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Morphology and molecular orientation of ethyl-substituted dicyanovinyl-sexithiophene films for photovoltaic applications

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ABSTRACT

Enhancement of the efficiency of organic solar cell devices requires knowledge about the structure of the organic layers involved. Films of the donor material dicyanovinyl-sexithiophene bearing four ethyl side-chains at thiophenes two and five DCV6T-Et(2,2,5,5) (DCV6T-Et) are prepared by thermal evaporation in high vacuum at various thicknesses and substrate temperatures. Infrared spectroscopic ellipsometry is used for determination of the molecular orientation in the thin films grown on room temperature (RT) substrate. From simulation of the IR ellipsometric data, the film thickness and the anisotropic optical constants of the DCV6T-Et films are determined. It is found that the optical constants strongly depend on the film thickness. Different average molecular orientations are determined for a few molecules thin (4 nm) and somewhat thicker (20 nm) films. Furthermore, the evolution of the surface morphology of films deposited at elevated substrate temperatures (80 °C, 100 °C) is studied in comparison to the thick RT-film. Atomic force microscopy images indicate that the growth on heated substrate is accompanied by an increase in grain size and surface roughness of the films. Simultaneously, the measured optical absorption spectra display structured and increased absorption in the red spectral region for the DCV6T-Et films deposited at higher substrate temperatures. The changes in surface topography and optical response relate to improved molecular arrangement induced by the substrate heating. To demonstrate the morphological influence on solar cell performance, we finally discuss DCV6T-Et/C60 planar heterojunction solar cells composed of DCV6T-Et films deposited at different substrate temperatures.

1. Introduction

In recent years, conjugated oligothiophenes became an established class of organic materials for use in organic electronics [1]. Unsubstituted oligothiophenes have found frequent application in organic field effect transistors since they are easy processable and show high carrier mobilities due to their ability to grow crystalline and ordered thin films [2]. Currently, thiophene-based oligomers are extensively investigated for application in organic light emitting diodes and photovoltaic cells [3–7]. An advantageous characteristic of the oligothiophenes is their structural variety. Modifications of the thiophene core by substitution or incorporation of different functional groups as side chains, terminal groups, or chromophores are aiming at improved solubility, thermal stability, self-organization, and tuning of optical and electronic properties [8–11].

The potential of organic materials in electronic devices depends on their absorption properties and charge carrier mobility in thin films which in particular are defined by the molecular orientation and stacking. For vacuum grown films, the molecular orientation can be affected using physical parameters, such as deposition rate [12,13], substrate temperature [2,14], and vacuum level [15]. Additionally, substrates with different chemical natures may induce different orientations [16]. A significant reason to study the molecular orientation in amorphous thin films is the fact that it affects considerably their charge transport properties [17]. Therefore, determination of the molecular orientation in organic thin films and finding ways to control it are crucial for improving the device characteristics.

In the last decades, infrared (IR) transmission, reflection, and ellipsometry measurements have been established for determination of anisotropic optical constants and thus parameters such as molecular tilt angle or dichroic ratio in organic samples [18,20–24]. In addition to

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spectroscopy in the IR region, ultraviolet–visible (UV–vis) methods including variable spectroscopic ellipsometry (VASE) or polarized absorption spectroscopy have been implemented for characterization of anisotropic thin films of organic semiconductors [15,25–27,44]. Thus, the application of complementary IR and UV–vis spectroscopic techniques, combined with other thin film characterization techniques could result in improved understanding of the correlation between molecular orientation and packing and device performance.

In this work, IR spectroscopic ellipsometry (IRSE) is used for analyzing the molecular orientation of thin vacuum deposited films of dicyanovinyl-sexithiophene with four ethyl side chains at thiophenes two and five DCV6T-Et(2,2,5,5) (DCV6T-Et, the chemical structure of the material is presented in Fig. 1) [28] of various thicknesses grown on a substrate held at room temperature (RT). DCV6T-Et belongs to a class of low band gap dicianovinyl (DCV) end-capped oligothiophenes of proven merit for application as donor materials in small molecule solar cells [29–32]. We show that the molecular orientation changes from isotropic to preferentially parallel to the substrate surface upon increasing film thickness. Furthermore, we study the morphology of DCV6T-Et films at constant film thickness, however grown at different substrate temperatures. The evolution of surface morphology with increasing substrate temperature relates to changes of the optical absorption as evident from UV–vis absorption measurements. Finally, we present DCV6T-Et/C60 planar heterojunction solar cells, showing that the structure of the DCV6T-Et films grown at higher substrate temperatures is favorable for the device performance.

2. Experimental details

2.1. Film preparation

All samples were prepared by thermal evaporation in vacuum at a base pressure of less than 6×10^{-4} Pa and deposition rate of 0.1–0.2 Å/s. Nominal layer thicknesses were determined using quartz crystal monitors. The latter were calibrated prior to deposition using second crystal placed at the sample position. The thin DCV6T-Et films were deposited assuming a density of $\rho = 1.3$ g/cm^3. Si wafer and quartz glass were used as substrates for the conventional IR reflection absorption spectroscopy (IRRAS), IRSE, atomic force microscopy (AFM), and UV–vis absorption measurements. The substrates were cleaned in ultrasonic baths with acetone, ethanol, and isopropanol. For the IRRAS measurement, before deposition of the DCV6T-Et layer, the quartz glass substrate was pre-covered with 100 nm gold. IRRAS measurement was performed on 70 nm DCV6T-Et layer deposited on RT-substrate, while IRSE, AFM, and UV–vis absorption measurements were carried out on DCV6T-Et layers with nominal thickness of 4 nm or 20 nm grown on Si or quartz glass and kept at RT, 80° or 100 °C temperature during deposition.

2.2. IR spectroscopy

The bulk DCV6T-Et absorbance spectrum was calculated from the recorded transmission spectrum of the material pressed in a KBr pellet. The bulk sample was prepared using the milling technique by mixing 0.8 mg DCV6T-Et powder with 400 mg KBr. The reflection spectra of a 70 nm thin DCV6T-Et layer deposited on substrate at RT on gold were measured by IRRAS. The thickness of the gold layer was 100 nm. For subtraction of the background signal, spectra of 80 nm Au layer deposited on quartz glass were recorded. Bulk transmission and thin film reflection measurements were carried out by means of Fourier transform infrared spectrometer Equinox 55 (Bruker) in the spectral range 4000–600 cm^{-1} with a resolution of 2 cm^{-1}, with 32 or 500 scans co-added for one transmission or reflection spectrum, respectively. IRRAS spectra were recorded under p-polarized irradiation (KRS5 polarizer, SPECAC) and at a grazing angle of incidence of 80°. The IR transmission and reflection spectra were obtained using deuterated triglycine sulfate or mercury cadmium telluride (MCT) detectors, respectively.

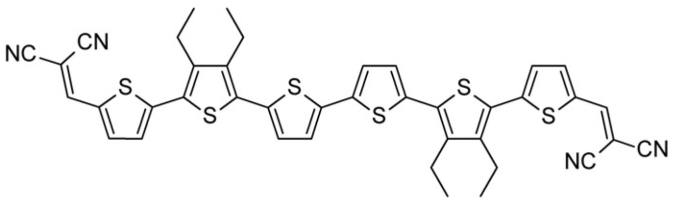

Fig. 1. Chemical structure of the dicyanovinyl-sexithiophene derivative DCV6T-Et(2,2,5,5).

2.3. IRSE measurements

The IR ellipsometric measurements were performed with a photometric ellipsometer [33,34], attached to a Bruker 55 Fourier transform spectrometer, in the mid-IR spectral range (4000–400 cm^{-1}). The state of polarization of reflected radiation, for a given angle of incidence, can be characterized by the experimental quantities tanψ and Δ. $\tan\Psi = |r_p|/|r_s|$ represents the ratio of the amplitudes of the p- and s-polarized complex reflection coefficients r_p and r_s (p: parallel, s: perpendicular to the incidence plane), and Δ which is the phase shift between them. Further details on the ellipsometric method can be found in Refs. [33–36]. The IRSE spectra were obtained with a resolution of 4 cm^{-1} using a MCT detector (KV104-1, Kolmar Technologies, Newburyport, MA). IRSE measurements were performed at angle of incidence at 55°, 60° and 65°. The probed spot on the surface was about 40 mm^2 at 65° incidence angle.

2.4. Optical simulation

Simulations for interpretation of infrared transmission, reflection, and ellipsometry measurements were developed in the recent decades [18–22,37]. In particular such simulations have been recently used for determination of tilt angles of alkanethiol molecules in self assembling monolayers [22]. A similar approach as used in Ref. [22] was taken for presented simulations of ellipsometric spectra of DCV6T-Et films. For optical simulation of the measured spectra a three-phase optical layer model was used. Vibrational bands are represented as Lorentzian oscillators with wavenumber ($\tilde{\nu}_{i0}$), parameters for the oscillator strengths (F_i) and full width at half maximum (Γ_i) to yield the complex dielectric function $\hat{\varepsilon} = \varepsilon' + i\varepsilon''$ with:

$$\varepsilon' = \varepsilon_\infty + \sum_i \frac{F_i\left(\tilde{\nu}_{i0}^2 - \tilde{\nu}^2\right)}{\left(\tilde{\nu}_{i0}^2 - \tilde{\nu}^2\right)^2 + (\Gamma_i\tilde{\nu})^2} \tag{1}$$

$$\varepsilon'' = \sum_i \frac{F_i\Gamma_i\tilde{\nu}}{\left(\tilde{\nu}_{i0}^2 - \tilde{\nu}^2\right)^2 + (\Gamma_i\tilde{\nu})^2}. \tag{2}$$

Transition dipole moments of the symmetric and asymmetric stretching vibrations of thiophene rings are defined with respect to the molecular geometry (see Fig. 2). The transition dipole moments of the bands are expected to be oriented in direction of the long axis of the molecules (asymmetric stretching vibration) and perpendicular to the long axis (symmetric stretching vibrations of the thiophene rings) [21]. The asymmetric band therefore can be used for the determination of the molecular orientation.

The parameter for the oscillator strength F from Eqs. (1) and (2) [22] can be converted into the dimensionless oscillator strength S (as defined in Ref. [38]) by dividing it by the square of the oscillator resonance frequency into wavenumbers $\tilde{\nu}_{i0}^2$. The parameters of the