Thickness dependent absorption spectra in conjugated polymers: Morphology or interference?

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The thickness dependence of the absorption spectrum of spin-coated films of poly[2-(2′-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] has been studied using reflectivity and variable angle spectroscopic ellipsometry measurements. It is found that, for films with thicknesses in the range of 18–178 nm, a single set of optical constants is sufficient to simulate accurately all the experimental data used, including the absorption spectra, independently of the film thickness or the processing conditions. Thus, the observed changes in the absorption spectrum with thickness can be fully accounted for by reflectivity and interference effects alone without the need to invoke morphology differences between films. © *2010 American Institute of Physics*.
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Since the discovery of electroluminescence in conjugated polymers (CPs),[1] this class of materials has been extensively studied for a wide range of optoelectronic applications such as polymer light emitting diodes,[1,2] organic photovoltaic devices,[3] and organic lasers.[4,5] A distinct advantage of CPs over other electronic materials is that they can be readily processed into thin films from solution using techniques such as spin-coating or inkjet printing,[6,7] therefore offering the prospect of low cost manufacturing processes.

One of the most widely used types of experimental data for the study of CP films is the absorption spectrum. This is because it is simple and convenient to measure, and gives information about the key electronic energy levels.[8–10] In view of its extremely widespread use, it is important to understand what factors affect it. It has been shown that the absorption spectra of CP films could depend on the film preparation conditions, such as solvent choice[11] or thermal annealing,[12] as well as spin-coating speed and solution concentration,[13] which in turn determine the thickness of the film. In all these reports, however, the observed changes in the absorption spectrum have been assigned to structural differences.

In this letter, we investigate the thickness dependence of the absorption spectra of spin-coated CP films using the prototypical CP poly[2-(2′-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH-PPV). We use measurements of reflectivity and variable angle spectroscopic ellipsometry (VASE) to identify the origin of the thickness dependence of the absorption spectrum. We show that the observed effects can be fully accounted for by reflectivity and interference effects, so that suggestions of thickness dependence of film morphology based on absorption spectra[13] need to be reexamined. Finally, we identify the conditions under which absorption spectra are most reliable.

We used soluble MEH-PPV with a weight average molecular weight of 1.0×10^5 Da and polydispersity of 2.5, formed by heating xanthate precursor polymer[14,15] in diphenylether. VASE measurements were performed in the reflection mode over the range of 190–1700 nm using a J. A. Woollam Co., Inc. M-2000DI system. Absorption spectra were acquired both using the M-2000DI system and a Cary 300 Bio UV-Vis spectrophotometer from Varian, Inc., as a comparison. The latter was also used for measuring near normal incidence (7° to the sample normal) absolute specular reflectance (ASR) spectra. Absorption and ASR spectra were measured using films on fused silica substrates. For the VASE measurements, both fused silica and silicon substrates were used. Prior to spin-coating, the substrates were cleaned by ultrasonication in acetone followed by propan-2-ol. Films were spin-coated from chlorobenzene solution and the thickness was varied by changing both the solution concentration (5–25 mg/ml) and the spin coating speed (1000–6000 rpm). All the measurements were performed in ambient conditions, but with a maximum of three hours between spin-coating and completion of the measurements. The VASE data, as well as the absorption and ASR spectra, were modeled by means of the WVASE32® analysis software, which uses formulae for the Fresnel reflection coefficients to predict experimental data and the Levenberg–Marquardt method to adjust the fitting parameters by minimizing the weighted mean squared error.[16,17] All the thicknesses were derived from the VASE measurements.

Figure 1 shows normalized absorption spectra measured for films with thicknesses of 18 and 178 nm. Each spectrum shows an absorption onset at ~590 nm (2.1 eV) and four absorption bands, as expected for films of PPV-derivatives,[8,9] which are labeled as peaks I–IV, respectively, from the lowest to the highest energy peak, in conformity with previous reports.[9,10] Significant differences between both spectra can be observed. First, the maximum of peak I occurs at $\lambda_{max} = 501 \pm 3$ nm (2.47 eV) in the 18 nm-thick film, but is blue-

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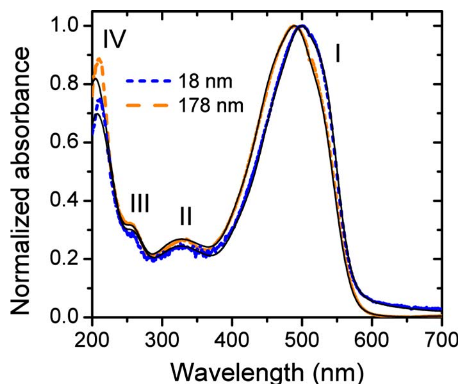

FIG. 1. (Color online) Experimental (short dashed and dashed lines) and simulated (black solid lines) normalized absorption spectra measured for two films of MEH-PPV with thicknesses of 18 and 178 nm. The spectra are shown referenced to the substrate.

shifted by 13 nm, at $\lambda_{max}=488\pm2$ nm (2.54 eV), in the 178 nm-thick film. Second, on the red side of peak I, the absorbance does not increase in proportion to the film thickness, but is found to be stronger in the 18 nm thick film.

The standard way of interpreting absorption data is to subtract the absorbance of the substrate and then assume that the resulting absorbance is equal to the product of the film ordinary (in-plane) absorption coefficient α_0 and the film thickness d, divided by the natural logarithm of 10 (Beer's law[18]). In this procedure, changes in the absorption spectrum can only arise from differences in the absorption coefficient of the film, and are therefore interpreted as differences in the film morphology.

However, this procedure assumes that the effect of reflectivity on the absorption spectrum is negligible. The ASR measurements in Fig. 2 show that is not the case since reflection coefficients up to 25% are observed. In order to gain a better understanding of the optical properties of the film, we performed VASE measurements. The ellipsometric Ψ and Δ data were acquired for several films with significantly different thicknesses, up to 178 nm, and angles of incidence (AOIs) from 45° to 75°. The VASE data were processed by means of a multisample analysis,[16] which combined not only the Ψ and Δ data, but also the absorption spectra,[17] and for some samples, the ASR spectra as well. This procedure has two advantages. First, it greatly reduces correlations between parameters.[16,17] Second, it leads to a single set of CP film optical constants averaged over the whole range of experimental data types and thicknesses. We stress here that the data are fitted with the same optical parameters for all film thicknesses. We used an air-CP film-substrate model, with the CP film being optically uniaxial with the optic axis perpendicular to the plane of the film.[19] Both the ordinary and extraordinary dielectric functions were described using a Kramers–Kronig consistent parametric functional model, in which the CP film absorption bands were described using a sum of Gaussian oscillator functions.

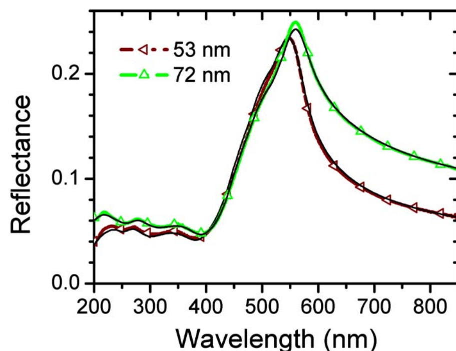

FIG. 2. (Color online) Experimental (symbols) and simulated (black solid lines) ASR spectra measured for two films of MEH-PPV with thicknesses of 53 and 72 nm.

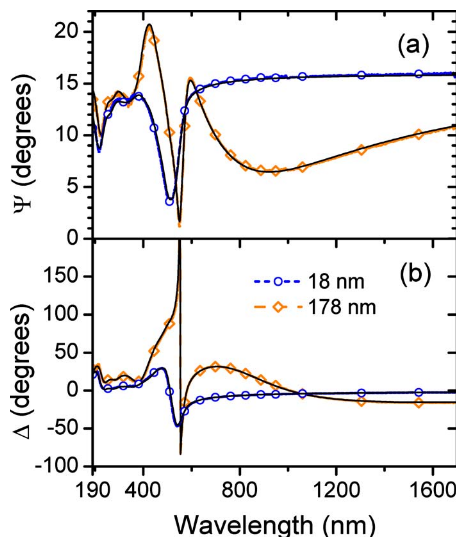

FIG. 3. (Color online) Experimental (symbols) and simulated (black solid lines) ellipsometric Ψ and Δ data measured at an AOI of 65° to the sample normal for the two films of MEH-PPV shown in Fig. 1.

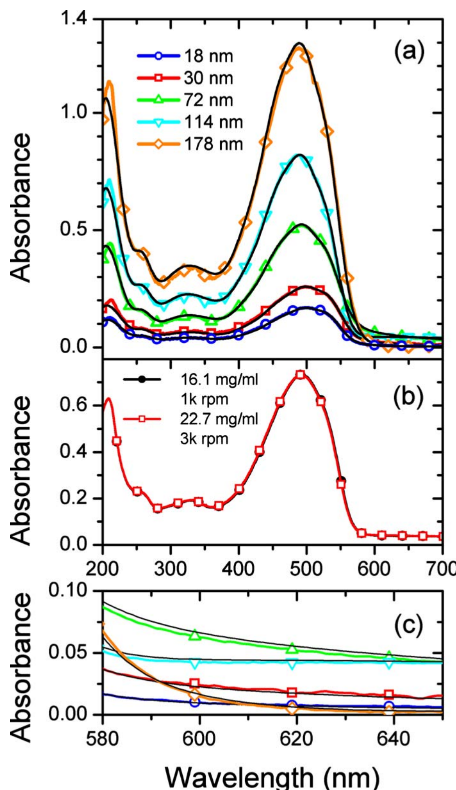

FIG. 4. (Color online) (a) Experimental (symbols) and simulated (black solid lines) absorption spectra measured for five films of MEH-PPV of different thicknesses in the range of 18–178 nm. (b) Experimental absorption spectra measured for two films of MEH-PPV. The two films have the same thickness of 102.5 ± 0.5 nm but were prepared from two solutions of different concentration and using two different spin speeds as follows: 16.1 mg/ml and 1000 rpm (black plain circles), and 22.7 mg/ml and 3000 rpm (red open squares). (c) Same data as in (a) but over the range of 580–650 nm. In all cases the spectra are shown referenced to the substrate.

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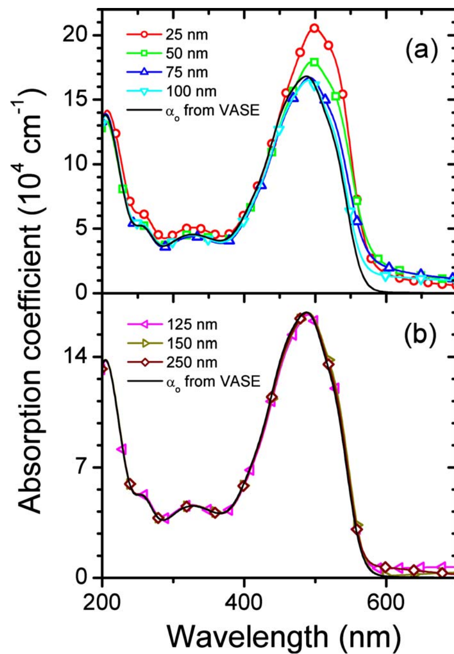

FIG. 5. (Color online) Symbols: Ordinary (in-plane) absorption coefficient, α_{oAbs}, derived using Beer's law (see text) for several (symbols) for several simulated absorption spectra of MEH-PPV films on fused silica substrates, with thicknesses in the range of 25–100 nm (a) and 125–250 nm (b). Black solid lines: Ordinary absorption coefficient, α_{oVASE}, of spin-coated films of MEH-PPV derived from VASE measurements.

Experimental and simulated Ψ and Δ data, measured at an AOI of 65° for the two films of Fig. 1, are shown in Figs. 3(a) and 3(b), respectively. Using these data together with measured transmission and reflectivity data we found that all the data for the nine film thicknesses could be fitted by a single set of optical constants for MEH-PPV, even though the thicknesses ranged from 18 to 178 nm. Examples of these fits for five film thicknesses are shown in Fig. 4(a). The normalized simulated absorption spectra for the 18 and 178 nm thick films are also reported in Fig. 1 and simulated ASR spectra are shown in Fig. 2. It can be clearly seen that a very close fit to all the data and all film thicknesses is achieved. Close fits to the Ψ and Δ data were also obtained for all AOIs or thicknesses used.

We first conclude from this that there is no significant dependence of the optical constants of MEH-PPV films on film thickness, for the wide range of thicknesses considered here, which is consistent with the work of Koynov *et al.*[20] but contradicts the study of Shi *et al.*[13] Our study shows that there is no measurable change of optical constants in MEH-PPV even for films as thin as 18 nm. A second important aspect of the result is that the same optical constants fit all the films, regardless of concentration of solution or spin-coating speed used to prepare the film. Our study therefore demonstrates the consistency and flexibility of spin-coating as a simple film preparation procedure.

The insensitivity of optical constants to the spin-coating conditions is illustrated in Fig. 4(b), which shows that two MEH-PPV films having the same thickness but spin-coated from two different solution concentrations and using two different spin speeds, have identical absorption spectra. A third conclusion is that the thickness dependence of the absorption spectra of MEH-PPV films can be fully accounted for by means of reflectivity and interferences rather than morphology changes between films.[13] The effect of interference is particularly noticeable in the spectral region corresponding to the red tail of peak I, where it can be seen in Fig. 4(c) that the absorbance first increases for films with thicknesses up to 72 nm, and then decreases for thicker films.

Finally, in addition to the above conclusions, we consider the conditions under which a simple measurement of an absorption spectrum of a CP film gives an adequate estimate of the ordinary absorption coefficient, Fig. 5(a) shows both α_o determined using VASE, noted α_{oVASE}, and a set of α_o values, noted α_{oAbs}, derived from simulated absorption spectra for films of increasing thickness up to 100 nm. It can be clearly seen in Fig. 5(a) that there is a significant discrepancy in between α_{oVASE} and α_{oAbs}, especially in the case of peak I. Figure 5(b) shows equivalent data for three films with thicknesses in the range of 125–250 nm. In the absorbing region, a good match between α_{oVASE} and α_{oAbs} is now obtained in the three cases, although a close inspection would reveal that complete overlap of α_{oAbs} with α_{oVASE} in the spectral region of peak I is still not achieved, particularly for the 125 nm thick film. On the red side of peak I, however, the effect of reflectivity can still be clearly observed, even for the 250 nm thick film. Hence it appears that effects of reflectivity and interference on the absorption spectra are mitigated for films with a thickness of 125 nm or higher but only in the absorbing region and with thicker films yielding a more accurate description of the absorbing properties.

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