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The Investigation of Thermal and Optical Properties of Semiconducting Nanostructural Hybrid Films

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In this work, we study the physical properties of hybrid organic/inorganic mixture semiconducting layers. Materials selected for the research were poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] and nanostructured cadmium sulfide (CdS) powder. These materials have been chosen due to their narrow optical band gap combined with high charge-carrier mobility, which makes them interesting for application as components of active layers in bulk p–n heterojunctions. In particular, we present the results of studies on the influence of CdS content on the physical properties of thin hybrid films. The ellipsometric measurements showed that the composition of the base layers influenced their optical properties without significantly influencing their thermal stability.

topics: nanocomposite, organic layer, thermal properties, semiconductors

1. Introduction

Hybrid organic/inorganic electronic materials offer greater possibilities for tuning electronic parameters to specific applications of electronic devices [1–4]. In particular, conducting or semiconducting polymers have found wide application in many organic electronic devices [5, 6]. The functional properties of organic materials, such as high mechanical flexibility, and ease of processing and recycling, combined with their electronic properties, are the main reasons for their use as active materials in third-generation solar cells. Organic photovoltaic cells (OPV) enable ecological and economical obtaining of solar energy. The highest average efficiency of devices obtained in laboratory conditions is within 15% [7]. In the case of polymer solar cells, there is a problem of a fairly rapid decrease in energy conversion efficiency (PCE) associated with their low thermal stability. One of the solutions to this problem is the use of hybrid organic/inorganic layers in the cell architecture, which allow for extending the working time of the cells, and at the same time, do not deteriorate their thermal stability.

The presence of semiconductor nanoparticles (NPs) may increase the intensity of light absorption and may result in the appearance of an additional absorption band. The energy gap of nanocomposites can be controlled by both the percentage content of NPs and their size and shape [8, 9]. In hybrid systems, morphological changes and discontinuities in the photoactive layer, agglomerates of nanoadditives, and the oxidation processes of the reactive metal cathodes may be present [10].

It should be noted that a complex system containing NPs causes a number of interactions at the nano-structured level that require careful studies. Understanding the physical relationships of these systems is a primary task in hybrid solar cell design.

The authors focus on the investigation of the influence of CdS nanoparticles on the physical properties of the nanocomposite layers PCPDTBT:CdS. In this work, the dielectric properties and the energy gap of the composite films were determined by spectroscopic ellipsometry. The glass transition temperature Tg of tested films has been determined using temperature-dependent spectroscopic ellipsometry.

2. Experimental

The materials used in the work are low band-gap polymer semiconductor poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3benzothiadiazole)]–PCPDTBP, with molar mass M_w = 33 kDa (96 wt% purity), supplied by Ossila, and cadmium sulfide CdS nanopowder, M_w = 144.48 kDa (99.9 wt% purity, APS 60 nm), supplied by Sigma-Aldrich. The nanocomposite layers were coated

TABLE I

Thickness of samples deposited on quartz and silicon substrates depending on the CdS nanoparticles content.

CdS content [%]	Thickness [nm]	
0	1142	1072
25	1110	1187
50	1063	1371
75	1078	–
substrate	quartz	silicone

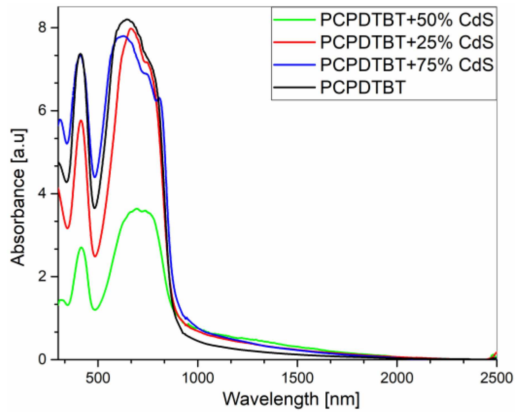

Fig. 1. Absorbance spectra for PCPDTBT/CdS nanoparticles films.

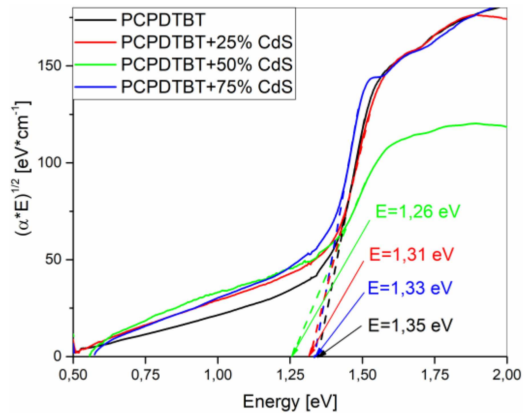

Fig. 2. Band gap width for PCPDTBT/CdS layers.

with polymer-NPs solutions, with increasing NPs percentage content. The weight concentrations of all solutions were 30 mg/ml. The percentage content of nanoparticles was 0, 25, 50, and 75%. All the solutions were homogenized at 16 kJ for 20 min, using a Bandelin Sonoplus homogenizer. In the next step, the layers have been cast onto silicone (with 400 nm SiO_2 layer) and quartz substrates. The thickness of obtained layers is presented in Table I.

The ellipsometric investigation has been carried out using SENTECH SE850E spectroscopic ellipsometer (SENTECH Instruments GmbH, Berlin, Germany), using dedicated SpectraRay/3 software and working within 240–2500 nm wavelength range. The temperature-dependent ellipsometric measurements have been done using a temperature chamber, working at lowered pressure, and an INSTEC mK1000 temperature controller (Instec, Inc., Boulder, CO, USA).

All samples were annealed at 300°C for 2 min and then cooled to −50°C. The annealing temperature value was lower than the thermal degradation point of the polymeric material. Temperature-dependent ellipsometric measurements were performed in the wavelength range 240–930 nm, with a constant angle of incidence of 70°, using 10-second intervals between measurements. The measurements were performed under a vacuum of 0.1 Tr. The heating rate was equal to 2 °C/min. The thickness of the layers was determined using the Cauchy dispersion in ellipsometric data analysis.

3. Results and discussion

3.1. Band gap energy investigation

Optical absorbance spectra of composite hybrid layers deposited onto quartz substrates are shown in Fig. 1.

Two peaks are clearly visible, with a maximum around 400 and 700 nm wavelength. The thickness of the layers is presented in the experimental section in Table I. These spectra were obtained using ellipsometric transmission mode. The absorbance A was recalculated from the transmission, using

$$A = \log\left(\frac{1}{T}\right), \tag{1}$$

where T is the transmission. The values of energy gaps E_g of composites were obtained using linear extrapolation to the plot $(\alpha)^{1/2}$ (where α is absorption coefficient) vs E, for $E > E_g$ (where E is energy), as presented in Fig. 2.

The obtained results show that the E_g value of PCPDTBT is equal to 1.35 eV. This value is slightly lower in two cases, for 25 and 75% CdS content (1.31 and 1.33 eV, respectively). The value of the energy gap in the case of 50% CdS content is 1.26 eV, which means that in this case, the content of nanoparticles is the most optimal.

3.2. Optical properties

The refractive index and extinction coefficient dispersions, fitted in the 260–730 nm range, are shown in Figs. 3 and 4, respectively. In the remaining range of wavelength, the degree of depolarization was higher than 5%.

Both optical coefficients were determined using the ellipsometric sandwich model. The composite layer was fitted with point by point model, where the values of refractive index n and extinction

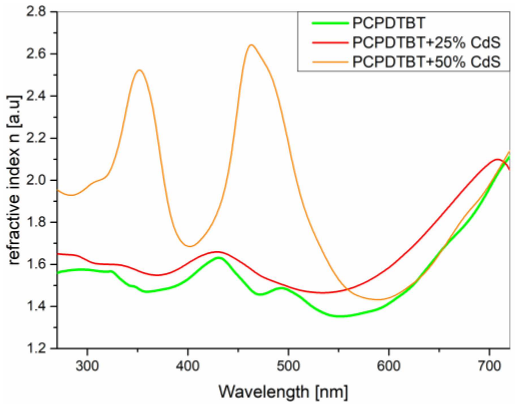

Fig. 3. Refractive index spectral dispersion of PCPDTBT and its composite films.

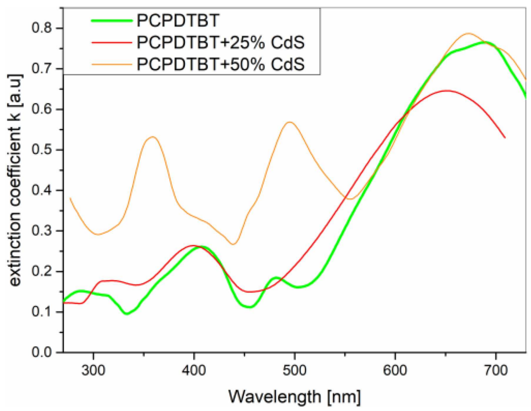

Fig. 4. Extinction coefficient spectral dispersion of PCPDTBT and its composites.

coefficient k were fitted to individual λ wavelengths. The silicon oxide SiO_2 and Si layers were fitted with Cauchy and file layers.

3.3. Temperature-dependent ellipsometry results

The values of the glass transition temperature T_g were determined for the layers deposited on the SiO_2/Si substrates. The thickness values of these layers are presented in the experimental part in Table I. The ellipsometric angle Δ at the wavelength of 930 nm as a function of temperature for PCPDTBT and its composite layers is shown in Fig. 5.

Glass transition temperature T_g of tested layers was determined as the intersection point of the two curves fitted by the linear regression (see Fig. 5). There are a few articles regarding the glass transition of PCPDTBT. Fanta et al. [14] were investigating amorphous/semicrystalline conjugated polymer blends. They have found, using differential scanning calorimetry, that the T_g of PCPDTBT is around 112°C. In our case, the glass transition for the PCPDTBT layer is around 152°C. The glass transition temperatures of composite films

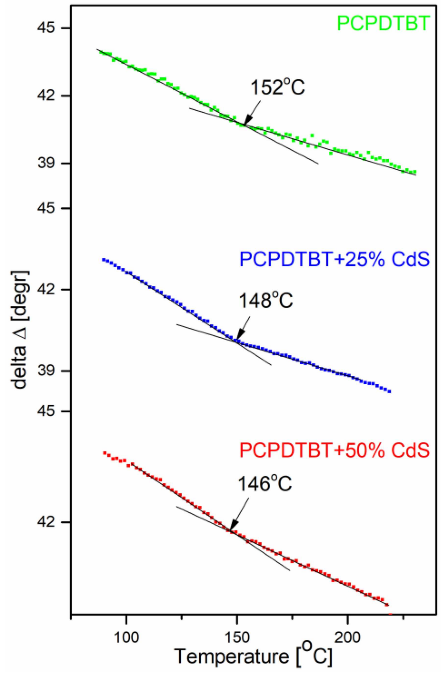

Fig. 5. Ellipsometric angle Δ at $\lambda = 930$ nm as a function of temperature.

with 25 and 50% CdS content determined by us are 148 and 146°C, respectively. The determined T_g value shows a slightly decreasing tendency along with the increase in the content of nanoparticles in the layers. Therefore, it can be assumed that even a significant percentage of CdS nanoparticles does not significantly affect the thermal properties of PCPDTBT/CdS-nanoparticles layers, and thus does not deteriorate their thermal stability.

4. Conclusions

The article presents the results of research into the physical properties of semiconducting polymer/nanoparticle (PCPDTBT/CdS) composite films, with particular emphasis on optical and thermal properties. In principle, the produced nanocomposite layers with a semiconductor polymer matrix and a significant proportion of the inorganic semiconductor nanoparticles phase can be used as a component of active bulk layers in the architecture of hybrid photovoltaic structures. The results showed that the tested layers have a low energy gap value, and the addition of CdS nanoparticles can reduce it and improve electron transport. The thermal stability of composite films is maintained even at high concentrations of nanoparticles.

Acknowledgments

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