



Optical constants of diindenoperylene in the dependence of preparation temperature and pressure

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ARTICLE INFO

Article history:

Received 30 May 2012

Received in revised form 1 March 2013

Accepted 4 March 2013

Available online 21 March 2013

Keywords:

Diindenoperylene

Small molecule materials

Optical constants

Organic vapor phase deposition

Physical vapor deposition

ABSTRACT

We determine the optical constants, that is, refractive index n , extinction coefficient k , and absorption coefficient α , of diindenoperylene (DIP) films deposited by organic vapor phase deposition (OVPD®) on quartz glass at different substrate temperatures between 60 °C and 140 °C and chamber pressures between 0.08 and 1.10 kPa. The corresponding optical properties of the OVPD-films are compared with those of DIP layers deposited by physical vapor deposition (PVD) in high vacuum ($\sim 10^{-5}$ kPa) at substrate temperatures of 20 °C–140 °C. Measured transmission/reflection spectra are evaluated numerically by a dielectric function of a sum of Lorentz oscillators to reproduce the optical properties of the DIP films. The optical results are analyzed in relation to the morphological and structural properties of the DIP films investigated by scanning electron microscopy. The optical and structural properties of the PVD-DIP films show a weak dependence on substrate temperature. A similar temperature behavior is observed for OVPD-DIP films for the chamber pressure range of 0.08–0.18 kPa. For these conditions, we found from the optical calculations in the spectral range 250–660 nm that (i) n varies between 1.4 and 1.9, (ii) k increases from 0.02 to 0.6, and (iii) α varies between $3.0 \times 10^5 \text{ cm}^{-1}$ and $5 \times 10^4 \text{ cm}^{-1}$. These data allow satisfactory determinations of thin film thicknesses by optical methods. At OVPD chamber pressures higher than 0.18 kPa, the growth of spongelike film structures is observed which induce large deviations from computed film thicknesses. Nevertheless, the high absorption coefficients in the visible spectral region make all the investigated DIP films suitable for application as absorber in organic solar cells.

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1. Introduction

Organic semiconducting thin films became of elevated interest due to their potential application in such devices as organic-based displays, e-paper, chemical sensors, field-effect transistors, organic light-emitting diodes or/and solar cells [1,2]. The main advantage of organic materials for implementation in electronics and optoelectronics resides in their large variety and easily adjustable physical parameters. Recently, small molecule materials proved their high potential for application in organic photovoltaic (PV) devices. Organic solar cells based on small molecules achieved efficiencies of 5.0% [3]. Efficiencies of 10.7% were recently reported on small molecule-based tandem PV devices [4]. Among other small molecule materials, diindenoperylene (DIP; $\text{C}_{32}\text{H}_{16}$) represents a promising material for PV application. DIP-donor/ C_{60} -acceptor solar cells with high fill factors of up to 74% and

power conversion efficiency close to 4% were recently demonstrated by Wagner et al. [5]. DIP is a perylene-based molecule with a very high hole mobility (of up to $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) already in thin films, good film forming properties, and thermal stability [2,6]. The crystalline perfectness of DIP films could be influenced by the substrate temperature [5]. Terrace structures parallel to the substrate surface (quartz glass) were demonstrated by Heilig et al. [7]. Structural variations imply changes of optoelectronic properties, for example, optical properties of DIP thin films can be adjusted by the deposition conditions [8,9].

In this work, we investigate the influence of the substrate temperature (T_s) and deposition pressure (P) on the optical constants (refractive index n , extinction coefficient k , and absorption coefficient α) of DIP thin films deposited by organic vapor phase deposition (OVPD®) method [10,11] in comparison with those of DIP layers prepared in high vacuum ($\sim 10^{-5}$ kPa) by physical vapor deposition (PVD). With the spectral (n, k) data set, one has moreover an elegant nondestructive optical method to determine the film thickness which can even be implemented for an in situ monitoring.

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2. Experimental details

DIP was delivered by Menachem and deposited in thin films by OVPD [10,11] and PVD under various preparation conditions. Quartz glass (1 mm thick) was chosen as substrate because of its high optical transmission above 180 nm, which permits a precise evaluation of the optical spectra. The quartz glass was cleaned with organic solvents (acetone, 2-propanol) in an ultrasonic bath, rinsed with deionized water, and dried in N₂-flux before the deposition.

The OVPD-DIP films were deposited at substrate temperatures of 60 °C, 100 °C, and 140 °C at OVPD chamber pressures of 1.1, 0.18, and 0.08 kPa, respectively. All OVPD processes were performed at a constant source flow of 150 standard cubic centimeters per minute, which ensured a nominal deposition rate of 1.8 Å/s. Further details on the OVPD method can be found elsewhere [10,11]. The PVD-DIP layers were deposited in high vacuum (10⁻⁵ kPa) at substrate temperatures of T_S = 20 °C, 60 °C, 100 °C, and 140 °C. The deposition rate was monitored by a quartz microbalance and was regulated to 0.6 Å/s.

The surface morphology and the thickness of the DIP layers were investigated by scanning electron microscopy (SEM) using a commercial Gemini LEO 1530 microscope at an operating voltage of 5.0 kV. The cross-sectional images were used for the determination of the film thickness, *d*_{SEM}.

Immediately after the film preparation, transmission (*T*) and reflection (*R*) spectra were measured in air by a Varian Cary 500 UV-Vis-NIR spectrophotometer with an integrating sphere in the interval of 250–660 nm. The used light sources were a deuterium lamp (250–380 nm) and a tungsten halogen source (>380 nm). Using the optical model air/DIP/quartz glass/air (see Section 2.1), the measured curves were fitted numerically with RIG-VM, a program calculating *T/R* spectra for multiple stack layers [12,13].

2.1. Optical model

The multilayer optical model describes each layer by its frequency-dependent dielectric function $\varepsilon(\omega)$, thickness, and coherence type [14] and uses the transfer matrix method to calculate the propagation of the electromagnetic wave [15]. The complex dielectric function is

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) = (n(\omega) + ik(\omega))^2, \quad (1)$$

where *n* and *k* are the refractive index and extinction coefficient, respectively. They determine the Fresnel coefficients for the transmission and reflection coefficients for each layer [15,16].

The extinction coefficient *k* is connected to the absorption coefficient as $\alpha = 4\pi k / \lambda$, where λ is the wavelength of the incident light.

The optical stack for DIP on quartz glass is presented in Table 1. For the quartz glass substrate, a standard (*n_q*, *k_q*) data set was used. As a dielectric function for the DIP film, a sum of Lorentz oscillators is used [16]:

$$\varepsilon_{DIP}(\omega) = \varepsilon_{\infty} + \sum_j \frac{A_j \Gamma_j E_j}{E_j^2 - \omega^2 - i\Gamma_j \omega} \quad (2)$$

where *E_j*, *A_j*, and Γ_j is the energetic position, the amplitude, and the broadening parameter of the *j*th oscillator, and the constant ε_{∞} =

Table 1
Model stack for DIP on quartz glass.

Layer	$\varepsilon(\omega)$	Thickness	Type
Air	1	∞	Incoherent
DIP	$\varepsilon(\omega)$	<i>d</i> _{DIP}	Coherent
Quartz glass	(<i>n_q</i> + <i>ik_q</i>) ²	1 mm	Incoherent
Air	1	∞	Incoherent

Light enters the stack from the top. The quartz glass is described by a (*n_q*, *k_q*) data set.

$\varepsilon(\omega \rightarrow \infty)$ considers all other high energy contributions. The amount of oscillators is initially assumed to be equal to the number of peaks observed with corresponding energetic positions in the experimental absorption spectra. By choosing a starting set of values for *E_j*, *A_j*, and Γ_j , the dielectric function is calculated with the help of Eq. (2). Further, Eq. (1) is used to determine the spectral dependence of *n* and *k* and then to calculate the Fresnel coefficients. The latter coefficients are used by Harbecke [15] to calculate the transmittance and reflectance of the DIP layer. The calculated and measured spectra are compared for minimum deviation. The latter is achieved through adapting the fitting parameters in Eq. (2). When a good agreement between the calculated and the measured *T/R* data is achieved, the values of the extinction coefficient are used to calculate the absorption coefficient of the films.

3. Results

Fig. 1 shows the SEM images that demonstrate the morphological evolution of the OVPD-grown DIP layers on quartz glass for different substrate temperatures and chamber pressures. The DIP film at T_S = 60 °C and *P* = 1.1 kPa in Fig. 1(a) shows a spongelike structure. With the substrate temperature increase to T_S = 100 °C and with the chamber pressure decrease to 0.18 kPa, a compact film with elongated grains with the size of ~100 nm is observed in Fig. 1(b). At T_S = 140 °C and *P* = 0.08 kPa, the film shows (see Fig. 1(c)) larger grain dimensions of approximately 150 nm, which result probably from the coalescence of the smaller DIP grains. Thus, more compact layers with a smoother morphology are observed for intermediate deposition parameters. Similar observations were reported by Rusu et al. [11] on the formation of Cu-phthalocyanine thin films. The film thicknesses determined from cross-sectional SEM measurements are summarized in Table 2. The lowest film thickness is observed for samples prepared at T_S = 100 °C/*P* = 0.18 kPa. Because the nominal deposition rate and the deposition time were kept constant, it can be concluded that the effective OVPD-DIP film thickness is directly influenced by the process conditions.

The SEM images of the PVD-DIP films in Fig. 2 show elongated rodlike grains with sizes of approximately 100 nm independent of the deposition temperature. The film thicknesses determined from SEM measurements vary only slightly around values of 50 nm (see Table 2). With increasing substrate temperature, an increased formation of voids in the film is observed.

Fig. 3 shows the measured transmission and reflection spectra of all DIP samples as well as the absorption $A = 1 - T - R$. All samples exhibit similar absorption peaks between 260 and 430 nm. The most pronounced peaks are recorded at lower wavelengths centered at 260 nm (4.8 eV) and 290 nm (4.2 eV) as well as at 365 nm (3.4 eV). In the wavelength range between 430 and 550 nm (2.2–2.8 eV), all spectra show an absorption feature consisting of four overlapping absorption peaks. The DIP films hardly absorb any light for wavelengths above 600 nm. The optical *T/R* spectra of the PVD-deposited DIP films in Fig. 3(a) display only a slight dependence on the substrate temperature. In contrast, the differences in the spectra are more pronounced for the samples prepared at different temperatures/chamber pressures by OVPD (Fig. 3(b)). A shift toward lower reflectivity and higher absorption between 430 and 520 nm is especially pronounced for OVPD-DIP sample deposited at a pressure of 1.1 kPa. When comparing the OVPD-DIP films with PVD-DIP films, one has to consider the difference in film thickness (see Table 2), which explains the higher transmission/lower absorption of the thinner PVD-DIP films.

Motivated by the structure of the absorption spectra (see Fig. 3), we used eight oscillators (*j* = 8) for the dielectric function in Eq. (2). Thus, in combination with the DIP film thickness, there are 26 fitting parameters. The fits were calculated by a simplex and Marquardt–Levenberg algorithm implemented in RIG-VM where all fit parameters that

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