¹Department of Physics and Photonics, Platov South-Russian State Polytechnical University (NPI), Novocherkassk 346421, Russia

Abstract. Influence of morphology of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) layer on performance of bulk heterojunction (BHJ) organic solar cells is analysed. Morphology depends on next technological factors: dispersity of PEDOT:PSS solution, substrate treatment, drying, PEDOT:PSS treatment. It is shown that samples with layer roughness less 10 nm have the best performance. Layer roughness was studied by atomic force microscopy (AFM).

1. Introduction
The growing need of mankind for electric energy, along with the limited reserves of hydrocarbons on the planet, stimulates research and engineering aimed at finding alternative sources of energy. The most perspective research area is using solar energy because this kind of energy is almost inexhaustible and available in the most part of the world. The last few decades organic solar cells (OSCs) and organic semiconductor materials have been more extensively researched. In perspective, these devices must replace silicon solar cells (SSC) because of low-cost production. Currently, organic solar cells with a bulk heterojunction are considered the most promising in mass application. Such devices have worse performance than tandem and multi-junction OSCs, but because of simple structure they have significantly more low-cost [1]. In organic solar cells (OSCs) poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) is intermediate layer between anode contact made of indium tin-oxide (ITO) and active layer. As the active layer, the blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) was used in experiment. PEDOT:PSS reduce the potential barrier during hole injection and provide ohmic contact between anode and active layer [2]. Influence of PEDOT:PSS morphology on performance of OSCs is shown in this paper.

2. Experimental
Glass substrates with size 2.5x2.5 cm and ITO layer with thickness of 150 nm were sonicated in surfactant solution for 15 minutes at 70 °C. After sonication they were washed in deionized water and treated in acetone at ambient temperature. The next steps of preparing substrates were sonication in isopropyl alcohol (IPA) at 65 °C and drying for 10 minutes at 140 °C with further ultraviolet-ozone (UV-Ozone) treatment for 30 minutes.

PEDOT:PSS was spin coated at 2500 rpm. Layer thickness was 80 nm. For better uniformity PEDOT:PSS was treated by ultrasonic disperser and filtered by syringe polytetrafluoroethylene (PTFE) filters.
Blend P3HT:PCBM (concentration 20 mg·mL⁻¹, weight ratio 1:1) was prepared in the glove box at nitrogen atmosphere. It was soluted in chlorobenzene and spin coated for 2 minutes at 1000 rpm with further drying for 15 min at 140 °C. The layer thickness was 100 nm.

Aluminum electrode with thickness of 100 nm was deposited in the thermal evaporation chamber.

PEDOT:PSS morphology was studied by nondestructive [3] atomic force microscopy (AFM). For excluding the influence of AFM on OSCs performance, two samples were fabricated with PEDOT:PSS, which was spin coated for each sample in the same way. Before next technological steps the AFM was made on one of them. If performance difference of both samples was more than 10%, these samples were discarded and the results were not used for analysis.

3. Results and discussion

Experiments shows that PEDOT:PSS layer morphology significantly depends on dispersion of solution, as well as substrate preparing, drying and solution treatment. Optimization of these processes allows to reach repeatable PEDOT:PSS layer uniformity with roughness less than 10 nm, that is shown on figure 1. J-V curves of such structure are shown on figure 2 (blue curve). It is visible that this structure has the best performance.

![Figure 1. AFM-image of PEDOT:PSS layer with roughness less 10 nm](image1)

![Figure 2. J-V curves of OSCs with different roughness](image2)

J-V curves of devices with PEDOT:PSS roughness 20 nm (orange dashed curve) and 30 nm (green dash-dotted curve) are shown on figure 2. It is clearly seen that roughness increasing provides monotonically but not harsh decreasing of OSCs performance. Roughness increasing is due to complicated chain-like chemical structure of PEDOT and PSS molecules. It makes dense packing of molecules in uniform layer difficult.

Another reason for nonuniform PEDOT:PSS layer is large particle agglomeration from aqueous solution. Hydrophobicity of PEDOT is due to this agglomeration. Because of that reason roughness of PEDOT:PSS layer can be 70 nm and more. OSCs with such structure contain many vertical conductive channels and as a consequence leakage currents. On J-V curve this case is shown on figure 2 (red curve). Open circuit voltage is significantly decreased and current density-voltage characteristic becomes linear.

Properties of J-V curve of OSCs could be explained by simple model, which is shown on figure 3.
In this model a real OSC, connected into the load network, is replaced by current source and diode with series resistance $R_S$ and shunt resistance $R_{SH}$. Series resistance accounts power losses because of semiconductor resistance itself and bond between the cell and connections to a load. It increases when layers thickness increases and also defects in border regions. Shunt resistance $R_{SH}$ accounts leakage currents. Leakage currents is any reverse biases in OSC and recombination processes, which reduces number of electron-hole pairs, which could be useful for increasing power conversion efficiency (PCE). As we can see from figure 3, if load resistance equals zero, then current doesn’t depend on shunt resistance. Terminals are shorted together and that’s why current through them called short-circuit current $I_{sc}$.

Also, when load has infinity value, the voltage doesn’t depend on series resistance. There is only voltage across the terminals which is equal to diode voltage – open circuit voltage. These circumstances allow to consider all technological parameters.

This model not always describe accurately the principle of solar cells. For real, real processes affecting on PCE couldn’t be described only by shunt and series resistances [5].

According to the model, described above, J-V curves on figure 2 can be explained. With increasing roughness of PEDOT:PSS layer (green dash-dotted curve and dashed yellow curve) series resistance increase and shunt resistance decrease. Decreasing shunt resistance is more noticeable because short circuit current drops more than open circuit voltage. The reason of roughness more than 30 nm is recombination processes and as a result leakage currents increase not so significantly, comparing to contact resistance of PEDOT:PSS. Reason of further roughness increasing is not loose packaging of branched PEDOT:PSS molecules, but embedding of large undissolved agglomerated PEDOT:PSS particles. These particles have sizes of 50-150 nm and do not absorbed by PTFE filters. According to this, their embedding in OSC structure leads to big leakage currents as it is shown in table 1.

| PEDOT:PSS roughness (nm) | Series resistance ($\Omega \cdot \text{cm}^2$) | Shunt resistance ($\Omega \cdot \text{cm}^2$) | Short-circuit current (mA/cm$^2$) | Open circuit voltage (mV) | Fill Factor | PCE (%) |
|--------------------------|---------------------------------|-----------------|-------------------------------|---------------------|-----------|--------|
| $<10$                     | 3                               | 200             | 10.3                          | 520                 | 0.68      | 4.2    |
| 20                        | 3.5                             | 180             | 9.5                           | 490                 | 0.65      | 3.9    |
| 30                        | 4.2                             | 150             | 8.4                           | 470                 | 0.64      | 3.6    |
| $>70$                     | 90                              | 2               | 1.9                           | 70                  | 0.45      | <0.1   |

In this experiment, PEDOT:PSS was treated by ultrasonic disperser was used to prevent emerging of large agglomerated particles.
4. Conclusions
PEDOT:PSS layer morphology significantly affects on performance of OSCs. The higher the value of roughness, the worse performance of OSCs. The main reason of high values of roughness is large undissolved agglomerated PEDOT:PSS particles. This leads to non-uniform layer and as a consequence worse performance. To prevent such negative factors PEDOT:PSS was treated by ultrasonic disperser. In this experiment, roughness varies from <10 nm to >70 nm. It is seen from obtained J-V curves, the best performance is observed with roughness less 10 nm. Performance becomes worse in the values of roughness 10-30 nm. Further increase of roughness make performance much worse because of particle agglomeration with particles size more than 70 nm.

References
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