Retrieval of Optical and Dielectric Constants of PBDTTTPD Polymer Film by Unconstrained Optimization Method

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Keywords: PBDTTTPD thin film, ITO substrate, Unconstrained optimization method, Optical and dielectric constants.

Abstract. Till now, optical and dielectric constants of polymer based on poly(benzo[1,2-b:4,5-b’]-dithiophene–thieno [3,4-c]pyrrole-4,6-dione) (PBDTTTPD) incorporated into thiophene (PBDTTTPD) have not been systematically investigated. In this work, PBDTTTPD thin film was prepared on ITO glass substrate. Transmittance spectra of ITO and PBDTTTPD films were measured. Based on unconstrained optimization method, the glass was firstly as the substrate, the thickness and the refractive index of the ITO were retrieved. Then the refractive index data of the ITO thin film were added to the PUMA program and the ITO was taken as the new substrate, the thickness, optical and dielectric constants of the PBDTTTPD film were further simulated only via the transmittance spectra. These optical and dielectric parameters are promising useful in design optical devices related to PBDTTTPD polymer.

Introduction

In recent years, polymer solar cells (PSCs) have been attracted much attention and vigorously investigated due to their potential applications for low-cost, light weight, and large-area processability [1-3]. For obtaining high power conversion efficiencies (PCEs), donor-acceptor (D-A) conjugated polymers have been used in PSCs for their low-band-gap and easy modulating electronic properties [1,2]. PBDTTTPD is a type of donor-acceptor (D-A) conjugated polymer based on the electron-rich unit of benzodithiophene (BDT) and the electron-deficient unit of 5-octylthieno[3,4-c]pyrrole-4,6-dione (TPD) along the polymer backbone [4-7] with a band gap of 1.82 eV [4]. Among π-conjugated polymer donors for efficient bulk-heterojunction (BHJ) solar cells, PBDTTTPD polymers produced some of the highest open-circuit voltages ($V_{oc}$, ca. 0.9 V) and proper short circuit current density ($J_{sc}$>12 mA/cm²) in conventional (single-cell) BHJ devices with PCBM acceptors [5]. The BHJ single solar cells based PBTD(T)PD (X=furan(F), thiophene(T), and selenophene(S) ) has high $V_{oc}$≈1 V, span a broad range of PCEs (3–8.5%) in optimized solar cells with improved thin-film morphologies through use of the additive 1,8-diiodooctane(DIO). PBTD(T)PD polymers are promising candidates for use in the high-band gap cell of tandem solar cells [5-7]. Although PBTDTTTPD is a promising D-A polymer used in organic photovoltaic, up to now, except for band gap [6], its optical and dielectric parameters including absorption coefficient ($\alpha(\lambda)$), extinction coefficient ($k(\lambda)$), refractive index ($n(\lambda)$) and dielectric constant ($\varepsilon_1(\lambda),\varepsilon_2(\lambda)$) have not been systematically investigated. It is well known that these optical and dielectric constants are necessary parameters in the design of optoelectronic devices.

In experiment, it is easy to measure the transmittance spectrum of a film. But it is a challenge to estimate the thickness and the optical constants of thin film only using transmission data. In many cases it is a very ill-conditioned inverse problem with many local-nonglobal solutions [10,11]. For solving this problem, pointwise constrained optimization approach [10-14] and unconstrained optimization algorithm [15-19] were proposed respectively. The core thought of the two
optimization methods is the theoretical transmittance of the thin film is equal to the measured one in every measurable wavelength. That is to say, the estimation problem takes the form [10-13, 15-17]:

$$
\text{Minimize } \sum_{i=1}^{N} \left[ T_{\text{theoretical}}(\lambda_i) - T_{\text{measurement}}(\lambda_i), s(\lambda_i), d, n(\lambda_i), \kappa(\lambda_i) \right] 
$$

subject to Physical Constraints.

Where \( \lambda \) is the wavelength, \( s \) indicates the refractive index of the substrate, \( d, n \) and \( \kappa \) are the thickness, the refractive index and the extinction coefficient of the under studied film. In general, \( s, n \) and \( \kappa \) are the functions of the wavelength. In nature, the constrained optimization algorithm is a nonlinear programming problem, the unknown variables (\( d, n(\lambda), \kappa(\lambda) \)) in (1) are the coefficients to be simulated. It is obvious that these physical constraints may depend on the material made up the thin film. A prior knowledge about the under studied material is needed. It is necessary to impose a functional form to \( n(\lambda) \) and \( \kappa(\lambda) \) for the constrained optimization approach [10-13]. Different from the method of Swanepoel [20, 21], the retrieval of the correct thickness and optical constants of the film by pointwise constrained optimization approach does not rely on the existence of interference fringes of the measured transmittance spectrum [10-13]. The main inconvenience of the pointwise constrained optimization approach is that it is a rather complex large-scale linearly constrained nonlinear programming problem whose solution can be obtained only by means of sophisticated and not always available computer codes that can deal effectively with the sparsity of the matrix of constraints [16, 17]. This problem can be resolved by the unconstrained optimization approach. Instead of imposing a functional form to \( n(\lambda) \) and \( \kappa(\lambda) \), automatic differentiation [22] and nonmonotonic spectral projected gradient techniques [15, 16] are used for solving the potentially large-scale unconstrained minimization problem.

![Figure 1. Measured and simulated transmittance spectra of ITO thin film.](image)

**Unconstrained Optimization Method**

For reduction the range of the variables of \( n(\lambda) \) and \( \kappa(\lambda) \), the physical constraints near the fundamental edge are used [16],

PC1. \( n(\lambda) \geq 1 \) and \( \kappa(\lambda) \geq 0 \) for all \( \lambda \in [\lambda_{\text{min}}, \lambda_{\text{max}}] \),

PC2. \( n(\lambda) \) and \( \kappa(\lambda) \) are all decreasing functions of \( \lambda \),

PC3. \( n(\lambda) \) is convex,

PC4. \( \kappa(\lambda) \) is convex if \( \lambda > \lambda_{\text{infl}} \) and concave if \( \lambda < \lambda_{\text{infl}} \), \( \lambda_{\text{infl}} \in [\lambda_{\text{min}}, \lambda_{\text{max}}] \).

In which, \( \lambda_{\text{infl}} \) is the inflection point wavelength of the extinction coefficient.

By suitable variable substitution and differentiation, objective function (1) can be represented as an expression only related to the second derivatives of \( n(\lambda) \) and \( \kappa(\lambda) \) plus functional values and first derivatives at \( \lambda_{\text{max}} \) [16]. Thus the constraints of the problem will be eliminated as far as possible. The physical constraint is changed into \( \kappa_{\text{infl}} \geq \kappa_{\text{infl}} \) [16]. This constraint is irrelevant when thickness \( d \) is determined since it is automatically satisfied by the convexity of \( \kappa \) and the fact that the derivative of \( \kappa \) at \( \lambda_{\text{max}} \) is nonpositive. In the process of determination of \( \lambda_{\text{infl}} \), \( n(\lambda) \) and \( \kappa(\lambda) \), the constraint can be neglected [16]. Thus the constrained optimization problem is transferred into an unconstrained one.
Numerical Results and Discussion

The PBDTTTPD polymer was synthesized according to the method in [6]. Spin coating method was used to fabricate the PBDTTTPD film on ITO glass substrate. The PUMA program (The software used in this work is freely available through the PUMA Project web page (http://www.ime.usp.br/~egbirgin/puma/)] was to be used to simulate the thickness, the optical and dielectric constants of the PBDTTTPD film only via its transmittance spectrum. There are five substrates in the standard PUMA program for choosing, but not including in the ITO. So we first took the glass as the substrate and retrieved the thickness and the refractive index of the ITO. Then the refractive index data of the ITO thin film were added to the PUMA program and the ITO was taken as the new substrate, the thickness, optical and dielectric constants of the PBDTTTPD film were further simulated.

![Refractive index curve of the ITO thin film](image)

**Figure 2. Simulated refractive index curve of the ITO thin film.**

**Retrieval of the Refractive Index of the ITO Film**

A Lamda-25 UV-Vis spectrophotometer (PerkinElmer company) was used to measure the transmittance spectra. Figure 1 shows the transmission spectrum of the ITO film. In ultraviolet, visible and near-infrared range, the ITO thin film has high transmittance. From 300 nm to 360 nm, the transmittance increase quickly from 0 to 0.84. In the range of 360-600 nm, the transmittance first decrease then increase. And there is almost a stable transmittance of 0.83 in the range of 600-800 nm.

By using PUMA program, the retrieved thickness of the ITO film (the substrate is glass) is 170 nm, which exactly coincides with the experimental result (The thickness of the film was measured by a Veeco Dektak 150 surface profiler). In the minimization process, the quadratic error and the trial thickness step were gradually decreased till the quadratic error is $10^{-4}$, the trial thickness step 1 nm, the iteration times 20000.

In the simulation of the refractive index of the ITO thin film, the thickness of the ITO film was seen as a constant. Three calls were carried out by gradually decreased the quadratic error and increased the iteration times. The three simulation results are almost same. Figure 2 shows the best result. The refractive indices decrease quickly from 2.276 at 350 nm down to 1.937 at 433 nm. In the range of 433-560 nm, the refractive indices decrease slowly, till 1.803 at 560 nm. In the range of 560-800 nm, the refractive index almost keeps this value. Our simulated result of the refractive index about the ITO thin film agrees well with the published result [23-25]. In [23], the experimental result of the refractive index of the ITO film by ellipsometric spectroscopy at 550 nm is about 1.85. Our result is 1.867. The above result indicates that the unconstrained optimization method is reliable to simulate the optical constant of the ITO thin film. By this method, the thickness and the refractive index of the ITO thin film can be determined only via the transmittance spectrum of the ITO film.
Simulation the Optical and Dielectric Constants of PBDTTTPD Thin Film

The measured transmittance spectrum of PBDTTTPD was shown in Figure 3 (red line). The transmittance is up to 0.85 in the range of 680-900 nm. But within 500-640 nm the transmittance is very low (~0.3). So The PBDTTTPD film can be used in tandem solar cells.

In the retrieval process of the optical constant of the PBDTTTPD film, the substrate is the ITO film. The simulated thickness of the PBDTTTPD is 145 nm. The measured thickness is 130 nm. We guess the thickness error mainly comes from the roughness of the polymer, which is not a ideal smooth film. Another reason is that the position measured the thickness and the position measured the transmittance spectrum are not the same places. The retrieved transmittance curve was indicated in Figure 3. There is a better agreement between the measurement and the simulation.

The simulated refractive indices of the PBDTTTPD were shown in Figure 4. In the range of 350-680 nm, the refractive indices decrease from 2.927 to 2.414. After 680 nm, the refractive index is almost a constant of 2.414.

The extinction coefficient as the function of wavelength was shown in Figure 5. \( \kappa(\lambda) \) increases with the wavelength in the range of 350-594 nm. At 594 nm, \( \kappa(\lambda) \) gets to the maximum of 0.419. After that, \( \kappa(\lambda) \) decreases with the wavelength till 0.013 at 683 nm. In the range of 683-900 nm, \( \kappa(\lambda) \) keeps this value.

The complex dielectric constants characterizes the optical properties of solid material. The real and imaginary components of the dielectric constants can be calculated according to \( \varepsilon_1 = n^2(\lambda) - \kappa^2(\lambda) \) and \( \varepsilon_2 = 2n(\lambda)\kappa(\lambda) \) [26]. The simulated real component of the dielectric constant of the PBDTTTPD was indicated in Figure 6. The changing trend of \( \varepsilon_1 \) is similar to the refractive index. From 350 nm to 680 nm, \( \varepsilon_1 \) decreases from 8.56 down to 5.82. In the range of 680-900 nm, \( \varepsilon_1 \) almost keep a constant of 5.82.

Figure 3. Measured (red) and simulated (black) transmittance spectra of the PBDTTTPD thin film. The inset is the chemical structure of the PBDTTTPD.

Figure 4. Simulated refractive index curve of the PBDTTTPD thin film.
Figure 5. Extinction coefficient curve of the PBDTTTPD thin film.

Figure 6. Real component of complex dielectric constant of the PBDTTTPD thin film.

The imaginary component of the dielectric constant ($\varepsilon_2$) was shown in Figure 7. $\varepsilon_2$ monotonically increases from 0.020 to 2.135 in the range of 350-594 nm, then monotonically decreases to 0.064 at 700 nm. In the range of 700-900 nm, $\varepsilon_2$ is almost a constant.

Figure 7. Imaginary component of complex dielectric constant of the PBDTTTPD thin film.

Figure 8. Plot of $\left(\frac{\alpha}{hv}\right)^{3/2}$ vs photon energy for direct transition of PBDTTTPD thin film.
Combined Tauc equation [27]
\[
\alpha(\lambda)h\nu = A(h\nu - E_g)^m
\]
and \(\alpha = 4\pi A_0 h\nu\lambda\), the band gap of the PBDTTTPD can be determined. In which, \(h\) is the Planck’s constant, \(\nu\) is the frequency of the photon, and \(A\) is a constant. For the direct band gap semiconductor, \(m=1/2\) or \(2/3\) [26]. When \(m=2/3\), the calculated results give the best linear plot in the band edge region for the PBDTTTPD thin film. Representative plot of \((\alpha h\nu)^{3/2}\) verses photon energy was showed in Figure 8. The band gap of PBDTTTPD thin film was obtained by extrapolation \(\alpha h\nu\) to zero. So \(E_g\) is 1.901 eV, which is almost as same as [6] (1.86 eV).

Conclusion
In this paper, PBDTTTPD thin film was prepared on ITO glass substrate. The transmittance spectra of ITO and PBDTTTPD films were measured. The thickness and refractive indices of the ITO film were simulated by PUMA program based on the unconstrained optimization method. We first took the glass as the substrate and retrieved the thickness and the refractive index of the ITO. Then the refractive index data of the ITO thin film were added to the PUMA program and the ITO was taken as the new substrate, the thickness, optical and dielectric constants of the PBDTTTPD film were further simulated.

The simulated thickness of the ITO film (170 nm) is exactly as same as the measured one. At 500 nm, the refractive index of ITO is 1.846. In the range of 550-800 nm, the refractive indices are almost a constant of 1.797. The refractive index of the ITO thin film is almost as same as the previously published result. Furthermore, taking the ITO as the substrate, the optical and dielectric constants, such as refractive index, extinction coefficient, real component and imaginary component of the dielectric constants and optical band gap of PBDTTTPD polymer thin film were also retrieved based on the unconstrained optimization method. At 500 nm, \(n, \kappa, \epsilon_1, \epsilon_2\) and \(E_g\) are 2.738, 0.295, 7.411, 1.617 and 1.901 eV respectively. The unconstrained optimization method is an easy and economic method to obtain the thicknesses, optical and dielectric constants of thin film only via transmittance spectrum. These optical and dielectric parameters are promising useful in design optical devices related to PBDTTTPD polymer.

Acknowledgement
The authors deeply thank the National Nature Science Foundation of China for supporting this work (granted No. 41172110).

References


