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Functional Properties of Thin Films of Deoxyribonucleic Acid with Poly(3,4-ethylenedioxythiophene) and Poly(styrenesulfonate) Complex and Bistability of Their Photocurrent

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Functional photo- and electrical properties of thin films of DNA:PEDT-PSS were investigated. The sample current-voltage dependencies were linear and symmetrical down to liquid nitrogen temperature; the sample conductivity at 300 K was found to be $10^{-10}\ \Omega^{-1}\text{cm}^{-1}$. The thermal activation energy of the dark conductivity was about 33 meV independently on the applied bias in the temperature region between 200 K and 300 K. Carrier trapping was evidenced by the Thermally Stimulated Current method. Nevertheless this effect was weakly expressed, most probably because of the fast recombination of generated carriers. Notably, a "bistable" photoconduction behaviour was identified below the room temperature at constant light excitation. Upon illumination of the samples by ~500 nm – 800 nm light a marked increase of the photocurrent took place by cooling them below 140 K – 160 K. In contrast, by heating the photosensitivity remained increased up to 230 K – 240 K. This effect could be associated with the light-induced modification of charge transport conditions in the samples.

Keywords: deoxyribonucleic acid, poly(3,4-ethylenedioxythiophene), poly(styrenesulfonate), light absorption, electrical and photoconductivity, thermally stimulated conductivity, charge carrier trapping.

INTRODUCTION

Nucleic acids and their derivatives are mostly investigated because of their important biological role [1, 2]. Though, deoxyribonucleic acid (DNA) also exhibits a charge migration, being therefore a subject of interest for its physical properties, and particularly for a great potential of application in photonics and molecular electronics. Such applications include: devices based on second and third order nonlinear optical effects [3], low loss optical waveguides [4], holography [5, 6], organic photovoltaics and organic field effect transistors [7]. However, pure DNA is electrically passive material. In order to render it active the poly(3,4-ethylenedioxythiophene) (PEDT) and poly(styrenesulfonate) (PSS) complex can be used. This enables engineering of material electrical properties. Nevertheless to assure the controllable purposeful modification of these properties, extensive investigations are required. In this paper we report investigations of electrical and optical properties of DNA:PEDT-PSS thin films. The films were characterized by the UV and visible spectroscopy and their electrical conductivity depending on the temperature and excitation by light was analysed.

SAMPLES AND EXPERIMENT

Poly(3,4-ethylenedioxythiophene) and poly(styrene-sulfonate) (Fig. 1) aqueous dispersion of the electrically conductive polymer PEDT-PSS is commercially available as the trade mark of BAYTRON® PH 500. It is specially homogenized to achieve small size particles. The weight ratio of PEDT to PSS is about 1 : 2.5.

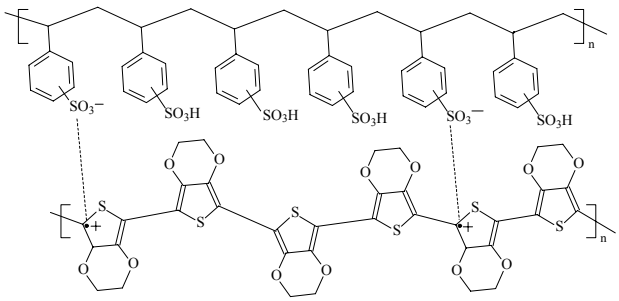

Fig. 1. Chemical structure of PEDT-PSS

This waterborne dispersion is ready to use and can be deposited by spincoating with viscosity max. 30 mPa·s [8]. It is tailored to a high conductivity and forms conductive coatings. This kind of polymer has high conductivity, transparent, colourless to bluish coatings, good resistance to hydrolysis, good photo stability and good thermal stability, high absorption in the range of 900 nm to 2000 nm, and no absorption maximum in the visible spectrum up to 800 nm [9].

DNA sodium salts, extracted from salmon milt and roe were provided by the Chitose Institute for Science and Technology (CIST). Their molecular weight was M_W = 106 Daltons (Da). The high molecular weight DNA rendered inhomogeneous film thickness due to high solution viscosity. In order to reduce the viscosity of the DNA-based solutions an ultrasonic procedure was used [10]. After sonication of DNA (8 g/L) in 18 MΩ cm deionized water, at 20 °C, it was blended using a magnetic

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stirrer overnight and then DNA solution was added to PEDT-PSS aqueous solution with different volume ratios 1 : 0.2 and 1 : 0.5 of DNA:PEDT-PSS. The solutions of polymers were spin-coated at 500 rpm or 1200 rpm on the ITO glass substrates which were cleaned in various solvents. The thickness of the thin solid films was measured by profilometer Tencor, ALFA-Step and was found 0.3 μm – 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 glass substrates.

The films were characterized by the UV and visible spectroscopy. Their Current-Voltage (IV) and conductivity temperature dependencies were measured by Keithley electrometer-voltage source Model 6430 from 77 K up to 300 K depending on the light excitation.

RESULTS AND DISCUSSION

Electrical Conductivity

Sample conductivity at room temperature was in average about $(1-5)\times10^{-10}\ \Omega^{-1}\text{cm}^{-1}$, 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. Current-Voltage (IV) curves were linear and symmetrical down to 78 K (Fig. 2). The samples were photosensitive in the whole temperature region. At 300 K the photosensitivity was about 10 %, and it increased up to a factor of two at the low temperature. Moreover, its dependence was quite complex as it will be discussed below.

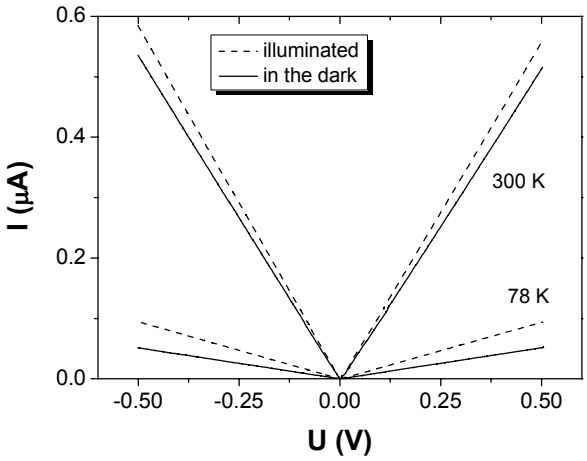

Fig. 2. IV curves of the sample upon illumination by white light (dashed curves) and in the dark (solid lines) at 300 K and 78 K as indicated on the Figure

Typically, 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 on Fig. 3 by the solid line. In the present case time constant of the exponential increase was ~80 sec, and this value decreased 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 generation of carriers occurs from their transport and/or trapping states.

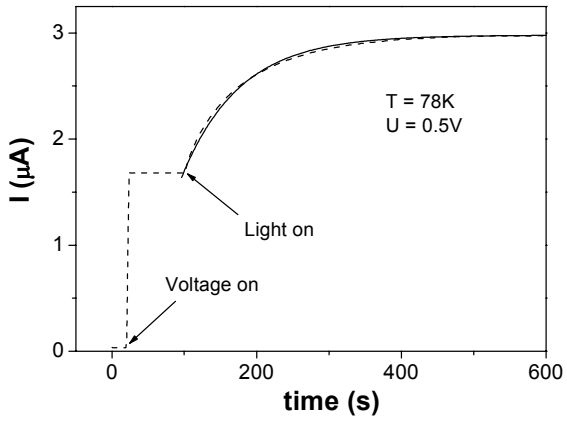

Fig. 3. Sample reaction on applied voltage pulse and white light pulse (dashed curve) as indicated on the Figure. The photocurrent growth could be approximated well by exponential dependence as indicated by the solid curve

Spectral Data

The UV-VIS-NIR absorption spectra of studied thin films deposited on glass substrates were measured at room temperature with a PERKIN ELMER UV/VIS/NIR Lambda 19 spectrometer. In Fig. 4 absorption spectrum of a DNA:PEDT-PSS (1 : 0.5) thin film is presented. The strong UV absorption band is seen at 260 nm – 280 nm which corresponds to the π-π* transition of electrons of the C=C bond of the DNA bases [11]. Another wide and low absorption band at around 900 nm is associated with conductive polymer PEDT-PSS.

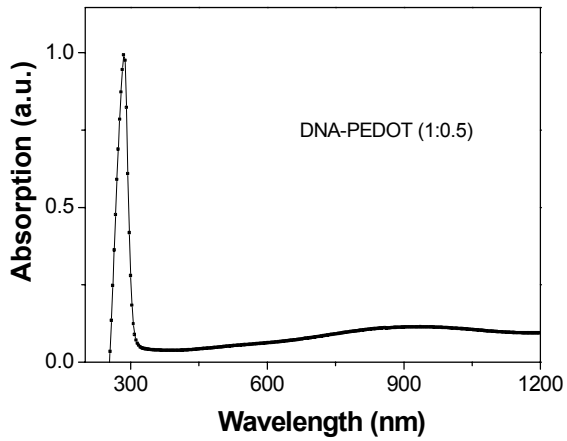

Fig. 4. Absorption spectrum of a DNA:PEDT-PSS (1:0.5) thin film

Thermally Stimulated Currents

To investigate carrier transport and thermal generation processes versus temperature, temperature scans of the dark current, Thermally Stimulated Currents (TSCs) and photocurrent were measured. In Fig. 5 the dark current temperature dependencies are presented for two samples. It

can be seen that close to the room temperature thermal activation energy is 0.033 eV – 0.035 eV. These values were not dependent on the applied bias. Below 130 K – 140 K a characteristic kink appears, and the thermal activation energy drops in below 0.014 eV, approaching in some samples zero value. To investigate this peculiar behaviour, TSC, and temperature dependencies of photocurrent were analysed. The details of the TSC method are presented in [12 – 14]. The TSCs obtained in different samples are shown in Fig. 6.

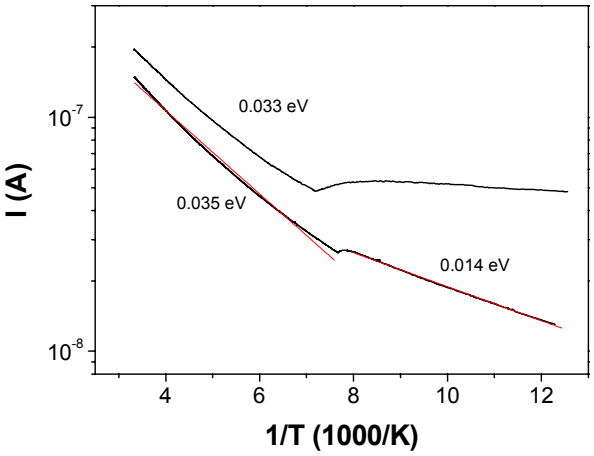

Fig. 5. Dark current temperature dependencies in two samples, measured at 0.5 V applied bias

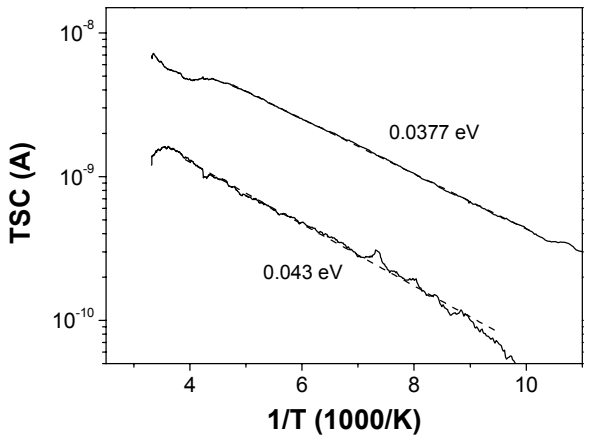

Fig. 6. TSC scans in two samples grown on the same substrate, measured at 0.5 V applied bias after the white light excitation (solid curves). Dashed curves indicate linear fits in Arrhenius scaling

Characteristically TSCs are low as compared with both dark current and current after the light excitation. 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 0.036 eV – 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 the 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 [15]. This assumption is realistic having in mind complicated hopping transport character in disordered organic materials. Therefore the evaluated activation energies could probably reflect the energetic spread in the charge transporting levels, resulting in distribution of the density of transporting states (DOS). To confirm this possibility by direct mobility measurements either by Time-of-Flight (TOF) method, Charge Extraction by Linearly Increasing Voltage (CELIV) method or by other methods used for low mobility materials, special sample preparation and experimental arrangements are necessary, and this is our future task.

Photoconduction and its Bistability

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 of the dark current and photocurrent is presented in Fig. 7.

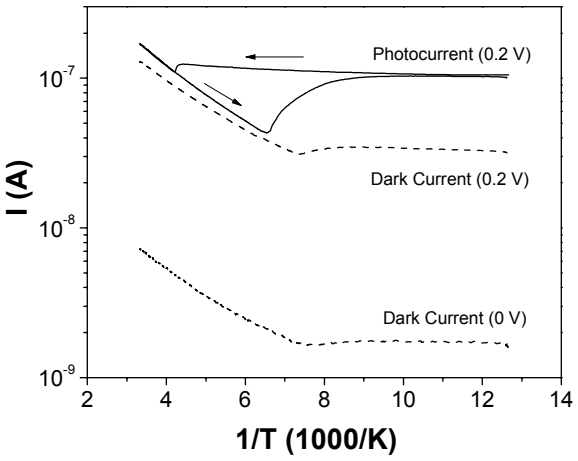

Fig. 7. Temperature dependencies of the photocurrent (PC – solid curves), upon scanning the temperature down and up as indicated by the arrows and the dark current (DC – dashed curves) at 0.2 V bias and without any applied bias

It can be seen that by decreasing the temperature the photocurrent starts growing at 145 K – 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.

SUMMARY AND CONCLUSIONS

Investigations of the electrical, optical and charge transport properties of DNA:PEDT-PSS thin films are presented. Sample conductivity at room temperature was in average about $(1-5)\times10^{-10}\,\Omega^{-1}\mathrm{cm}^{-1}$, 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 LN 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. *Id est*, a notable increase of the photocurrent could be observed below 140 K – 160 K by cooling the samples. Meanwhile by heating the photosensitivity remained increased up to 230 K – 240 K. Most probably such phenomenon could be attributed to the light-induced carrier transport changes of the samples.

Acknowledgments

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