

Properties of functional DNA:PEDOT layers

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We report investigations of functionalized DNA:PEDT-PSS films. The electrical conductivity of the samples material at the room temperature was about $(1-5) \cdot 10^{-10} \Omega^{-1} \text{cm}^{-1}$. 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 white light a remarkable increase the photocurrent could be observed below 145–155 K by cooling the samples. Meanwhile by heating the photosensitivity increased up to 235–245 K. Such phenomenon could presumably be attributed to light-induced morphology changes of the sample material.

Описаны исследования функционализированных пленок DNA:PEDT-PSS. Электропроводность образцов материала при комнатной температуре составляла около $(1-5) \cdot 10^{-10} \text{ Ом}^{-1} \text{ см}^{-1}$. Кривые ВАХ образцов были линейными и симметричными в области температур от комнатной до азотной. Энергия термоактивации проводимости при температурах, близких к комнатной, составляла около 0,033 эВ независимо от напряжения смещения. Методом термостимулированного тока обнаружен слабый захват носителей, свидетельствующий о быстрой рекомбинации фотовозбужденных носителей. В частности, при постоянном фотовозбуждении обнаружена "бистабильная" фотопроводимость при температурах ниже комнатной. Т.е. при возбуждении белым светом можно наблюдать значительное увеличение фототока при температурах ниже 145–155 К при охлаждении образцов. В то же время при нагревании фоточувствительность оставалась повышенной до 235–245 К. Это явление предположительно объясняется фотоиндуцированными изменениями морфологии материала образцов.

1. Introduction

Nucleic acids and their derivatives attract a great attention of researchers due to their important biological role [1, 2]. At the same time, deoxyribonucleic acid (DNA), which exhibits a charge migration, is of interest due to its physical properties, and particularly to a great potential of application in photonics and 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 an electrically inactive material. In order to render it active, it is necessary to functionalize it with poly(3,4-ethylenedioxythiophene) (PEDOT, PEDT) and poly(styrenesulfonate) (PSS) complex. This enables the development of its electrical properties.

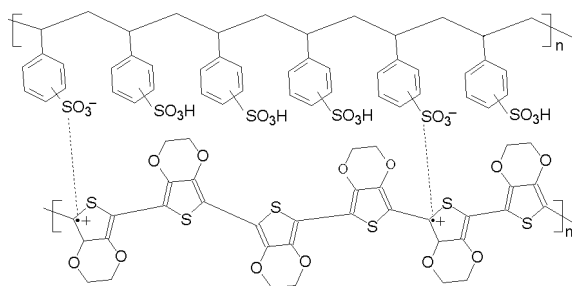


Fig. 1. Chemical structure of PEDOT-PSS polymer complex.

Nevertheless, to assure the controllable purposeful modification of these properties, extensive investigations are still required. In this work, we report investigations of optical and electrical properties of DNA:PEDT-PSS thin films. Their electrical conductivity dependence on temperature and excitation with light was analysed.

2. Samples and experiment

An aqueous dispersion of the poly(3,4-ethylenedioxythiophene) / poly(styrenesulfonate) intrinsically conductive PEDT-PSS polymer (Fig. 1) being commercialized under the trade mark BAYTRON^R PH 500 is especially homogenized to achieve small size particles. The weight ratio of PEDT to PSS was about 1:2.5. This aqueous 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. This kind of polymer forms highly-conductive, transparent, colourless to bluish coatings with good resistance to hydrolysis, good photo stability and good thermal stability, high absorption in the range of 900 to 2000 nm, with 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, the mix was stirred overnight using a magnetic stirrer and then DNA solution was added to PEDT-PSS aqueous solution at different DNA:PEDT-PSS volume ratios 1:0.2 and 1:0.5. The solutions of polymers were spin-

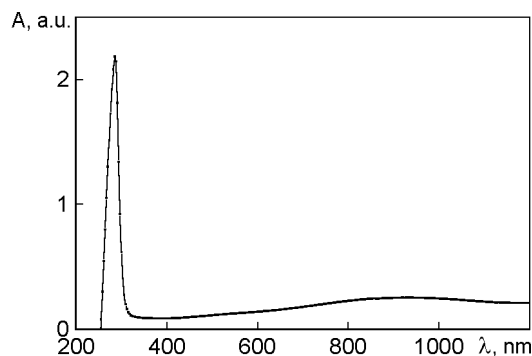


Fig. 2. Absorption spectrum of a DNA-PEDOT (1:0.5) thin film.

coated at 500 or 1200 rpm on the ITO glass substrates cleaned in various solvents. The thin solid film thickness was measured by a profilometer Tencor, ALFA-Step and was found to be 0.3–1.5 μm. The semi-transparent aluminium contacts were evaporated onto the upper surface. Alternatively, some samples were deposited on gridded intercalated electrodes initially evaporated on glass substrates. The films were characterized by the UV and visible spectroscopy using a PERKIN ELMER UV/VIS/NIR Lambda 19 spectrometer. Their Current-Voltage (IV) and conductivity temperature dependences were measured by Keithley electrometer-voltage source Model 6430 in the 77 K–300 K range depending on the light excitation.

3. Results and discussion

The UV-VIS-NIR absorption spectra of studied thin films deposited on glass substrates were measured at room temperature. 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 $\pi-\pi^*$ electron transition of the C=C bond in the DNA bases. Another broad and low absorption band around 900 nm is associated with the PEDT-PSS conductive polymer.

The average sample conductivity at room temperature was about $(1-5) \cdot 10^{-10} \Omega^{-1} \text{cm}^{-1}$, though it could deviate by up to two orders of magnitude even in the samples produced on the same substrate, evidencing the sensitivity of their properties to the technological conditions. The IV curves were linear and symmetrical down to 78 K as it is shown in Fig. 3. The samples had demonstrated photosensitivity starting from the room temperature down to 78 K. At room temperature, the photosensitivity was about

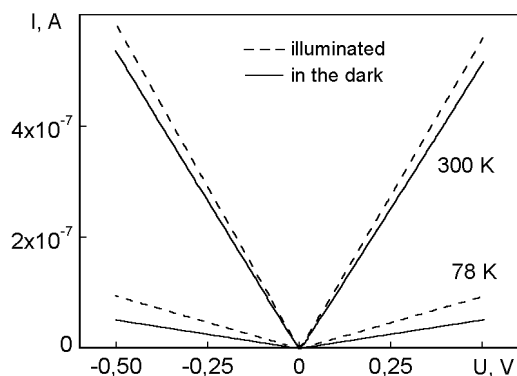


Fig. 3. IV curves of a sample upon white light illumination (dashed curves) and in the dark (solid lines) at 300 K and 78 K (as indicated in the Figure).

10 per cent, and it increased by a factor of up to two at the low temperature. Its temperature dependence was quite complex as it will be discussed below.

Characteristically, the sample response to 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 in Fig. 4 by the solid line. In the present case, the time constant of the exponential increase was ~ 80 s and tended to shorten with temperature. Nevertheless, this process still has to be investigated in more detail. The current decay after the light is switched off occurs in a similar manner. 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, a slower light-induced generation of carriers occurs from their transport and/or trapping states.

To investigate the temperature dependences of carrier transport and thermal generation processes, temperature scans of the dark current, Thermally Stimulated Currents (TSCs), and photocurrent were measured. In Fig. 5, the dark current temperature dependences are presented for two samples. It can be seen that close to room temperature, thermal activation energy is about 0.033–0.035 eV. These values are independent of 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

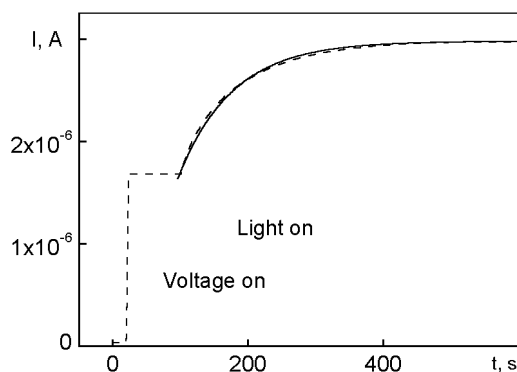


Fig. 4. Sample response on applied voltage pulse and white light pulse (dashed curve) as indicated in the Figure. The photocurrent increase could be approximated well by exponential dependence as indicated by the solid curve, $T=78$ K, $U=0,5$ V.

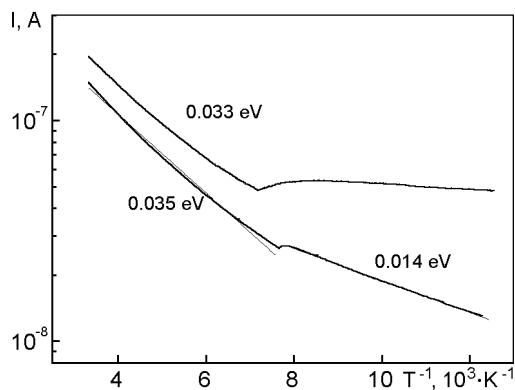


Fig. 5. Dark current temperature dependences for two samples measured at 0.5 V bias.

samples zero values. To investigate this peculiar behaviour, Thermally Stimulated Current (TSC) and temperature dependences of photocurrent were analysed. The details of the TSC method are presented in [10–12]. The TSCs obtained in different samples are shown in Fig. 6.

Typically, TSCs are low as compared with both dark current and current after the light excitation. This indicates that a relatively small number of carriers becomes trapped, and most of them recombine after the light excitation is over. 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 indicate that the current increase is related to transport phenomena, i.e., increased carrier mobility, rather than to their thermal generation. A similar conclusion was made also for disordered P3HT-

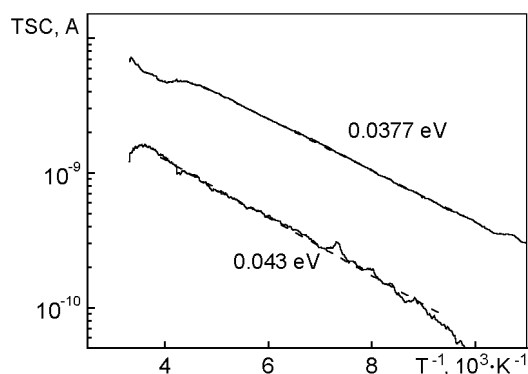


Fig. 6. TSC scans in two samples measured at 0.5 V bias after the white light excitation (solid curves). Dashed curves indicate linear fits in Arrhenius scaling.

PCBM bulk-heterojunction organic solar cell structures [13]. This assumption is realistic by having in mind a complicated hopping transport character in disordered organic materials. Therefore, the evaluated activation energies could probably reflect the energy spread in the charge transporting levels resulting 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. As mentioned above, a characteristic kink was observed in dark current measurements that becomes even more expressed upon light excitation. A typical behavior is presented in Fig. 7. It is seen that at lowering temperature, the photocurrent starts grow at about 145–155 K and reaches saturation level that is by a factor of about 2 to 2.5 higher than that in the minimum. Afterwards, when the temperature is increased, the photocurrent changes relatively little up to about 235–245 K, forming a "bistable" loop. This behavior does not change with applied bias, indicating that the effect is light-induced. Most probably such phenomenon could be attributed to the light-induced sample morphology changes resulting in a sudden increase of material photosensitivity at low temperatures. Nevertheless, to reveal its exact nature, further investigations are necessary.

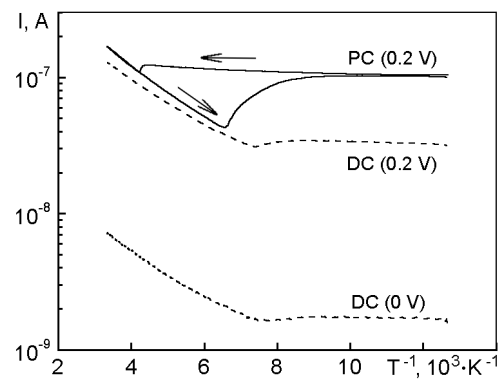


Fig. 7. Temperature dependences of photocurrent (PC-solid curves), upon the temperature variation down and up (as indicated by the arrows) and the dark current (DC-dashed curves) at 0.2 V bias and without any bias.

4. Summary and conclusions

We report investigations of DNA:PEDT-PSS thin films. After sonication of DNA in deionized water, DNA solution was added to PEDT-PSS aqueous solution at different DNA:PEDT-PSS ratios 1:0.2 and 1:0.5. 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 onto the upper surface. The films were characterized by the UV and visible spectroscopy. Their conductivity temperature dependences were measured from 77 K up to 300 K depending on the light excitation.

The sample conductivity at room temperature was in average about $(1-5) \cdot 10^{-10} \Omega^{-1}\text{cm}^{-1}$, though it could deviate by up to two orders of magnitude even in the samples produced on the same glass substrate, thus indicating sensitivity of their properties to the technological conditions. The 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 independent on the applied bias.

We have identified weakly expressed carrier trapping using the Thermally Stimulated Current method, what proves the fast recombination and/or retrapping of light-generated carriers. Though, under constant light excitation, a "bistable" photoconduction below the room temperature was evidenced. I.e., a notable photocurrent increase could be observed below 140–160 K at cooling the samples. Meanwhile, under 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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Властивості функціоналізованих шарів DNA:PEDOT

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Описано дослідження функціоналізованих плівок DNA:PEDT-PSS. Електропровідність зразків матеріалу при кімнатній температурі становила близько $(1-5) \cdot 10^{-10} \text{ Ом}^{-1}\text{см}^{-1}$. Криві ВАХ зразків були лінійними та симетричними в області температур від кімнатної до азотної. Енергія термоактивації провідності при температурах, близьких до кімнатної, становила приблизно 0,033 eV незалежно від напруги зміщення. Методом термостимульованого струму виявлено слабе захоплення носіїв, яке свідчить про швидку рекомбінацію фотозбуджених носіїв. Зокрема, при постійному фотозбудженні виявлено "бістабільну" фотопровідність при температурах нижче від кімнатної. Тобто при збудженні білим світлом можна спостерігати значне збільшення фотоструму при температурах нижче від 145–155 K при охолодженні зразків. В той же час при нагріванні фоточутливість залишалася підвищеною до 235–245 K. Це явище пояснюється можливими фотоіндукованими змінами морфології матеріалу зразків.