



Shift of absorption energy during thin dye film growth: interpretation by geometric models of the growth morphology



Ines Trenkmann, Christian von Borczyskowski, Harald Graaf*

Technische Universität Chemnitz, Institute of Physics, Optical Spectroscopy and Molecular Physics, Reichenhainer Str. 70, 09126 Chemnitz, Germany

ARTICLE INFO

Article history:

Received 11 March 2014

Received in revised form 19 September 2014

Accepted 24 October 2014

Available online 5 November 2014

Keywords:

Film growth

Organic semiconductor

Optical absorption spectroscopy

Transition band energy shift

ABSTRACT

We measure absorption spectra of two different perylene molecules in thin films with thicknesses varied between 1 and 30 nm physical vapor deposited on glass substrates. Atomic force microscopy (reveals the formation of crystallized needles for N, N'-dimethyl perylene tetracarboxylic acid diimide and amorphous round-shaped islands for 1,6,7,12-tetrachloro-N,N'-dimethyl perylene tetracarboxylic. For both molecules, a spectral shift of the lowest energy transition to lower energies was observed with increasing film thickness. Common models taking electric fields, electronic coupling or exciton confinement into account cannot completely describe the observed spectral shift. Here we show that the experimental values can be fitted with an advanced layering model based on the energetic difference between bulk and interface/surface materials. In contrast to the known simple d^{-1} model, which describes the energetic shift for the special case of a layer-by-layer growth, we extend this idea to other film morphologies.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Organic dye molecules with semiconducting behavior are an increasing class of materials with a wide range of potential applications in electronics and optics. In the last decades numerous experimental studies of this class of material, especially perylene pigments, are replenished with theoretical analysis of the crystallochromy [1–4]. For a deeper physical understanding of the aggregation and coupling mechanisms of such molecules in thin films optical investigations are a suitable, non-destructive method to obtain insight in the intermolecular interactions. Perylene dyes are subject to extensive studies especially by optical absorption measurements regarding their optical constants [1], surface states in molecular chains [2] coherent external phonons (lattice phonons) and internal phonons (intramolecular vibrations) [3] as well as effects of the deposition conditions [4]. The obtained optical spectra are a combination of different parameters such as intermolecular interactions, molecular deformations and vibrational degrees of freedom. These parameters depend on the amount of molecules forming the solid state, which leads to a slight change in the optical absorption spectrum during the growth of thin films. Different studies reveal a red shift of the lowest energy absorption with increasing amount of molecules during deposition [5,6].

In literature, different explanations are given to interpret these observations:

- The first model describes the energetic shift induced by strong intermolecular interactions between chromophores in an ordered array: this leads to a coupling of excitons resulting in a red shift due to classical Davydov splitting in the case of a parallel arrangement of transition dipoles. The magnitude of the shift depends on the exact alignment of the molecules and increases with the number of interacting molecules. Since the interaction is localized, the maximum shift is reached within a few numbers of molecules. In the case of flat lying phthalocyanine molecules, just 5 monolayers are essential to reach the maximum shift [7]. We demonstrated recently, that in the case of more or less upright standing chromophores like perylene pigments the maximum energetic shift is reached within one monolayer [8].
- The second one was given by So et al. [5]. They demonstrated in multilayer devices consisting of alternating layers of perylene-tetracarboxylic-dianhydrid (PTCDA) and naphthalene-tetracarboxylic-dianhydrid an energetic shift of the lowest energy transition of the PTCDA absorption spectra while varying the individual layer thickness from 1 to 20 nm. They explained their findings by an exciton confinement which can be seen, if the thickness of the absorbing layer (here PTCDA) decreases. The restriction of the free exciton wave function results in a $1/d^2$ dependence of the transition maximum. But this effect is only relevant for films up to 10 nm [5,9].

* Corresponding author. Tel.: +49 371 531 33015; fax: +49 371 531 21819.
E-mail address: graaf@uni-bremen.de (H. Graaf).

c. The third explanation by local electrical fields considers interaction of the dye molecules at the interfaces with the underlying substrate and/or surrounding atmosphere leading to slight variations of the electronic properties and thereby the optical properties compared to the bulk material. Therefore, the observed spectra are a superposition of the absorption bands of molecules at interfaces and bulk molecules. The influence of the interfaces decreases with increasing film thickness resulting in a $1/d$ dependence. [10,11]. This dependence is only valid for films thicker than 1–2 nanometers (equivalent to 1 monolayer). The first monolayer itself is either influenced by substrate–molecule interactions [12] or as we showed recently by intermolecular interactions with strong dipole–dipole interactions [8]. It has to be emphasized that this easy assumption is only suitable for films showing mainly a layer-by-layer growth [8,12].

The present study focuses on two different perylene pigments as model substances. This class of molecules is often investigated and shows n-type semiconductor characteristics and is highly photostable. The chosen materials are characterized by quite similar optical and electronic properties [13] and show an island growth mode: N, N'-dimethyl perylene tetracarboxylic acid diimide (MePTCDI) forms crystalline needles [6], with the lattice constants $a = 0,3874$ nm, $b = 1,558$ nm and $c = 1,4595$ nm [14], and its chlorinated derivative 1,6,7,12-tetrachloro-N,N'-dimethyl perylene tetracarboxylic ($\text{Cl}_4\text{MePTCDI}$) forms amorphous lentil like islands [15]. The reason for the different arrangements is the chlorination in the bay-position, which leads to a twisting of the aromatic perylene core compared to the flat unchlorinated perylene core [16]. The chemical structures of both molecules are depicted in Fig. 1.

The intermolecular interactions between MePTCDI molecules are higher than between $\text{Cl}_4\text{MePTCDI}$ molecules, leading for example to a reduction of the evaporation temperature and an increased solubility of $\text{Cl}_4\text{MePTCDI}$ [15]. Additionally these smaller interactions are also responsible for the formation of amorphous thin films. The different strength of the intermolecular interaction of both perylenes is also evident in the optical absorption spectra of both dyes. While the crystalline MePTCDI is characterized by a clear excitonic splitting in the electronic transition [6], the amorphous $\text{Cl}_4\text{MePTCDI}$ spectra showed only an energetic shift but no splitting compared to the solution [15]. Like shown in earlier studies absorption spectra of both perylene exhibit a red-shift of the lowest transition peak with increasing film thickness [6,15].

We will discuss the observed red-shift of the lowest energy transition during film growth under the assumption of a superposition of absorption bands of molecules in interface layers and that of molecules in the bulk. For both materials the relation of these molecules depends on the number of islands or needles formed on the surface. It is known that this number depends on substrate temperature and deposition rate [17,18].

The electric properties of thick polycrystalline films are influenced by grain boundaries, which are caused by the size and number of grown islands. The knowledge of how this parameter affects the optical properties of the film can be used in reverse to determine them. This opens a non-destructive, easy and fast experimental way to prove the quality and reproducibility of thin films consisting

of organic semiconductors not only prepared by physical vapor deposition, but also solution processed films.

2. Experimental

MePTCDI was purchased from Hoechst, and $\text{Cl}_4\text{MePTCDI}$ was synthesized according to the procedure described by Sadrai et al. [16]. First, both perylenes were purified with a three-zone-sublimation apparatus from Lindberg at a pressure of 1 mPa. Sample preparation and optical absorption measurements were carried out in a vacuum chamber to avoid the impact of ambient atmosphere, especially oxygen and hydrogen. The samples were prepared on cleaned glass substrates using physical vapor deposition at pressure of 10^{-2} Pa with deposition rates of 0.02 to 2 nm min^{-1} . The temperature of the sample was held at a constant value of 318 K. The average film thicknesses were controlled with a quartz crystal microbalance by measuring the resonance frequency change of the oscillator crystal (6 MHz, Conrad Electronic). The optical absorption spectrum of each film thickness was measured in-situ with a Cary 4 Spectrophotometer (Varian). For a systematic analysis of the observed shift, the complete absorption spectrum for each film thickness was fitted with a sum of Gaussian peaks. For this step a self-written Python code based on the Levenberg–Marquardt algorithm of NumPy was used. For the ex-situ characterization of the film morphology an atomic force microscope (AFM, Smena-B from MT-MDT) was used in tapping mode with a silicon tip.

3. Results

AFM measurements of MePTCDI and $\text{Cl}_4\text{MePTCDI}$, shown in Figs. 2 and 3 (a) respectively, clearly illustrate the mentioned structural difference of both film morphologies. While MePTCDI crystallizes in needles, the twisted $\text{Cl}_4\text{MePTCDI}$ shows a Volmer–Weber mode with spherical caps. The MePTCDI needles exhibit no preferred growth direction, however all needles have similar dimensions. Shown here is a 26 nm thick film (see Fig. 2); the needles have a length of around 400 nm and an average thickness of 60 nm. In Fig. 3(a), the caps in the shown 30 nm thick $\text{Cl}_4\text{MePTCDI}$ film have an average height of 50 nm and a diameter of 375 nm. Moreover, it can be noticed, that first caps have already grown together. With further increasing film thickness, the caps grow more and more together until no separated single cap is noticeable, as can be seen in Fig. 3(b) for a 70 nm thick film.

In Fig. 4, the absorption spectra for both dyes are shown exemplarily for four different film thicknesses. The recorded spectra of $\text{Cl}_4\text{MePTCDI}$ are due to the small intermolecular interactions between the chlorinated perylene dye molecules confirm with reported solution spectra [16]. The peaks at 2.31 eV and 2.49 eV as well as the shoulder at about 2.70 eV belong to vibrational satellites of the $S_0 \rightarrow S_1$ transition, and the peak at 2.88 eV corresponds to the $S_0 \rightarrow S_2$ transition. The strong π – π interaction between the unchlorinated dye molecules in the crystalline MePTCDI film leads to the formation of charge transfer states, which are visible in the spectra as broad band at ~ 2.6 eV besides the $S_0 \rightarrow S_1$ transition peak at 2.17 eV [4,19–21].

Both materials show no significant changing of the absorption spectra, but a red-shift of the $S_0 \rightarrow S_1$ transition peak with increasing film thickness d . For a better visibility, the normalized absorption of

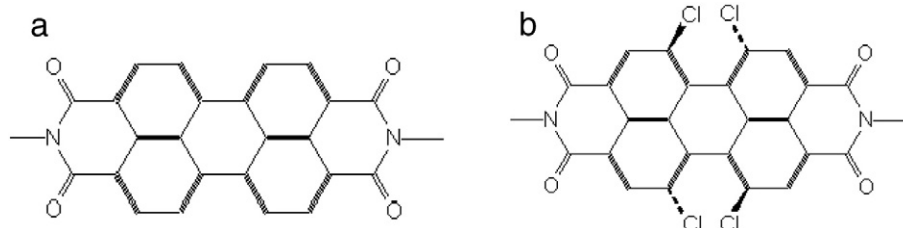


Fig. 1. (2-dimensional) picture of the chemical structure of (a) MePTCDI and (b) $\text{Cl}_4\text{MePTCDI}$. $\text{Cl}_4\text{MePTCDI}$ has a twisted aromatic perylene core due to chlorine atoms at the bay-position.

Download English Version:

<https://daneshyari.com/en/article/1665055>

Download Persian Version:

<https://daneshyari.com/article/1665055>

[Daneshyari.com](https://daneshyari.com)