

## RAPID COMMUNICATION

# The optical constants of emitter and electrode materials in polymer light-emitting diodes

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Online at [stacks.iop.org/JPhysD/36/L29](http://stacks.iop.org/JPhysD/36/L29)**Abstract**

The optical constants of spun-cast films of several polyfluorene derivatives were examined using a combination of reflection and transmission spectroscopic ellipsometry. Results for both unannealed films and films annealed at 150°C are presented. For some polymers, annealing allowed the polymer chains to re-organize such that the films became more isotropic. The optical constants of two common metal cathodes, calcium and aluminium, were investigated using reverse ellipsometry. Multi-layer structures incorporating both polymer and metal layers were also successfully modelled.

**1. Introduction**

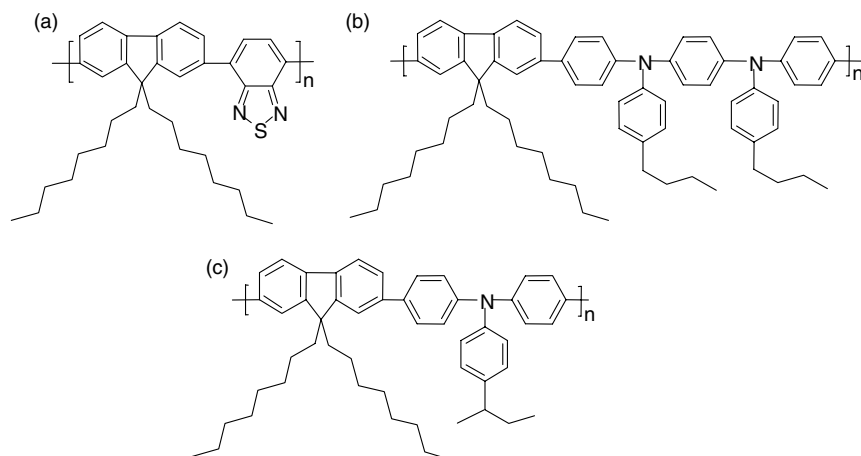
Conjugated polymers are attractive materials for use as the active semiconductor in large-area, low-cost electronic devices. Polymer light-emitting diodes (LEDs) are already finding commercial applications in displays, and the performance of polymer-based photovoltaic devices is improving rapidly. Both these types of device involve multi-layer structures incorporating electrode materials and polymer layers with thicknesses comparable with the wavelength of optical radiation. Optimization of device performance requires modelling of the emission and absorption of light within the device. This is particularly important in polymer LEDs, where the efficiency and angular distribution of the emission depends strongly on the position and orientation of the emitting dipoles within the device [1–4]. If the optical constants (refractive index and absorption coefficient as a function of wavelength) of the polymer and electrodes are known, it is possible to determine the position at which constructive interference occurs between directly emitted light and light reflected at the cathode, thus maximizing the radiative rate and providing maximum emission in the forward direction. Modelling of non-radiative energy transfer to the cathode also requires the imaginary part of the dielectric function of the cathode to be known [5].

Determination of optical constants for conjugated polymer films is complicated by the high degree of uniaxial anisotropy

due to preferential alignment of polymer chains parallel to the plane of the film [6]. The amount of anisotropy is sensitive to the deposition conditions, and to subsequent processing steps such as annealing, which is often used during the manufacturing process in order to optimize device performance and lifetime. In this paper, we use the technique of variable-angle spectroscopic ellipsometry to determine accurate anisotropic optical constants for thin films of a number of polyfluorene derivatives which are commonly used in polymer LEDs and photovoltaic devices [7, 8]. We study the effect of annealing on the degree of anisotropy in these materials. We also determine the optical constants for evaporated films of calcium and aluminium which are commonly used as electrodes in polymer devices, and we show that these data can be combined to form consistent optical models for multi-layer device structures.

**2. Experimental methods**

The polyfluorenes investigated in this work are F8BT [poly(9,9'-dioctylfluorene-co-benzothiadiazole)], PFB [poly(9,9'-dioctylfluorene-co-bis-*N,N'*-(4-butylphenyl)-bis-*N,N'*-phenyl-1,4-phenylenediamine)] and TFB [poly(9,9'-dioctylfluorene-co-bis-*N,N'*-(4-butylphenyl)diphenylamine)]. Their chemical structures are shown in figure 1. TFB and F8BT are often blended together for use in organic LEDs [9], whilst



**Figure 1.** The chemical structures of (a) F8BT, (b) PFB, and (c) TFB.

PFB and F8BT are often used in organic photovoltaic devices due to their efficient charge transfer properties [8].

The polymers were separately dissolved in *para*-xylene at concentrations of 25 g l<sup>-1</sup> for TFB and 15 g l<sup>-1</sup> for F8BT and PFB. They were spin-coated in a nitrogen atmosphere at 2500 rpm for 60 s onto quartz substrates which were pre-cleaned with acetone and propan-2-ol in an ultrasonic bath. Thicknesses determined by ellipsometry were confirmed using atomic force microscopy or surface profilometry, which gave good agreement. Prior to annealing, the thicknesses of the PFB, F8BT and TFB layers were 75 nm, 133 nm and 115 nm, respectively. Annealing was carried out in a nitrogen atmosphere at 150 °C for 2 h, after which samples were rapidly cooled by placing them in contact with a cold surface. The thicknesses were not significantly changed by annealing. Normal-incidence UV–visible transmission measurements which were made using a Hewlett-Packard 8453 spectrophotometer in order to confirm the in-plane extinction coefficients determined by ellipsometry.

Metal films were prepared by thermal evaporation at pressures of ~10<sup>-6</sup> Torr onto glass cover slips which had been cleaned in acetone and propan-2-ol in an ultrasonic bath. Thicknesses were measured using a quartz crystal oscillator. Aluminium and calcium films were approximately 100 nm thick. The calcium films were capped with an aluminium layer, 150 nm thick.

Ellipsometry measurements were made using a J.A. Woollam M-2000 diode-array rotating compensator ellipsometer with a xenon light source, over a wavelength range of 245–900 nm. Ellipsometry measures the change in polarization of light as a function of incident angle and wavelength for *p* (parallel) or *s* (senkrecht) polarized light after reflection or transmission by the sample. The experimental values determined are  $\Psi$  and  $\Delta$ , which are related to the reflection and transmission coefficients by

$$\frac{\hat{R}_p}{\hat{R}_s} = \tan \Psi_r e^{i\Delta_r}, \quad \frac{\hat{T}_p}{\hat{T}_s} = \tan \Psi_t e^{i\Delta_t},$$

where  $\hat{R}_p$ ,  $\hat{T}_p$ ,  $\hat{R}_s$  and  $\hat{T}_s$  are the complex amplitude reflection ( $\hat{R}$ ) and transmission ( $\hat{T}$ ) coefficients (taking into account all interfaces within the sample), for *p* and *s* polarized light.

Unfortunately, there is no simple inverse transformation from the  $\Psi$  and  $\Delta$  values to the optical constants,  $n$  (refractive index) and  $k$  (extinction coefficient). They are usually determined using an optical model in which the parameters are adjusted iteratively to give the best fit. Samples investigated in this work were modelled using J.A. Woollam Co. WVase32 software, which uses a Levenberg–Marquardt algorithm for fitting.

The strategy for modelling varies depending on the material under examination. In the case of anisotropic conjugated polymers, reflection ellipsometry alone is often insufficient to allow determination of in-plane ( $n_o, k_o$ ) and out-of-plane ( $n_e, k_e$ ) optical constants across both the absorbing and emissive regions, due to a high degree of correlation between the model parameters [10]. The correlations can be reduced by analysing multiple samples with different layer thickness [11], or by combination with transmission measurements [12] or transmission ellipsometry measurements [10]. Here, we have combined reflection and transmission ellipsometry measurements, which we have previously shown to be particularly effective in determining accurate optical constants in anisotropic conjugated polymer films, including F8BT [10].

Reflection ellipsometry was performed at angles between 60° and 70°, and transmission ellipsometry at angles between 40° and 50°. Anisotropic refractive indices,  $n_o$  and  $n_e$ , were first fitted in the transparent region, above ~650 nm, using the Cauchy equation

$$n_{o,e}(\lambda) = A_{o,e} + \frac{B_{o,e}}{\lambda^2} + \frac{C_{o,e}}{\lambda^4}.$$

In addition to the Cauchy parameters,  $A_{o,e}$ ,  $B_{o,e}$  and  $C_{o,e}$ , the thickness was also included as a fitting parameter. Once the thickness was determined it was fixed and the optical constants,  $n_o$ ,  $n_e$ ,  $k_o$  and  $k_e$  were fitted independently over the spectral region between 245 and 900 nm. The use of transmission ellipsometry measurements requires that the substrate is optically transparent. Consequently, for the polymers described in this work, a transparent quartz substrate was used and one incoherent reflection from the bottom of the substrate was taken into account when modelling the reflection ellipsometric data. Kramers–Kronig consistency is not ensured when  $n_o$ ,  $k_o$ ,  $n_e$ ,  $k_e$  are fitted independently.

Therefore, the optical constants were verified using a Kramers–Kronig consistent model combining Cauchy dispersion and several Gaussian oscillators.

For the examination of metal films by ellipsometry other issues must be addressed. Calcium and aluminium films are isotropic and hence the optical constants can be determined from fewer data sets than are needed for polymers and only reflection data are required. However, aluminium forms a surface oxide when exposed to air and calcium degrades rapidly unless protected by a capping layer. It is therefore not possible to determine the optical constants using the conventional reflection ellipsometry technique. Consequently, reverse ellipsometry, where the incident beam traverses the substrate before hitting the layer of interest, was employed to determine the values of the optical constants in these cases. In this case the angles of incidence used were between  $40^\circ$  and  $50^\circ$ . Partial overlapping of reflected beams in the reverse ellipsometry measurement can make it difficult to extract the optical constants of a film. Hence thin glass cover slips ( $\sim 0.1$  mm) were used as substrates to maximize the overlap between the glass–air reflection and the glass–metal reflection. The optical constants of calcium and aluminium were modelled using a combination of Lorentz oscillators with oscillator strengths, centre frequencies and widths which were allowed to vary. Three oscillators were needed to give a good fit to the data, including one with a centre frequency of zero to represent free-electron Drude conductivity.

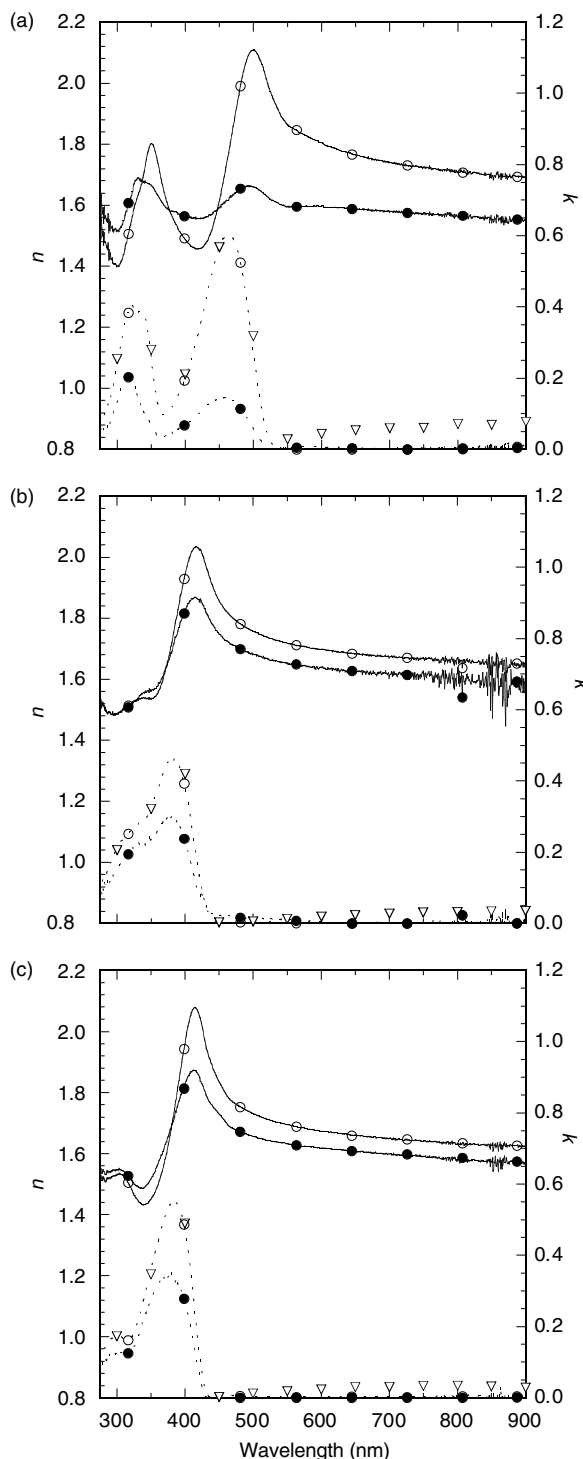
### 3. Results and discussion

Figure 2 shows the anisotropic optical constants of F8BT, PFB and TFB before annealing, determined using ellipsometry. The in-plane extinction coefficients extracted from UV–visible transmission measurements are also plotted in figure 2 (open triangles). The mean-squared error (MSE) values were lower than 2.5 for all of the polymer films tested here, indicating good agreement between the model and the experimental data.

Whilst there is evidence that thick films of poly(9,9'-dioctylfluorene), F8, are almost isotropic in nature [13] the films under investigation here are sufficiently thin to exhibit significant anisotropy. F8BT is the most anisotropic of the three polyfluorene derivatives under investigation, showing a birefringence of 0.19 at 633 nm compared to 0.06 for PFB and 0.05 for TFB at the same wavelength. The maximum birefringence (at the onset of the  $\pi$ – $\pi^*$  transition) is 0.45 in F8BT whilst in PFB and TFB the birefringence is again substantially lower at only 0.16 and 0.21, respectively.

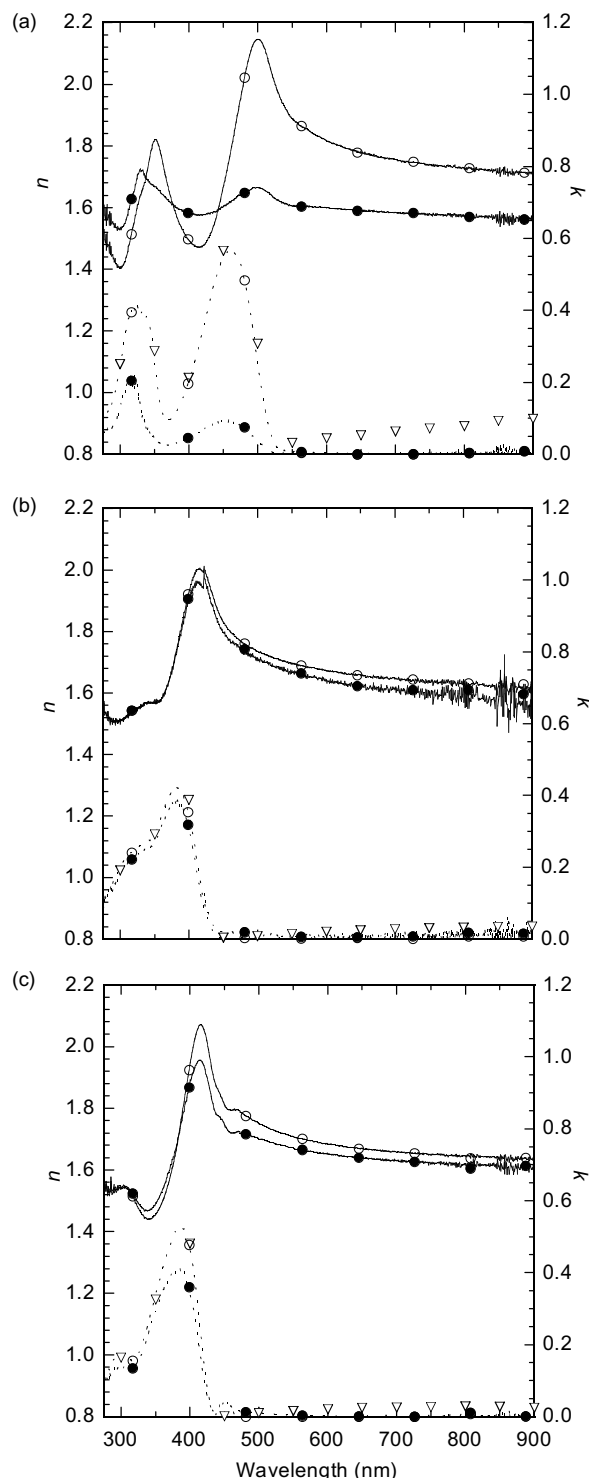
The results in figure 2 indicate that there is a greater degree of chain alignment in the F8BT film than in either PFB or TFB, assuming that their transition dipole moments are all oriented along the chain. In all three cases the out-of-plane optical constants are all slightly blue-shifted with respect to the in-plane values, as a result of the decreased conjugation length for chains lying perpendicular to the plane of the film. The transmission measurements agree with the ellipsometrically determined in-plane extinction coefficients.

Figure 3 shows the optical constants of F8BT, PFB and TFB after annealing and quenching the films. The annealing



**Figure 2.** The ordinary (○) and extraordinary (●) values for the refractive index (—) and extinction coefficient (---) for unannealed films of (a) F8BT, (b) PFB, and (c) TFB determined by ellipsometry. The ordinary extinction coefficients extracted from UV–visible transmission measurements are also plotted (▽).

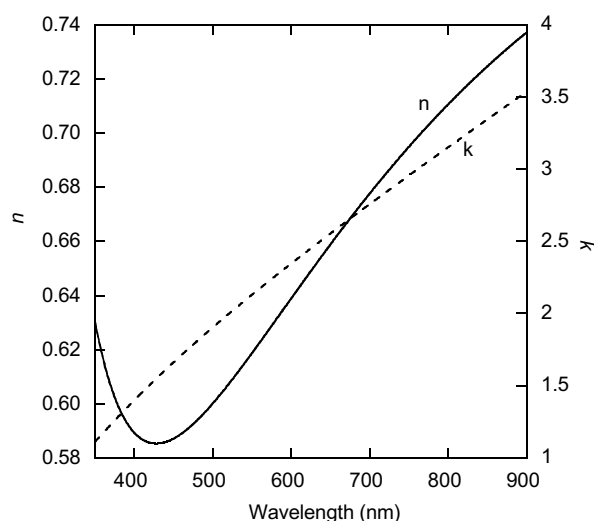
was carried out at  $150^\circ\text{C}$  which is expected to be above the glass transition temperature for all of these polyfluorene derivatives. The optical constants of F8BT remain unchanged and therefore there is still a large degree of anisotropy in these films. PFB and TFB, however, are much more isotropic after annealing. In PFB the film is almost completely isotropic, with a maximum



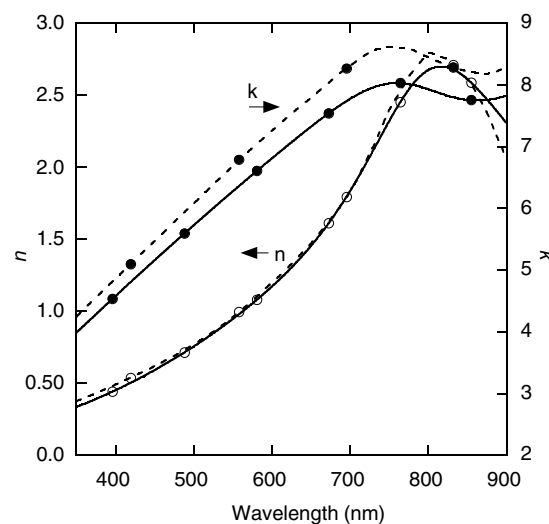
**Figure 3.** The ordinary (○) and extraordinary (●) values for the refractive index (—) and extinction coefficient (---) for annealed films of (a) F8BT, (b) PFB, and (c) TFB determined by ellipsometry. The ordinary extinction coefficients extracted from UV-visible transmission measurements are also plotted (▽).

birefringence of 0.04, at 415 nm. In TFB the maximum birefringence is higher, 0.12, but still much reduced compared to the unannealed case.

The results in figures 2 and 3 suggest that the spin-coating process forces the polymer chains into a higher energy



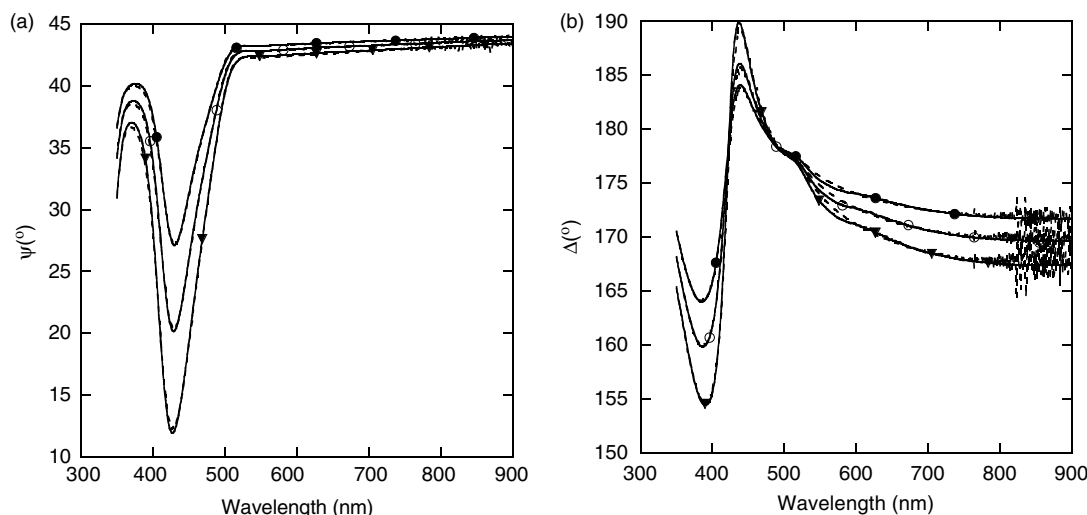
**Figure 4.** The refractive index (—) and extinction coefficient (---) of calcium.



**Figure 5.** The refractive index (○) and the extinction coefficient (●) determined for aluminium (—) and the literature values (---) [14].

conformational state from which they can, in PFB and TFB films, relax upon annealing. In the case of F8BT the degree of anisotropy cannot be altered by thermal annealing at this temperature. The rigidity of the polymer backbone in this material may prevent significant conformational alteration. The optical constants of samples which were cooled slowly after annealing were identical to those of the rapidly cooled samples shown in figure 3. The out-of-plane constants for the annealed films show a small red shift with respect to the out-of-plane indices for unannealed films. This is likely to be due to an increased conjugation length in the direction perpendicular to the substrate surface after the films have been annealed.

The  $n$  and  $k$  values for optically thick calcium and aluminium films were obtained by reverse ellipsometry, and are shown in figures 4 and 5, respectively. The glass cover slip absorbs at wavelengths below 350 nm and so data below this wavelength are not plotted. The optical constants of aluminium are in reasonable agreement with literature



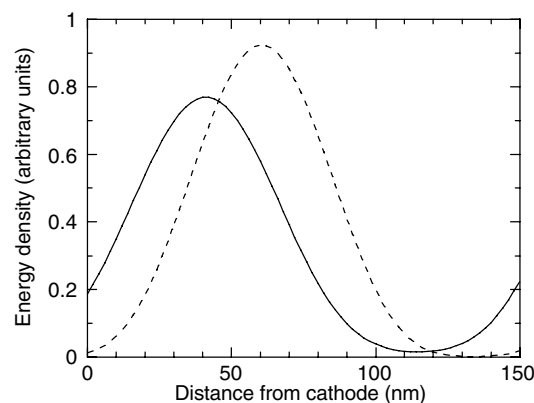
**Figure 6.** The experimentally determined reverse ellipsometry data (---) and the model fit (—) for (a)  $\Psi$  and (b)  $\Delta$  for the structure glass | F8BT | Ca | Al at 40° (●), 45° (○) and 50° (▼).

values [14] (figure 5, dotted lines), confirming the validity of our technique. Published data for the refractive index of calcium in this spectral region are conflicting [15, 16]. The  $n$  and  $k$  spectra here concur in shape with those outlined by Potter and Green [15] although our  $n$  values are slightly higher (0.59 at 400 nm compared with  $\sim 0.4$  reported by Potter and Green).

Having determined the optical constants for several polymer and metal films, a multi-layer structure incorporating F8BT, calcium and aluminium was fabricated. Again reverse ellipsometry was employed to examine this structure. The model was constructed using the optical constants determined for F8BT and calcium. The F8BT layer was 94 nm thick and the calcium layer was  $\sim 150$  nm thick. Since light cannot penetrate the calcium layer, the capping layer of aluminium was not included in the model. The fit of the model to the experimentally determined  $\Psi$  and  $\Delta$  data is shown in figure 6.

An intermixed layer of 2.1 nm between the calcium and polymer layer was found to improve the model fit. The final MSE of 7.0 confirms that it is possible to study multi-layer structures of this type using reverse spectroscopic ellipsometry, and that data obtained for separate polymer and metal films can be combined to give a consistent description of the optical properties of more complicated structures.

The optimum position of the recombination zone in LEDs is affected by the phase shift on reflection of light incident at the polymer/cathode boundary [1]. The phase shift on reflection in these systems differs significantly from the  $\pi$  phase shift seen in perfect reflectors. For the case of F8BT, for example, we can calculate normal incidence reflection coefficients for polymer/metal interfaces at 550 nm (the peak emission wavelength of F8BT), using the complex refractive indices measured in this paper. Aluminium gives a phase shift of  $1.18\pi$  and an intensity reflection coefficient of 0.85. Calcium is a less good reflector, and gives a phase shift of  $1.44\pi$  and an intensity reflection coefficient of 0.57. The reflection coefficient calculated with our measured value of the refractive index of calcium is significantly smaller than that which would be calculated using the literature value taken from Nilsson and Forssell [1, 16]. Figure 7



**Figure 7.** Energy density as a function of distance from cathode for normal emission in an F8BT ( $n = 1.866$ )/cathode structure at 550 nm. The cathode is calcium (—,  $n = 0.619 + 2.134i$ ) or aluminium (---,  $n = 0.949 + 6.28i$ ). The data are normalized such that a perfectly reflecting cathode would give a maximum energy density of 1.

shows the energy density distributions for normal emission in polymer/cathode structures, taking into account interference between directly emitted light and light reflected at the cathode. The optimum dipole positions to maximize forward light output are 41 nm and 60 nm from the cathode for calcium and aluminium cathodes, respectively. We note that absorption in a calcium electrode will provide a significant loss mechanism in an organic LED, and that accurate measurements of polymer and cathode refractive indices are essential to quantify absorption losses and optimum dipole positions.

#### 4. Conclusions

The anisotropic optical constants of several polyfluorene derivatives have been determined and the effect of annealing has been studied. The optical constants of F8BT were found to be unaffected by the annealing process. For both PFB and TFB the anisotropy was much reduced such that the films

were almost isotropic after annealing. The optical constants of calcium and aluminium thin films were also determined using reverse ellipsometry, and were used to model the optical properties of polymer/metal structures.

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