Analysis of Electrical and Optical Properties
of DNA:PDT-PSS Thin Films

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We report investigations of functionalized DNA:PEDT-PSS films. The electrical conductivity of the sample material at the room temperature was about \((1–5) \times 10^{-10} \, \Omega^{-1}\, cm^{-1}\). The IV curves of the samples were linear and symmetrical in the region from the room temperature down to the liquid Nitrogen temperature. The thermal activation energy of the conductivity near the room temperature was about 0.033 eV independently on the applied bias. The weak carrier trapping was identified by the Thermally Stimulated Current method, proving the fast recombination of light-generated carriers. Notably, by constant light excitation a “bistable” photoconduction below the room temperature was evidenced. i.e., upon excitation by a white light a remarkable increase of the photocurrent could be observed below 145–155 K by cooling the samples. Meanwhile by heating the photosensitivity remained increased up to 235–245 K. Such phenomenon could presumably be attributed to the light-induced morphology changes of the sample material.

Keywords: Deoxyribonucleic acid (DNA), PEDOT, electrical conductivity, photoconductivity, carrier trapping, light absorption.

1 INTRODUCTION

Nucleic acids and their derivatives attract a lot of attention due to their important biological role [1, 2]. At the same time deoxyribonucleic acid (DNA), which exhibits a charge migration, is a subject of interest for its potential of
application in photonics and in molecular electronics [3–5]. However, pure DNA is electrically passive material. In order to render it active one has to functionalize it with poly(3,4-ethylenedioxythiophene) (PEDOT, PEDT) and poly(styrenesulfonate) (PSS) complex. This enables engineering of its electrical properties. Nevertheless, to assure the possibility of the controllable purposeful modification of these properties, extensive investigations are required. In this paper we report investigations of optical and electrical properties of DNA:PEDT-PSS thin films.

2 SAMPLES AND EXPERIMENT

Poly(3,4-ethylene-dioxythiophene) and poly(styrenesulfonate) aqueous dispersion of the intrinsically conductive polymer PEDOT (PEDT-PSS) is available as the trade mark of BAYTRON® PH 500. The chemical structure of polymer complex PEDOT (PEDT-PSS) is presented in Fig. 1. The weight ratio of PEDT to PSS is about 1:2.5. This waterborne dispersion is ready to use and can be deposited by spincoating with viscosity max. 30 mPa·s. It is tailored to a high conductivity and forms conductive coatings.

DNA sodium salts, extracted from salmon milt and roe were provided by CIST. After sonication of DNA in deionized water, DNA solution was added to PEDT-PSS aqueous solution with different ratios 1:0.2 and 1:0.5 of DNA:PEDT-PSS. The solutions of polymers were spin-coated at 500 or 1200 rpm on the glass substrates coated by Indium-Tin-Oxide (ITO). The thickness of the thin solid films was 0.3–1.5 µm. The semi-transparent aluminium contacts were evaporated on the top. Alternatively some samples were deposited on gridded intercalated electrodes initially evaporated on the glass substrates.
The films were characterized by the UV and visible spectroscopy. Their Current-Voltage (IV) characteristics and conductivity temperature dependencies were measured from 77 K up to 300 K depending on the white light excitation.

3 RESULTS AND DISCUSSION

3.1 Optical Properties

In Fig. 2 absorption spectrum of a DNA-PEDT-PSS (1:0.5) thin film is presented. A strong UV absorption band is seen below 280 nm. It corresponds to the $\pi-\pi^*$ transition of electrons of the C=C bond of the DNA bases. The another wide and low absorption band at around 900 nm is associated with the conductive polymer PEDT-PSS.

3.2 Electrical properties

Sample conductivity at room temperature was in average about $(1–5) \times 10^{-10} \, \Omega^{-1} \cdot \text{cm}^{-1}$, though it could deviate by up to two orders of magnitude even in the samples produced on the same substrate, indicating sensitivity of their properties to the technological conditions. IV curves were linear and symmetrical down to 78 K temperature as it is shown in Fig. 3. The samples were photosensitive. At the room temperature the photosensitivity was about $\sim 10$ per cent, and it increased up to a factor of two at the low temperature. Its dependence on the temperature was quite complex as it will be discussed below.

Characteristically, sample reaction on the applied voltage and light pulses was different: upon application of a voltage step very fast increase of the current was observed, meanwhile the photocurrent growth was relatively slow and could be approximated well by the exponential dependence as it is indicated
FIGURE 3
IV curves of the sample upon illumination by white light (dashed curves) and in the dark (solid lines) at 300 K and 78 K as indicated on the Figure.

FIGURE 4
Sample reaction on applied voltage pulse and white light pulse (dashed curve) as indicated on the Figure. The photocurrent growth could be approximated well by exponential dependence as indicated by the solid curve.

on Fig. 4 by the solid line. In the present case time constant of the exponential increase was \(~80\) sec, and this value used to shorten with temperature. Nevertheless this process still has to be investigated in more detail. Current decay after the light is switched off occurs similarly. This evidences that different carrier transport mechanisms play a role in both cases. Upon application of the voltage pulse fast carrier injection from contacts takes place that is limited by ohmic conduction of the sample volume. Meanwhile slower light-induced generation of carriers occurs from their transport and/or trapping states.

To investigate carrier transport and thermal generation processes depending on temperature, temperature scans of the dark current, Thermally Stimulated
FIGURE 5
Temperature dependencies of the photocurrent (PC—solid curves), upon scanning the temperature down and up as indicated by the arrows and the dark current (DC—dashed curves) at 0.2 V bias and without any applied bias.

FIGURE 6
TSC scans in two samples, measured at 0.5 V applied bias after the white light excitation (solid curves). Dashed curves indicate linear fits in Arrhenius scaling.

Currents (TSCs) and photocurrent were measured as demonstrated in Figs 5, 6. The details of the TSC method are presented in [6–8]. Close to the room temperature the thermal activation energy of the dark current is about 0.033–0.035 eV (Fig. 5). These values were not dependent on the applied bias. Below about 130 K–140 K a characteristic kink appears, and the thermal activation energy drops in below 0.014 eV, approaching in some samples zero values.

Characteristically TSCs are low as compared with both dark current and current after the light excitation, as can be seen from Fig. 6. This indicates
that relatively small number of carriers becomes trapped, and most of them recombine after the light excitation is turned off. Nevertheless nearly the same activation energy values of about 0.036–0.043 eV were evaluated in a wider temperature region as compared to the dark currents. Such low activation energy values could be indication that current increase is related to transport phenomena, i.e., growth of carrier mobility, rather than change of the carrier density because of their thermal generation. Similar conclusion was made also for disordered P3HT-PCBM bulk-heterojunction organic Solar cell structures [9]. This assumption is realistic by having in mind complicated hopping transport character in disordered organic materials. Therefore evaluated activation energies could probably reflect the energetic spread in the charge transporting levels, resulting in distribution of the density of transporting states (DOS). As it was mentioned above a characteristic kink was observed in dark current measurements that becomes even more expressed upon light excitation. A typical behaviour is presented in Fig. 5.

It can be seen that by lowering the temperature the photocurrent starts growing at about 145–155 K and reaches saturation level that is by a factor of about (2–2.5) higher than that of the minimum. Afterwards, if the temperature is increased the photocurrent changes relatively little up to about 238 K, forming a “bistable” loop. This behaviour does not change with applied bias, indicating that the effect is light-induced. Most probably such phenomenon could be attributed to the light-induced morphology changes of the samples, resulting in a sudden increase of photosensitivity of material at low temperatures. Nevertheless to reveal its exact nature, further investigations are necessary.

4 SUMMARY AND CONCLUSIONS

We have investigated DNA:PEDT-PSS thin films that are of particular interest for their functional optoelectrical properties. After sonication of DNA in deionized water, DNA solution was added to PEDT-PSS aqueous solution with different ratios 1:0.2 and 1:0.5 of DNA:PEDT-PSS. The solutions of polymers were spin-coated on the ITO glass substrates. The thickness of the films was 0.3–1.5 µm. They were characterized by the UV and visible spectroscopy. Their conductivity temperature dependencies were measured from 78 K up to 300 K depending on the light excitation.

Sample conductivity at room temperature was in average about \((1–5) \times 10^{-10} \ \Omega^{-1} \text{cm}^{-1}\), though it could deviate by up to two orders of magnitude even in the samples produced on the same glass substrate indicating sensitivity of their properties to the technological conditions. IV curves were linear and symmetrical down to 78 K temperature. The thermal activation energy of the dark conduction near the room temperature was about 0.033 eV independently on the applied bias.
We have identified weakly expressed carrier trapping by the Thermally Stimulated Current method, what proves the fast recombination and/or retrapping of light-generated carriers. Though, by constant light excitation a “bistable” photoconduction below the room temperature was evidenced. i.e., a notable increase of the photocurrent could be observed below 140–160 K by cooling the samples. Meanwhile by heating the photosensitivity remained increased up to 230–240 K. Most probably such phenomenon could be attributed to the light-induced morphology changes of the samples.

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REFERENCES


