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ELECTRICAL CHARACTERIZATION OF PEDOT:PSS BASED FLEXIBLE ORGANIC OPTOELECTRONIC DEVICES

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Abstract- Electrical behavior of PEDOT:PSS films was investigated for potential application as anode in ITO-free flexible organic optoelectronic devices. Current-voltage, capacitance-voltage, capacitance-frequency and contact resistance-bending cycles characteristics were measured at different electrode configurations, as well as with and without post-deposition treatment procedure of the polymer film. Information about the hole mobility, conduction mechanism and electrical parameters' stability at defined operational voltage and mechanical loading was extracted. It was found that UV treatment of the polymeric films is favorable for the improvement of its mechanical stability and the contact resistance, but it results in increasing of the interface capacitance. Optimum electrode gap of 6 mm was established, based on the results obtained for the hole mobility and the specific zones of current saturation from the current-voltage characteristics. Operational voltage of the unipolar type structure PEDOT:PSS/copper was measured to be 3 V.

Keywords: Flexible Optoelectronic Device, Thin Polymeric Films, PEDOT:PSS, ITO-Free Transparent Electrode.

I. INTRODUCTION

In the recent years, a wide range of functional and substrate materials have been investigated for potential application in flexible organic optoelectronic devices [1]. One of the main difficulties that still should be overcome is the need of films durable at different mechanical loads (rolling, bending and folding) [2]. The poorest component in such devices is the transparent anodic film, typically produced of indium tin oxide (ITO). It has low electrical resistance of 30 ohms/square and high optical transmittance (>90%), which makes it excellent choice for glass optoelectronic devices [3].

However, the thin ITO films are brittle and easy damageable at continuous bending stress conditions [4]. Currently, new materials have been explored for replacing ITO anodes in the flexible organic light emitting devices (OLED) and solar cells [5]. Suitable alternatives seem to be metal nanogrids [6], ultra-thin metal films [7], metal nanowires [8], carbon nanotubes [9], graphene [10] and poly(3,4- ethylenedioxythiophene) polystyrene sulfonat (PEDOT:PSS) films [11]. Indeed, the most promising candidate is PEDOT:PSS, due to the low-cost fabrication of thin films by spin-coating and spray deposition. It can also serves as hole transporting and injecting material, when combined with the typically used electroluminescent organic substances.

Although the polymeric anodes have a number of advantages over ITO in terms of low cost, easy processing and mechanical strength, one of the drawbacks, stopping yet their commercial application, is their relatively low conductivity, high threshold operational voltage of the devices, using PEDOT:PSS and high interfacial capacitance [12]. For improving the electrical performance of PEDOT:PSS electrode, more information about its charge transport and interfacial properties is necessary. Mobility of the main charge carriers in PEDOT:PSS (holes) is one of the important parameters for tuning the polymer films thickness, regarding effective current supplying, optimal hole transport and hole injection/extraction ability. The optimized thickness will result in balanced mobilities of holes and electrons, causing higher probability for emissive recombination in OLEDs or efficient charges extraction in solar cells.

Based on the shape and slope of the current-voltage characteristics of the system organic film/metal interface, information about the injection and transport mechanism of the charge carriers at the interface and in the bulk of the structure can be received [13]. Different methods for interpretation of the electrical behavior of such structures have been reported in the literature, and variety of models have been applied to describe the progress of the *I-V* characteristics. The most popular models are Richardson–Schottky, Fowler-Nordheim and Space Charge Limited Current (SCLC) theories [14].

In the most of the cited papers, the structures are multilayer, independently of the used polymer type, but for the present study, space charge limited current in single PEDOT:PSS based structure is one of the most suitable approaches for extracting valuable information about the material behavior. Impedance spectroscopy (IS) also has been demonstratedas a powerful technique for exploring the charge carrier transport mechanisms in the organic based devices [15]. The electrical behavior of organic semiconductors have been studied using IS in combination with current-voltage characteristics measurements based on single layer structures [16]. It allows determination of the structures' contact resistance.

The aim of this study is application of the typical methods for organic materials electrical characterization to extract information about the main electrical parameters of PEDOT:PSS thin films with potential application as electrode in flexible optoelectronic devices. For this purpose current-voltage, capacitance-voltage, capacitance-frequency characteristics, and contact resistance as a function of bends number, were measured for samples with different electrode configurations and post-deposition treatment procedure. The voltage dependent hole mobility was determined for all cases and recommendations about the entire optoelectronic device architecture for high conversion efficiency obtaining were given.

II. EXPERIMENTAL SECTION

Pieces with size 2×1 cm were cut from polyethylene terephthalate (PET) foil with thickness of 200 µm. For studying the hole transporting properties of PEDOT:PSS, hole only devices were fabricated, by using copper top and bottom electrodes ("sandwich" type structures). Due to the big difference between the copper's work function (4.7 eV) and the lower unoccupied molecular orbital (LUMO) energy of PEDOT:PSS (2.4 eV), the electron injection at the interface PEDOT:PSS/Cu is blocked, but the hole injection is fluent. In this way hole current circulates in the structures prepared and all processes revealed can be attributed to single type charge carriers.

PEDOT:PSS solution was purchased from Sigma Aldrich and thin films were produced on the top of Cu/PET substrates by spin coating at 2 000 rpm for 40 sec. Afterward, the films were dried at 60 ^{o}C per 20 min. The resulted thickness of the PEDOT:PSS films was 35 nm, measured by Tencor Alpha-Step Surface Profiler. Copper adhesive tape was used as top electrodes, situated at different distances, respectively 2 and 6 mm from each other, which correspond to distances between segments for seven segment digital indicator (if we assume for example display application). In this way, the produced lateral conductive channel may give information about the range of revealing of the electrical processes. Configuration of the tested flexible devices is shown in Figure 1. Some of the samples were treated before and after PEDOT:PSS films deposition with UV exposure source, having wavelength of 365 nm for PET surface modification [17] and contact resistance reduction.

Current-voltage transfer characteristics (*I*-*V*) were measured by picoammeter Keithley 6485. Capacitance-voltage dependences (*C*-*V*) and contact resistance were recorded by LCR meter Instek 819. Impedance characteristics and capacitance-frequency dependences were measured in the range 100 Hz - 100 kHz at bias voltage of 2 V with same LCR meter. Repeating bending cycles were applied by homemade setup generating 25 N compression/tension force cycles. Schematic of the bending test setup is shown in Figure 2.

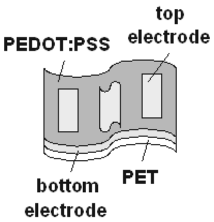

Figure 1. Configuration of the tested flexible devices.

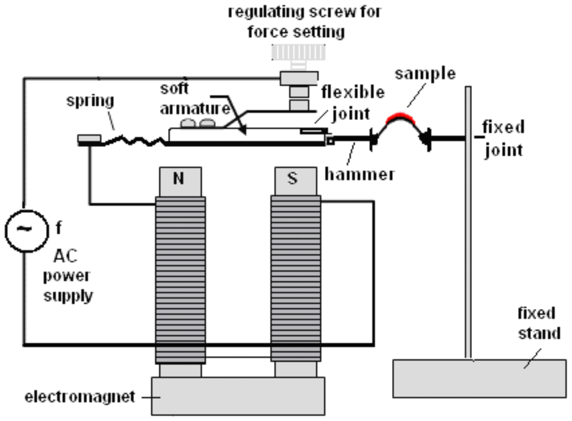

Figure 2. Schematic representation of the setup for bending cycles generation

III. RESULTS AND DISCUSSION

Figure 3 shows the I-V transfer characteristics of the hole only devices in p-channel operational mode, measured for different channel lengths and different samples treatments. As can be seen the current at the shorter channel length of 2 mm is the lowest and almost independent of the voltage applied. This effect, similar to structure saturation, can be ascribed to the space charges accumulated in the bulk between the neighboring electrodes, creating build-in potential near the electrodes and repulsing the new incoming positive charges.

The result is relatively sharply decreasing current (from 4 mA to 1 mA) at voltages higher than 3 V, compared to the 6 mm channel length device. It is also related to the low charge carriers mobility of PEDOT:PSS material. At higher distance for charge carriers collection of 6 mm, this effect is weaker and the space charges are distributed in such way in the electrode gap, that blocking effect for hole injection is not revealed. The abrupt increase of the current for the UV treated sample (almost 5 times higher compared to the non-treated samples) suggests hole traps activation. The traps restrict the current flow, due to recombination processes and capturing of the free charge carriers. The results obtained are in good agreement with the observed in the literature [18]. UV energetically activated trap centers release the trapped carriers, which contribute to the current flow. The electrical field additionally stimulates this process. This is the reason for increasing of the current with the voltage increase. At 3.5 V the current reaches 22.3 mA for UV treated sample with channel length of 6 mm.

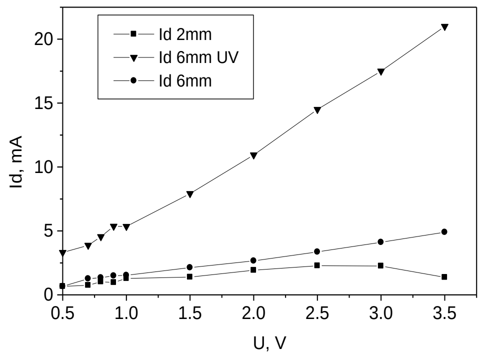

Figure 3. *I-V* characteristics of PEDOT:PSS based samples at different electrode distances (channel lengths) and post-deposition treatment procedures

The mobility of holes in this system was determined by using gradual channel approximation. In layers of disordered matter, such as polymers, charge carrier mobility is strongly dependent on the carrier concentration, i.e. the mobility is voltage dependent in channel type devices. In saturated mode (in our case after 3 V, where the current is limited by the space charge) the voltage dependent carrier mobility $\mu(U)$ is given by Equation (1) [19]:

$$\mu(U) = \frac{2l}{C_i.w}\left(\frac{\partial\sqrt{I_d}}{\partial U}\right)^2 \qquad (1)$$

where l is the distance between the electrodes (length of the channel), w is width of the channel (length of the electrodes), C_i is the capacitance per unit area (based on the relative dielectric permittivity of PEDOT:PSS, which is assumed to be 2.2 [20]); I_d is the current between the electrodes and U is the voltage.

In order to obtain reliable mobility values from the structure, the threshold voltage should be also taken into account. In our case, measurable noise-free current is generated at 0.5 V, which can be assigned as threshold value. This voltage is dependent on the contact injection barrier at the electrode/semiconductor layer interface, total trap density formed by the traps in the bulk and at the interface, capacitance and etc. The voltage dependent hole mobility for the studied samples is shown in Figure 4.

The responses of the hole mobility for all samples were similar in trend, but highly different in magnitude. All voltage dependent mobility curves reached a maximum at approximately 2 V and then started to decrease with further voltage increasing. In the treated by UV samples, the hole mobility was two orders of magnitude higher in comparison to the non-treated one, probably due to reorganization of the PEDOT particles and greater degree of ordering [21]. At the shortest channel, due to the space charge formation, the hole mobility is the smallest and its maximum barely reached 2.10^{-6} cm^2/V.s.

Contact resistance is another factor important for consideration during the electrical characterization of such structures. As has been reported in [17], UV treatment improves mechanical strength and adhesion of PEDOT:PSS polymer, deposited on flexible foils. In the present study, it was found that the post-deposition treatment by UV additionally improved the PEDOT:PSS surface conductivity.

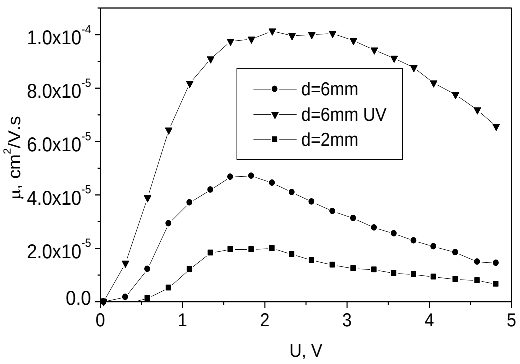

Figure 4. Voltage dependent hole mobility in PEDOT:PSS electrode film

Lack of such treatment leads to higher contact resistance of 59 Ω versus 53 Ω for treated one before bends, as can be seen in Figure 5. The instability of the contact PEDOT:PSS/Cu is within 1.1% for the treated samples after 20 000 bends applied. For comparison, non-treated ones exhibited over 6% change of the contact resistance at the same conditions. Further spectroscopic analyses will be conducted for the UV treated PEDOT:PSS films to clarify the mechanism of contact resistance reduction.

It should be mentioned that when the PET is bent by vibration, in certain moment one of the surface experiences tensile stress and the other one - compressive stress. In the next moment (defined by the frequency of the bending cycles), the situation is reversed. Films are one side deposited, so they are subjected to stress and strain forces.

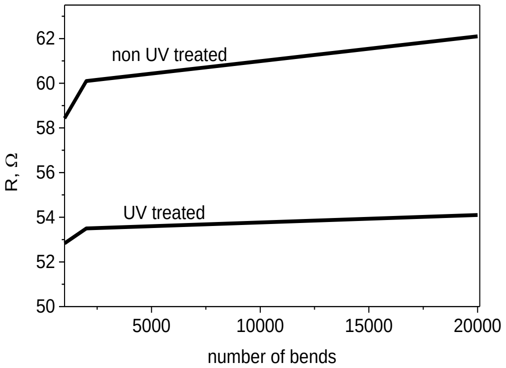

Figure 5. Contact resistance at the PEDOT:PSS/Cu interface after multiple bends for different post-deposition treatment conditions of PEDOT:PSS film

The results from the contact resistance measurements show that the devices exhibits high stability, in spite of the type of mechanical deformation that is applied. Moreover, all layers in the stack exhibit high durability and no stress is transferred between the contacting materials. Regarding the radius of curvature, set during the bending test, as the films are thinner compared to the substrate thickness (200 μm), the radius of curvature for the substrate is accepted as radius of bending for the whole device [22]. For the used setup the radius of curvature is 10 mm.

Capacitive-volt characteristics (*C-V*) provide useful information about the electrical properties at the junctions [23]. *C-V* characteristics (Figure 6) showed relatively small variations up to 1 V and then gradually increased with the voltage increasing. The results confirm the observations for the contact resistance, as for the UV treated sample, where the contact is highly adhesive and the interface contact is stable, the interface capacitance is also stable and almost unchanged with the voltage. Gradually decreasing of the capacity with the frequency increase can be related to the low charge carriers' mobility in organic materials. Thus, when a great number of charge carriers are injected into the organic layer, space carriers accumulated near the electrode interfaces act as barrier and restrict further injection, resulting in capacity decrease.

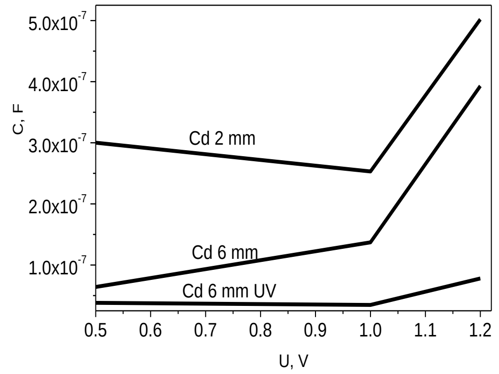

Figure 6. C-V characteristics of PEDOT:PSS based samples at different electrode distances and post-deposition treatment after 10 000 cycles of bending

Figure 7 presents the dependence of the junction capacitance on the frequency for PEDOT:PSS/Cu interface with UV treated and non-treated polymer layer. Both characteristics showed relatively small variations up to 1 kHz (within the same order of magnitude) and then gradually decrease with the frequency increasing. This trend is ascribed to the low charge carrier mobility in the polymer and the poor ability of the charges to follow the changes in the AC signal with the same rate. In the low frequency range, the capacitance depended stronger on the surface condition near the electrodes.

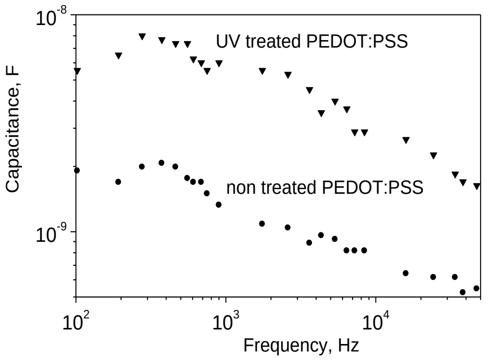

Figure 7. Capacitance versus frequency for PEDOT:PSS/Cu interface with UV treated and non-treated polymer film without bending

The UV treatment of PEDOT:PSS film led to average 3 times increasing of the capacitance in the whole frequency range in comparison to the interface with non-treated PEDOT:PSS. This can be explained with the enhancement of the conductivity of the PEDOT:PSS films when their surface is activated by UV exposure.

Although further study of the work function of PEDOT:PSS in needed, it can be concluded from Figures 5, 6 and 7, that the UV treatment of the PEDOT:PSS films probably shifts its work function. This is possible approach to tune the bulk electrical properties of the transparent anodic films and the interface injection properties. The second approach is variation of the electrode gaps and configuration.

IV. CONCLUSION

In a flexible organic optoelectronic device, the electrodes configuration should ensure path for the holes in a long distance, to prevent space charges accumulation, mobility decreasing, current flow saturation and hole injection (or extraction) blocking. The operational voltage range in PEDOT:PSS/Cu devices is up to 3-3.5 V, therefore the electron injecting/extracting electrodes and electron transporting layers should have operational voltage in the same range for high efficiency of the optoelectronic device. UV treatment of the PEDOT:PSS films make them suitable alternative to ITO with similar contact resistance. Although the UV treatment makes the resistance more stable to multiple bends, the interface is characterized by relatively higher transient capacitance, which may affect some dynamic parameters, such as switch rate, for example.

In summary, information about the electrical behavior of the charge carriers in a polymeric based device, based on typical electrical characteristics of the electrode interface was extracted. If the copper top electrode is replaced by organic film with energy of its highest occupied molecular orbitals similar to Cu work function, then the above described effects will take place. The approach used is helpful for optimizing the device performance. The results can be useful not only for flexible organic optoelectronic devices with patterned electrodes, but for organic thin film transistors as well.

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Mariya Aleksandrova was born in Sofia, Bulgaria, 1983. She received the B.Sc. and the M.Sc. degrees of electronic engineering from Technical University of Sofia, Department of Microelectronics in 2005 and 2007, respectively, and the Ph.D. degree in the field of interface optimization of molecular optoelectronic devices, at the same department, in 2010. Currently, she is Associate Professor in this department (Laboratory "Vacuum Deposition Processes"). Her research interests are in organic semiconductors, thin films, light emitting devices, material science for micro- and nanosystems. She is head of projects for fabrication of flexible OLED with new polymeric materials and technologies. Her academic activity during the last 2 years is related to establishing new M.Sc. degree program "Microtechnologies and Nanoengineering" in Technical University of Sofia. She serves as reviewer for the journals "Material Science and Engineering B", "Materials and manufacturing processes", and etc. She is member of the National Institute of Standardization of Bulgaria, "Nanotechnology" section.

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