Stability of Diodes with Poly(3-hexylthiophene) and Polyazomethines Thin Organic Layer

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Herein we report results of studies on stability of diodes based on organic semiconductors such as poly(3-hexylthiophene) (P3HT) and soluble derivative of polyazomethine poly(1,4-(2,5-bis(ethyloxy) phenylene)methyldiindenomethylidene) (BOO-PPI). Both polymers were deposited on glass/ITO substrate with or without covering with blocking layer: poly(3,4-ethylenedioxythiophene):poly(4-styrene sulfonate) (PEDOT:PSS) and finished with Al back electrode. Prepared devices were studied by monitoring their electrical conductivity under nitrogen atmosphere and ambient air conditions. Under nitrogen atmosphere a marked influence of presence of the blocking layer on the diodes electrical conductivity was revealed. The P3HT diodes prepared without PEDOT:PSS thin film showed quick degradation, whereas presence of these layers stabilizes electrical conductivity in these devices. Inversely, the PFI based diodes without the PEDOT:PSS revealed stable conducting properties, while corresponding diodes with PEDOT:PSS layer showed degradation traces of their conducting properties.

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1. Introduction

The optoelectronic devices based on organic semiconductor thin films have been recently extensively studied due to their possible low cost production, mechanical flexibility, and easiness of their preparation [1-3]. Much attention was put to experimental and theoretical studies of transport properties of organic semiconductors leading to marked increase in understanding mechanisms which play the key role in operational performance of i.e. photovoltaic devices [1-8]. Research done on poly(3-hexylthiophene) (P3HT) [9], the model material for organic solar cells, provided the substantial knowledge on such phenomena as current limiting mechanisms in ITO/P3HT/Al devices [9], the trap filling and the trap free transport properties [10] as well as on influence of various parameters on overall device performances [11-13].

Practical application in the optoelectronic devices of organic semiconductors is limited by very low stability under normal atmospheric conditions. Degradation processes in air, due to the diffusion of the atmospheric gases into organic layer, as well as oxidation of metal contacts, affect conductivity in organic semiconductors and are leading to decrease electrical parameters and overall device efficiency. Up to date influence of air on organic semiconductors stability has been intensively investigated [2, 4-8]. Additionally influence of metal-organic semiconductor interface on cell performance was studied by adding in the cell construction additional PEDOT:PSS layer. In this work we report results of stability study on organic diodes based on organic semiconductors such as P3HT, model material used as donor in organic solar cells, and derivative of the polyazomethine polymer, BOO-PPI. All devices prepared with and without PEDOT:PSS layer between indium tin oxide (ITO) and organic semiconductor, were studied under nitrogen and air atmosphere, by monitoring their electrical, optical and morphological properties, as function of time, using current-voltage ($I$-$V$) characteristics, UV-Vis spectroscopy and atomic force microscopy (AFM) imaging.

2. Polymer thin films preparation and experimental details

As a front electrode glass/ITO substrates (15Ω/□, KinTec Co.) pre-cleaned by subsequent ultrasonic washing with an acetone (10 min), isopropanol (20 min), and deionized water (10 min) were used. After cleaning ITO surface was dried with nitrogen. Part of the studied diode structures were prepared on the cleaned glass/ITO
substrate covered with PEDOT:PSS (Baytron P, Cleve-
vice Co.) interfacial layer. This interfacial layer was
spin coated from 70% solution of PEDOT:PSS diluted
in deionised water and dried in air on the hot plate at
150°C for 5 min. In our study, soluble derivative of poly-
thiophenes, regioregular poly(3-hexylthiophene) (98%,
Rieke Metals) was used without further purification. The
P3HT was dissolved in chlorobenzene (99%, Acros Or-
ganics) with a concentration of 10 mg/mL and BOO-PPI
was dissolved in chloroform (99%, SigmaAldrich) with
a concentration of 6 mg/mL. At a later stage both poly-
mers were deposited by spin coating on the glass/ITO
and the glass/ITO/PEDOT:PSS substrates.

Fig. 1. Polymer repeating units: (a) BOO-PPI,
(b) P3HT.

Structures of the polymers described used in this re-
search are presented in Fig. 1 for the BOO-PPI (a)
and the P3HT (b), respectively. For studying electrical
properties in the diode architecture a 100 nm thick
Al electrode was evaporated on the top of organic layer.
These structures were kept and characterized in a glove-
box under nitrogen atmosphere (Linz) or exposed in air
(Zabrze). In this manner, we compared the stability of
the diodes prepared in two different laboratories starting
from the same organic semiconductor basic materials and
we had a possibility to evaluate reproducibility as well as
quality of particular technological processes connected
with the devices fabrication, e.g. deposition of organic
thin film or metal electrode. It should be stressed that
stability of the organic layered structures without top
metallic electrode were monitored using UV-Vis JASCO
V-570 spectrometer and Topometrix AFM analysis, which
however have not revealed any visible changes in the po-
sition of optical absorption band maxima of the UV-Vis
spectra with time. However, we have observed small
changes (variations) in the absorbance level.

3. Results

Representative current–voltage characteristics taken
on ITO/X/BOO-PPI/Al and ITO/X/P3HT/Al (where
X represent lack or existence of PEDOT:PSS layer)
diodes under nitrogen gas atmosphere are compared in
Fig. 2 and Fig. 3, respectively. Numerical labels on the
curves indicate the time in days. The I–V charac-
teristics labeled by 1 were taken on the fresh diodes. As
can be seen, the BOO-PPI based diodes revealed relatively
stable electrical conductivity, irrespective of presence of
interfacial PEDOT:PSS layer. P3HT based diodes with-
out PEDOT:PSS layer showed a quick decrease of their
electrical conductivity, within first day, and then stabi-
li
d. It is important to note also significantly higher currents in BOO-PPI diodes without PEDOT:PSS layer on the ITO electrode.

Fig. 2. Comparison of the I–V characteristics for
the ITO/PEDOT:PSS/BOO-PPI/Al and ITO/P3HT/
BOO-PPI/Al diodes as measured on fresh devices (marked
by 1) and after 5 days (marked by 5). The devices were
kept in nitrogen gas atmosphere.

Fig. 3. Comparison of the I–V characteristics for
ITO/PEDOT:PSS/P3HT/Al and ITO/P3HT/Al
diodes as measured on fresh devices (marked by 1) and
after n days (number of days marked on the plots).
The devices were kept in nitrogen gas atmosphere.

To carry out studies under ambient air condition, sim-
ilar structures based on P3HT and BOO-PPI from the
same organic materials have been prepared in Zabrze.
All the studied structures, without or with PEDOT:PSS
interfacial layer, revealed quick degradation of their elec-
trical properties. Practically, within few days we have
observed total disappearance of their electrical conduc-
tivity. For instance, in Fig. 4 we show the I–V character-
istics for ITO/PEDOT:PSS/BOO-PPI/Al device mea-
sured in the dark immediately after preparation and after
24 h. One can observe a very quick complete disappearance of the electrical conduction in this case.

4. Discussion

To identify different electrical transport mechanisms, in the log-log scale, we fitted the experimental forward-dark current with the straight lines, corresponding to the currents with the power law voltage dependence $I \sim V^n$ where $n = 1$, 2 and 5. The linear and square voltage dependence can be attributed to the ohmic and the trap free space-charge limited conduction (SCLC), while $I \sim V^5$ indicates that either trapping or effect of field on mobility is important [14]. Such analysis applied to data presented in Fig. 3 (P3HT based diodes) revealed that the relatively large current $I \sim V^5$ disappeared within first day after the device preparation. Then, persisted currents follows Ohm’s law voltage dependence and SCLC law with $I \sim V^2$. Similar analysis performed on the data presented in Fig. 2 showed that in BOO-PPi based diodes, the linear $V$ dependence directly changes to the trap free SCLC ($I \sim V^2$) form. This finding allows for the quantitative analyses according to Refs. [9-14].

Most of the organic semiconductors due to the lack of air stability have a natural p-type doping in the range 10^{15–10^{17}} cm^{-3} and reveal ohmic conduction at low voltage (between the ohmic contacts) [9, 14]:

$$J = qn\mu \frac{V}{L},$$

where $q$ is the charge, $n$ — the charge carrier density, $\mu$ — the carrier mobility, $V$ — the applied voltage and $L$ — the thickness of the organic material. For higher voltage conduction changes to the trap free SCLC [9, 14]:

$$J_{SCLC} = \frac{9}{8} \varepsilon \varepsilon_0 n \mu \frac{V^2}{L^3},$$

where $\varepsilon$ is the dielectric constant of the organic material and $\varepsilon_0$ is the vacuum permittivity. When a transition from the Ohm law to the SCLC occurs, the both currents are equal at the transition voltage $V_{tr}$, which can be determined experimentally. In this case, the doping density $n$ can be calculated from the following relation [14]:

$$n = \frac{9\varepsilon \varepsilon_0 V_{tr}}{8qL^2}.$$  (3)

The last equation allows us to determine the charge carrier density $n$ from data presented in Fig. 1. In order to calculate corresponding densities, the thickness of the BOO-PP1 layer in the diodes $L = 160 \pm 10$ nm were measured using the AFM. Determined values of $n$ on fresh diodes for ITO/BOO-PP1/Al (ITO/PEDOT-PSS/BOO-PP1/Al) are 1.1 x 10^{16} (3.1 x 10^{15}) and after four days 1.5 x 10^{16} (5.3 x 10^{15}) cm^{-3}, respectively. Let us note, about one order of magnitude higher $n$ in diodes without PEDOT-PSS layer and visible increase of $n$ within the time. This result is attributed to an active role of ITO electrode in increasing doping of BOO-PP1. In this manner, we can regard on the PEDOT-PSS layer as on the buffer layer which prevent the doping by ITO.

We now turn to discuss the results presented in Fig. 2 in more detail. One can observe that $I-V$ characteristics for ITO/P3HT/Al device quickly changed with the time and became qualitatively similar to that presented in Fig. 1, whereas $I-V$ dependences for ITO/PEDOT-PSS/ P3HT/Al diodes behave differently. They are stable in time and do not reveal the SCLC in the range of applied voltages. Moreover, one can observe even an improvement of their conduction properties with time (compare corresponding plots 1 and 5), this feature can be attributed to the relaxation processes which increase spatial ordering of the P3HT layer. Nevertheless, the marked importance of the PEDOT-PSS layer in the P3HT based devices is clear. According to the mentioned similarity between the both figures, we can extend our interpretation on the P3HT based devices. Namely, we may also ascribe observed increase in the ohmic current at low voltage in glass/ITO/P3HT/Al device as to caused by the extra doping introduced by the ITO. Inversely, presence of the PEDOT-PSS layer prevents the doping in glass/ITO/PEDOT-PSS/P3HT/Al diodes.

5. Conclusions

The studies of stability of P3HT and BOO-PP1 based diodes performed under nitrogen atmosphere, clearly indicate an important role of the PEDOT-PSS thin layer on short time stability of electrical conduction in studied diodes. Studies performed on the BOO-PP1 based diodes revealed that irrespectively of the presence of the PEDOT-PSS thin layer their forward electronic conduction is dominated by the Ohm law type current at low voltage and by the trap free SCLC with current proportional to $V^2$ at higher voltage. The value of the doping density $n$ depends strongly on the presence of the PEDOT-PSS thin layer in the diodes architecture. We have presented convincing arguments that the PEDOT-PSS layer appears as the buffer layer which prevents the doping by the ITO substrate. Moreover, this interpretation is consistent also with our results obtained on the P3HT based diodes. Namely, we can ascribe observed in the time...
increase in the ionic current of ITO/P3HT/Al diodes as the result of doping introduced from ITO to interfacial P3HT, whereas in the diodes ITO/PEDOT:PSS/P3HT/Al presence of the thin PEDOT:PSS buffer layer prevents the extra doping, simultaneously stabilizing conduction. Performed studies on similar devices kept and measured in ambient air indicated their very low electrical conduction stability which undergoes fast and strong degradation.

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References