Optical spectroscopy of photovoltaic systems based on low-bandgap polymers

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ABSTRACT

We report on the optical characterization of a low-bandgap thieno[3,4-b]pyrazine phenylenevinylene copolymer. Individual layers on quartz and Si substrates as well as layered structures on indium tin oxide covered glass with and without a PEDOT:PSS (poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate)) layer were examined using spectroscopic ellipsometry, transmission, reflectance, electroreflectance and external quantum efficiency measurements. For comparison, current–voltage and capacitance–voltage characteristics were also measured. Changes in optical spectra of the pristine polymer due to an applied external voltage are analyzed quantitatively in terms of the Stark effect which allows the determination of the exciton radius, binding energy and ionization field strength. For structures with an inserted PEDOT:PSS layer, a significant charge trapping in the polymer layer is observed that considerably modifies both optical and electrical properties.

1. Introduction

The technology and cost benefit for reel to reel processed solar cells based on soluble conjugated polymers are undoubted. The development of low-bandgap polymers whose absorption matches the solar spectrum better than the well-known poly(3-hexylthiophene) (P3HT) is a key issue. In low-bandgap copolymers with alternating donor and acceptor segments in the repeat unit, delocalized excitons or polaron pairs may be formed under light absorption. Donor–acceptor copolymers with strong acceptors exhibit significantly larger polaron pair yields compared with P3HT which influences their recombination dynamics [1]. Up to now, only a few low-bandgap polymers really yield record power conversion efficiencies, while the majority of this kind of polymers typically show low cell efficiencies mostly linked to problems with the charge separation and charge transport. Understanding the fundamental properties of excitons and defect electronic states in low-bandgap polymers as well as electrical and optical properties of a common boundary to other materials such as widely exploited phenyl-C_{61}-butyric acid methyl ester or PEDOT:PSS (poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate)) where specific interface defects may be formed, is a challenge for researchers working in this field. In general, interfaces and defects can act as recombination centers and build up internal electric fields. As a consequence, they can exhibit a strong influence on the electrostatic potential and charge relief in layered structures thereby determining drift and diffusion currents and the resulting extraction of photogenerated carriers from a photovoltaic device.

In this work we report on the photovoltaic-relevant properties of a thieno[3,4-b]pyrazine phenylenevinylene low-bandgap copolymer (LBP) studied with a variety of experimental techniques. We present the determined exciton parameters and demonstrate the significance of charge trapping for photovoltaic structures containing LPB/PEDOT:PSS interfaces.

2. Experiment

The well-defined strictly alternating thieno[3,4-b]pyrazine phenylenevinylene copolymer (see Fig. 1) was synthesized by a Horner polycondensation route [2]. To determine its optical constants, spin-coated films of different thicknesses were deposited on quartz and Si substrates. The photovoltaic structures were prepared on indium tin oxide (ITO) covered glass substrates (Merck Displays, 125 nm ITO, 13 Ω/square). The usual device configuration was formed by spin coating a thin layer (~80 nm) of PEDOT:PSS; (Clevios P VP AI 4083, Heraeus Clevios GmbH/Germany) followed by a drying step (5 min at 120 °C). Subsequently, an active layer (pristine LBP; solvent: chlorobenzene) was deposited again by spin coating without any subsequent annealing. Then the aluminum cathode was thermally deposited (~50 nm) through a shadow mask. It followed a glass–glass encapsulation using a commercial standard epoxy adhesive. The cell area was 0.5 cm². The device structures investigated in this work are divided into two groups, with and without a PEDOT:PSS layer, respectively. Each group consists of four samples with different thicknesses of a pristine LBP layer which was spin coated at a speed of 700, 1000, 1400 and

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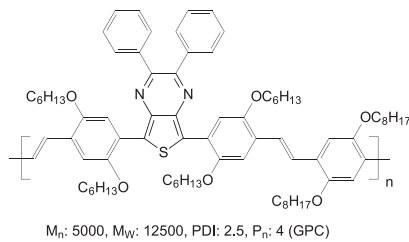E-mail address: Biankhans-christian.biank@tu-ilmenau.de (H.C. Biank).

M_n: 5000, M_W: 12500, PDI: 2.5, P_n: 4 (GPC)

Fig. 1. Chemical structure of the low-bandgap thieno[3,4-b]pyrazine phenylenevinylene copolymer.

2000 rpm resulting in the active layer thickness of 35.4, 30.8, 26.5 and 22.1 nm, respectively.

The optical characterization of individual layers deposited on quartz and Si substrates was carried out by spectroscopic ellipsometry (SE) and transmission (T) measurements in a spectral range 0.75–5 eV (250–1650 nm) using a rotating analyzer Woollam VASE® ellipsometer with an autoretarder. The spectral resolution was 3.5 nm (9 meV at a photon energy 1.8 eV).

Reflectance (R), electroreflectance (ER) and external quantum efficiency (EQE) spectra of photovoltaic structures were recorded in a spectral range 1.1–4.1 eV (300–1100 nm) using the same measuring setup which includes a monochromator, a halogen lamp as the light source, a calibrated UV-enhanced Si photodiode, and a lock-in detection technique. The spectral resolution was 0.6 nm (1.5 meV at 1.8 eV). The illuminated area of the cells was approximately 0.2 cm^2. The R and EQE measurements were done with the light beam mechanically chopped at a frequency 180 Hz. The internal quantum efficiency (IQE) was estimated by IQE = EQE / (1 − R). This equation is approximately fulfilled for the studied device structures in a spectral range 1.75–3.2 eV, as revealed by simulations considering optical constants and layer thicknesses of constituent materials. For the ER, a rectangular modulation voltage (frequency 980 Hz, peak-to-peak amplitude $V_{pp} = 0.4$ V) superimposed on a dc bias voltage V_{bias} was applied to the sample.

The capacitance–voltage (CV) and current–voltage measurements were conducted with a LabView® controlled Keithley 3330 LCZ Meter and a Keithley 2400 Source meter. During the capacitance measurement a 50 mV amplitude sinusoidal voltage (1 kHz) was superimposed on a dc bias voltage. All measurements were made in the dark.

3. Results and discussion

Fig. 2a–c shows the determined optical constants (n, k, α) of the pristine LBP as well as the typical IQE, R and ER spectra for device structures where the active layer consists of the pristine LBP (1400 rpm, 26.5 nm) while a PEDOT:PSS layer is absent. One could argue that each of the spectra possesses features corresponding to specific optical transitions. However, the ER provides much better resolved fine structure. In general, this is related to its derivative-like nature which makes it possible to detect relatively small changes in energy positions and oscillator strengths of optical transitions caused by an applied electric field.

To quantitatively analyze ER spectra, we performed a fit using a Lorentzian line shape [3]:

$$\Delta R = \text{Re}\left[A_0 + \sum_{j=1}^{n} A_j e^{i\Theta_j} \left(E - E_j + i\gamma_j \right)^{-2} \right]$$

where n is the number of resonances, A_0, A_j and Θ_j are the offset, amplitude and phase, and E_j and γ_j are the resonance energy and the broadening parameter, respectively. In this way we find four nearly equidistant (approximately 165 meV) resonances denoted by solid arrows in Fig. 2c as well as a well-separated and significantly broader
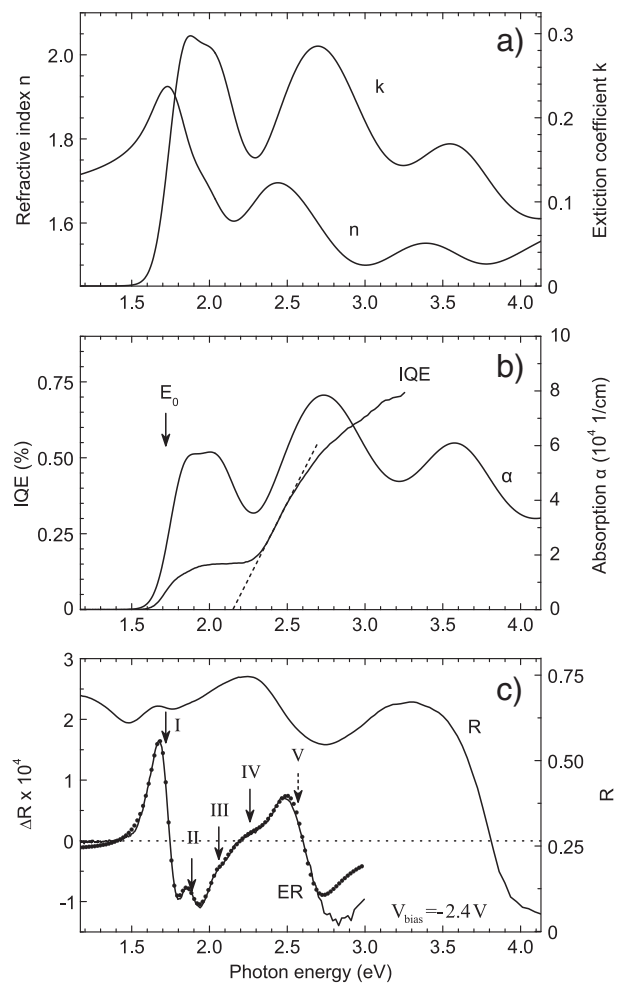

Fig. 2. Optical constants and typical measured spectra: (a) Refractive index (n) and extinction coefficient (k) of the studied LBP, (b) Internal quantum efficiency (IQE) for the pristine LBP compared to its absorption coefficient (α), (c) reflectance (R) and electroreflectance (ER) of a 1400 rpm sample without a PEDOT:PSS layer. The arrows mark resonance energies determined from fit (dotted line) to the experimental ER data (solid line).

resonance V centered at a photon energy of approximately 2.6 eV denoted by the dashed arrow.

In the interpretation of the experimental data we follow in particular Liess et al. [4] who examined the electroabsorption in poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenvinylene] (MEH-PPV) and Köhler et al. [5] who studied MEH-PPV by means of photocurrent measurements and quantum-mechanical calculations and discovered that excited states (excitons) generated by high-energy photons can be at least partially delocalized and facilitate charge separation. Further discussion of the role of delocalized states and other reasons for exciton dissociation and charge separation in polymer/fullerene blends can be found in [6–11] and references therein. Accordingly, we relate the low-energy absorption band at 1.7–2.2 eV (see Fig. 2b) to optically excited states where both the hole and the electron are localized (low-energy or localized excitons). ER spectra reveal the fine structure of this band with particular optical transitions (I to IV in Fig. 2c) due to the exciton ground state (I) and its phonon replica (II–IV), respectively. For these excited states we measure only a relatively low IQE (see Fig. 2b). The second absorption band at 2.3–3.1 eV is regarded as hot excitons, where the hole is localized while the electron is delocalized or vice versa or both the electron and the hole are delocalized. These are excited states which give rise to a considerably higher IQE. In ER only one resonance marked by V (Fig. 2c) is clearly resolved for hot excitons. Note a significantly larger broadening of hot