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V. Kažukauskas [a] , A. Arlauskas [a] , M. Pranaitis [a] , O. Krupka [b] , F. Kajzar [b] , Z. Essaidi [b] & B. Sahraoui [b]

[a] Semiconductor Physics Department and Institute of Applied Research of Vilnius University, Vilnius, Lithuania

[b] Laboratory POMA, UMR FRE, Angers University, Angers, France

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Thin Films of DNA:PEDOT-PSS – Electrical and Optical Properties

V. KAŽUKAUSKAS,[1] A. ARLAUSKAS,[1]
M. PRANAITIS,[1] O. KRUPKA,[2] F. KAJZAR,[2]
Z. ESSAIDI,[2] AND B. SAHRAOUI[2]

[1]Semiconductor Physics Department and Institute of Applied Research of Vilnius University, Vilnius, Lithuania
[2]Laboratory POMA, UMR FRE, Angers University, Angers, France

Electrical, charge transport and optical properties of DNA:PEDOT-PSS thin films were investigated. Sample conductivity at room temperature was about (1–5) $\times 10^{-10}\,\Omega^{-1}\,cm^{-1}$*, IV curves being linear and symmetrical down to Liquid Nitrogen (LN) temperature. The thermal activation energy of the dark conduction near the room temperature was about 0.033 eV independently on the applied bias. The small effect of carrier trapping was evidenced by the Thermally Stimulated Current method, proving the fast recombination of light-generated carriers. Though, by constant light excitation a "bistable" photoconduction below the room temperature was identified. I.e., upon excitation by light from the spectral region ~500–800 nm 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.*

Keywords Charge carrier trapping; deoxyribonucleic acid (DNA); electrical and photoconductivity; light absorption; poly(3,4-ethylenedioxythiophene) (PEDOT); poly(styrenesulfonate) (PSS)

PACS 73.50.Gr; 81.40.Rs; 81.40.Tv; 87.85.jc; 87.14.gk

I. Introduction

Nucleic acids and their derivatives attract a lot of attention of researchers 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 physical properties, and particularly for a great potential of application in photonics and in molecular electronics. Such applications include: devices based on second and third order nonlinear optical (NLO) effects [3], low loss optical waveguides [4], holography [5,6], organic photovoltaics and organic field effect transistors (FET) [7]. However, pure DNA is electrically passive material. In order to render it active one has to functionalize it

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Address correspondence to V. Kažukauskas, Department of Semiconductor Physics and Institute of Applied Research, Vilnius University, Saulėtekio 9, bldg.3, LT-10222 Vilnius, Lithuania. E-mail: vaidotas.kazukauskas@ff.vu.lt with poly(3,4-ethylenedioxythiophene) (PEDOT, PEDT) and poly(styrenesulfonate) (PSS) complex. This enables engineering of its 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:PEDOT-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.

II. Samples and Experiment

Poly(3,4-ethylenedioxythiophene) and poly(styrenesulfonate) (Fig. 1.) aqueous dispersion of the intrinsically conductive polymer PEDOT-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 PEDOT to PSS is about 1:2.5. This waterborne dispersion is ready to use and can be deposited by spin coating with viscosity max. 30 mPa · s [8]. It is tailored to a high conductivity and forms conductive coatings. The films are transparent and colourless to bluish. They have good resistance to hydrolysis, good photo stability and good thermal stability, high absorption in the range of 900 to 2000 nm, and no absorption maximum in the visible spectrum up to 800 nm.

DNA sodium salts, extracted from salmon milt and roe were provided by CIST. The molecular weight measured $M_W = 106$ 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 [9]. After sonication of DNA (8 g/L) in 18 MΩ cm deionized water, at 20°C, it was blended using a magnetic stirrer overnight and then DNA solution

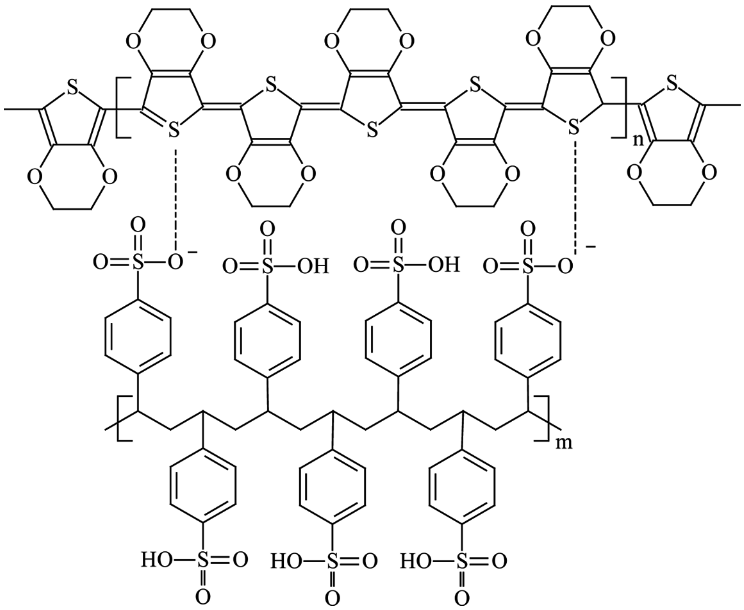

Figure 1. Chemical structure of polymer complex PEDOT-PSS.

was added to PEDOT-PSS aqueous solution with different volume ratios 1:0.2 and 1:0.5 of DNA:PEDOT-PSS. The solutions of polymers were spin-coated at 500 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 0.3–1.5 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.

III. Results and Discussion

III.1. *Light Absorption Spectra*

The UV-VIS-NIR absorption spectra of studied molecules in thin films deposited on glass substrates were measured at room temperature with a PERKIN ELMER UV/VIS/NIR Lambda 19 spectrometer. In Figure 2 absorption spectrum of a DNA:PEDOT-PSS (1:0.5) thin film is presented. The strong UV absorption band is seen below 280 nm which corresponds to the π-π^* 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 conductive polymer PEDOT-PSS.

III.2. *Electrical Conductivity*

Sample conductivity at room temperature was in average about (1–5) × $10^{-10}\,\Omega^{-1}\,\mathrm{cm}^{-1}$, 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 (Fig. 3). The samples had demonstrated photosensitivity starting from

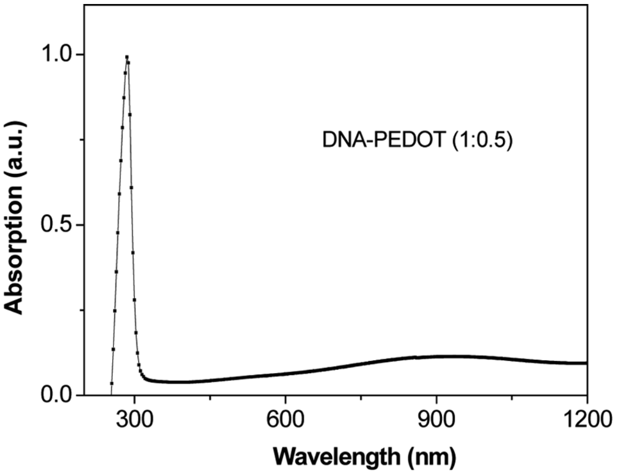

Figure 2. Absorption spectrum of a DNA-PEDOT (1:0.5) thin film.

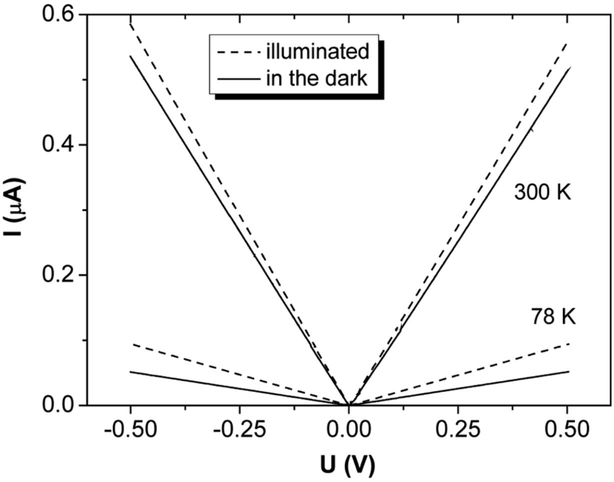

Figure 3. IV curves of the sample upon illumination by white light (dashed curves) and in the dark (solid lines) at 300 K and 78 K as indicated on the Figure.

the room temperature down to 78 K. At the room temperature the photosensitivity was about ~10 per cent, 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.

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 on Figure 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

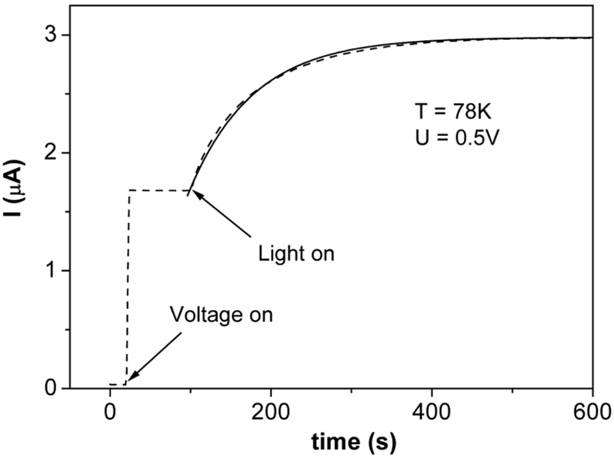

Figure 4. Sample reaction on applied voltage pulse and white light pulse (dashed curve) as indicated on the Figure. The photocurrent growth could be approximated well by exponential dependence as indicated by the solid curve.

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.

III.3. *Thermally Stimulated Current Spectra*

To investigate carrier transport and thermal generation processes depending on temperature, temperature scans of the dark current, Thermally Stimulated Currents (TSCs) and photocurrent were measured. In Figure 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 about 0.033–0.035 eV. 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 below 0.014 eV, approaching in some samples zero values. To investigate this peculiar behaviour, Thermally Stimulated Current (TSC), and temperature dependencies of photocurrent were analysed. The details of the TSC method are presented in [10,11,12]. The TSCs obtained in different samples are shown in Figure 6.

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 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 [13]. 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

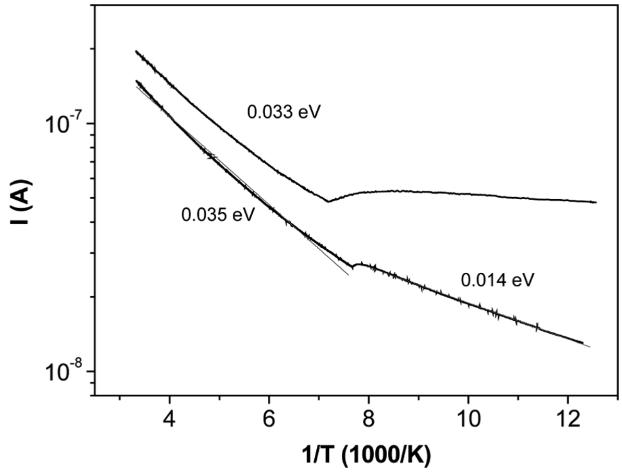

Figure 5. Dark current temperature dependencies in two samples, measured at 0.5 V applied bias.

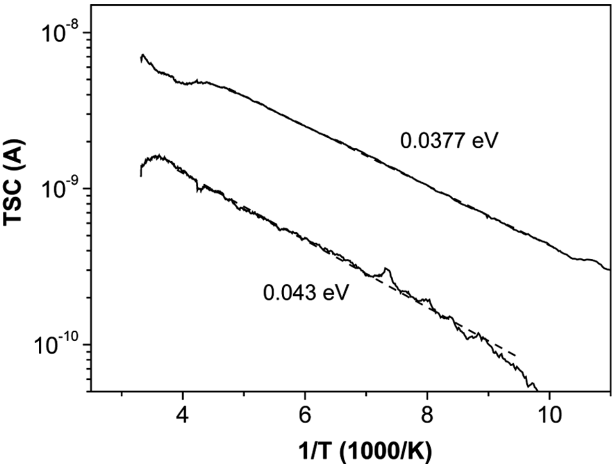

Figure 6. TSC scans in two samples, measured at 0.5 V applied bias after the white light excitation (solid curves). Dashed curves indicate linear fits in Arrhenius scaling.

in distribution of the density of transporting states (DOS). Nevertheless 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.

III.4. *Bistable Photoconductivity*

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 Figure 7.

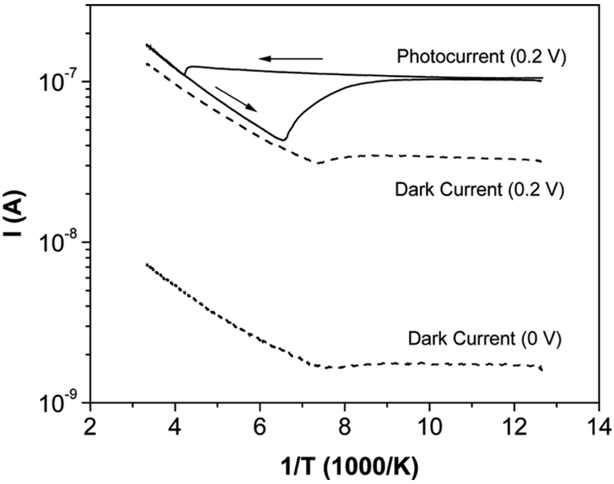

Figure 7. Temperature dependencies of the photocurrent (solid curves), upon scanning the temperature down and up as indicated by the arrows and the dark current (dashed curves) at 0.2 V bias and without any applied bias.

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.

Summary and Conclusions

Investigations of the electrical, optical and charge transport properties of DNA:PEDT-PSS thin films are presented. 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 obtained films was 0.3–1.5 μm. The semi-transparent aluminium contacts were evaporated on the top. The films were characterized by the UV and visible spectroscopy. Their conductivity temperature dependencies were measured from 77 K up to 300 K depending on the light excitation.

Sample conductivity at room temperature was in average about $(1\text{–}5) \times 10^{-10}\,\Omega^{-1}\,\mathrm{cm}^{-1}$, 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. 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.

Acknowledgments

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