Measuring the refractive indices of conjugated polymer films with Bragg grating outcouplers

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Photoluminescence trapped inside a polymer film can be scattered out with a Bragg grating. The refractive index in the plane of the film and in the normal direction can be determined as a function of wavelength by measuring the scattering angles of the TE- and TM-waveguide modes. For the polymer poly[2-methoxy-5-(3′,7′-dimethyloctloxy)-paraphenylenevinylene], which is commonly used in light-emitting diodes, the refractive index in the plane of the film drops from 2.0 to 1.8 as the wavelength increases from 600 to 750 nm, while the refractive index in the normal direction is relatively constant at 1.57. © *2003 American Institute of Physics.*
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The refractive index of conjugated polymers is an important parameter for modeling the angular dependence of emission from polymer light-emitting diodes (LEDs),[1,2] light extraction from LEDs with Bragg gratings,[3] emission from microcavities,[4,5] and waveguiding in potential polymer laser diode structures.[6] Typically, the refractive index of semiconducting polymers is determined by fitting variable-angle spectroscopic ellipsometry data to an optical model.[7–10] Since the films are anisotropic and the index changes quickly with wavelength, accurate interpretation of the ellipsometric data can be difficult.[9] Usually results from other techniques must be included to insure accurate results.[7,9,11] In this letter, we demonstrate a relatively simple method for measuring the anisotropic refractive index of light-emitting polymers. Polymer films are spin cast over a Bragg grating with period Λ. When the polymer is photopumped, the waveguided photoluminescence is scattered by the grating. The refractive index is determined by measuring the scattering angles for each wavelength and using the equation

$$k_0 \sin(\theta) = \beta_m \pm \frac{2\pi z}{\Lambda}, \tag{1}$$

where $\mathbf{k}_0$ is the free-space wave vector of light with wavelength λ, β_m is the propagation vector of the waveguide mode, z is the scattering order, and θ is the angle of emission with respect to normal.

We chose to demonstrate our method with the widely used light-emitting polymer, poly[2-methoxy-5-(3′,7′-dimethyloctloxy)-paraphenylenevinylene] (OC_1C_{10}–PPV), which has the chemical structure shown in Fig. 1(a). The substrates for our studies were silicon wafers with 1-μm-thick silicon dioxide (SiO_2) coatings. Bragg gratings with period $\Lambda = 405$ nm were patterned into the SiO_2 by exposing a film of photoresist to the interference pattern of two He–Cd laser beams ($\lambda = 325$ nm), developing the resist, and etching the SiO_2 in 50:1 hydrofluoric acid (HF). The gratings were determined to be between 15 and 25 nm deep using an atomic force microscope. Planar polymer waveguides were fabricated by spincasting a 1 wt % solution of OC_1C_{10}–PPV in 1,2-dichlorobenzene onto the SiO_2 gratings. Polymer film thicknesses ranged from 150 to 450 nm. The thickness was intentionally chosen to be thicker than the typical active layer in a LED ($\sim$100 nm) so that several waveguide modes would be supported and so the grating depth would be small compared to the thickness.

Samples were placed on a rotation stage and optically pumped by a He–Cd laser operating at 442 nm. Angularly resolved photoluminescence spectra were obtained by placing an iris in front of the collection optics of a grating spectrometer equipped with a charge coupled device camera. The collection angle was 1°. The polarization of the light was resolved by placing a linear polarizer in front of the spectrometer.

Waveguiding occurs when light propagating in a high-refractive-index material with wave vector $\mathbf{k}$ is internally reflected at the boundaries with the surrounding low-refractive-index materials. The waveguide modes can be described in terms of their polarization and their modal wave vector, β_m, which is the component of $\mathbf{k}$ parallel to the film. This wave vector can be written in terms of an effective refractive index as $\beta_m = 2\pi n_{\text{eff}}/\lambda$. TE modes have the electric field in the plane while TM modes have their magnetic field in the plane [Fig. 1(b)].

Figure 2 contains a few examples of angularly resolved

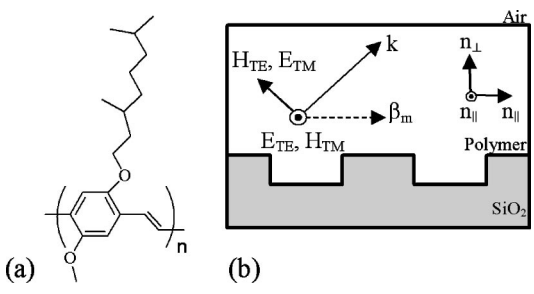

FIG. 1. (a) The chemical structure of OC_1C_{10}–PPV. (b) The fields and wave vectors for TE- and TM-polarized waveguide modes and the orientation of the uniaxial indices of the polymer film.

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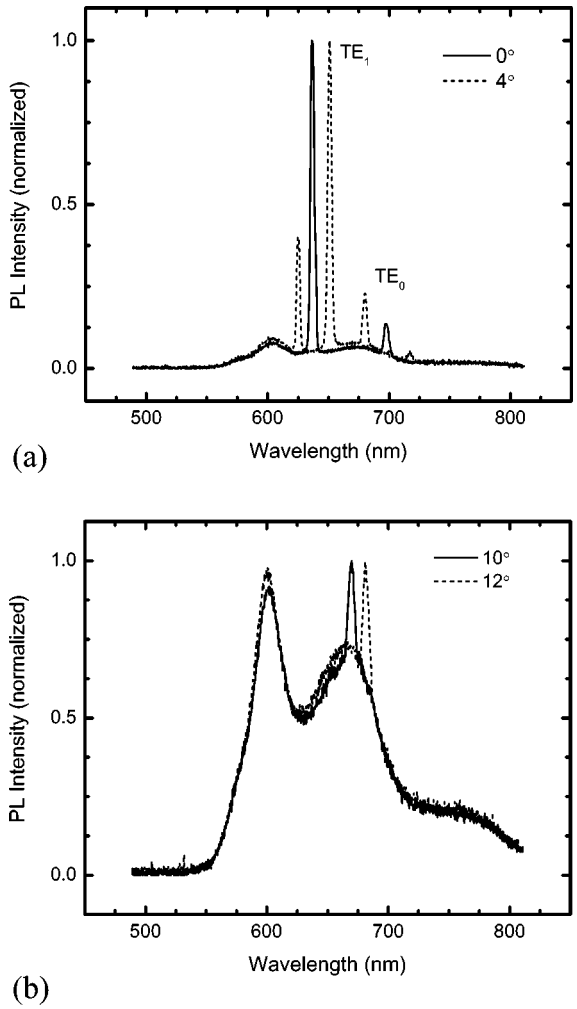

FIG. 2. (a) A few *s*-polarized photoluminescence spectra (corresponding to TE-polarized waveguiding) and (b) *p*-polarized photoluminescence spectra (corresponding to TM-polarized waveguiding).

polarized spectra. The *s*-polarized spectra contain sharp peaks from scattered TE waveguide modes. The scattered light is much stronger that the typical *s*-polarized emission spectra. The *p*-polarized spectra also contain sharp peaks from scattered TM waveguide modes. However, there is very little power in the TM modes so the peaks are small compared to the normal *p*-polarized emission spectrum. The effective refractive index can be calculated by inserting the peak wavelengths and emission angles into the following form of Eq. (1):

$$n_{\text{eff}} = \frac{\lambda}{\Lambda} \pm \sin(\theta). \tag{2}$$

The correct sign of the $\pm$ is chosen by observing the peak wavelength splitting as the angle is changed. The splitting occurs because the grating scatters waveguided light traveling in opposite directions. The positive sign should be used for peaks that move towards shorter wavelengths as θ is increased, while the negative sign should be used for peaks that move towards longer wavelengths.

The values of the effective refractive index for waveguide modes in a few representative OC_1C_{10}–PPV films are plotted versus wavelength in Fig. 3. While TM modes were only scattered out for very thick films, TE modes were extracted for all thicknesses across all emission wavelengths.

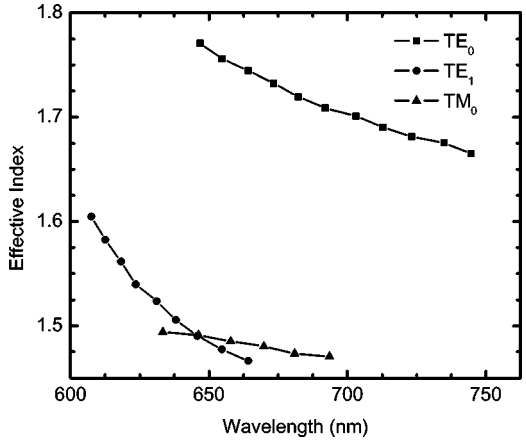

FIG. 3. The effective index vs wavelength for TE_0, TE_1 waveguided modes in a 380-nm-thick OC_1C_{10}–PPV film and TM_0 waveguided modes in a 420-nm-thick OC_1C_{10}–PPV film.

After the modes were determined, we used waveguide equations[12,13] to calculate the polymer indices. We assume the polymer film has uniaxial indices as shown in Fig. 1(b) where $n_{\parallel}$ is the refractive index in the plane of the film and $n_{\perp}$ is the refractive index normal to the film. The TE waveguide equation for this system is

$$\kappa_{\text{TE}} h - m\pi = \arctan\left(\frac{\gamma_{\text{air}}}{\kappa_{\text{TE}}}\right) - \arctan\left(\frac{\gamma_{\text{SiO}_2}}{\kappa_{\text{TE}}}\right), \tag{3}$$

where

$$\gamma_x = \left(\frac{2\pi}{\lambda}\right)\sqrt{(n_{\text{eff}}^2 - n_x^2)} \quad \text{for } x = \text{air, SiO}_2, \tag{4}$$

$$\kappa_{\text{TE}} = \left(\frac{2\pi}{\lambda}\right)\sqrt{(n_{\parallel}^2 - n_{\text{eff}}^2)}, \tag{5}$$

h is the thickness of the polymer film, and the integer m is the mode order.

Similarly, the TM waveguide equation is

$$\kappa_{\text{TM}} h - m\pi = \arctan\left(\frac{n_{\parallel}^2 \gamma_{\text{air}}}{n_{\text{air}}^2 \kappa_{\text{TM}}}\right) - \arctan\left(\frac{n_{\parallel}^2 \gamma_{\text{SiO}_2}}{n_{\text{SiO}_2}^2 \kappa_{\text{TM}}}\right), \tag{6}$$

where

$$\kappa_{\text{TM}} = \frac{n_{\parallel}}{n_{\perp}}\left(\frac{2\pi}{\lambda}\right)\sqrt{(n_{\perp}^2 - n_{\text{eff}}^2)}. \tag{7}$$

The value of h was obtained using a profilometer. For thick films, h could also be calculated by using Eq. (3) and n_{eff} for TE_0 and TE_1 modes at the same wavelength. We used $n_{\text{air}} = 1.00$, $n_{\text{SiO}_2} = 1.46$, and the experimental values of n_{eff} for the TE modes to solve for $n_{\parallel}$ using Eq. (3). We used the calculated values of $n_{\parallel}$ along with the experimental values of n_{eff} for the TM modes to solve for $n_{\perp}$ using Eq. (4).

The refractive index of our OC_1C_{10}–PPV films is plotted in Fig. 4 for a wide range of film thicknesses. Our measurements are very repeatable for films made with similar deposition conditions and do not depend on the grating period or film thickness. The refractive index is highly dispersive and anisotropic. The high degree of anisotropy is com-

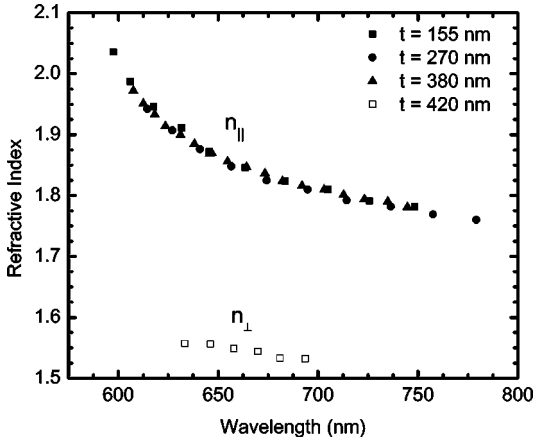

FIG. 4. The uniaxial index of refraction for our OC_1C_{10}–PPV films. The in-plane index was found for 150-nm-thick (closed squares), 270-nm-thick (closed circles), and 380-nm-thick films (closed triangles). The out-of-plane index was found for a 420-nm-thick-film (open squares).

mon for conjugated polymers and can be attributed to the polymer chains lying preferentially in the plane of the substrate.[2,14,15] This is significant because it implies that the majority of the emissive dipoles lie in the plane. Since dipoles emit strongly perpendicular to their orientation, light extraction efficiencies larger than the $1/2n^2$ isotropic limit can be obtained.[2] Also, the anisotropy indicates that the majority of the waveguided light in polymer LEDs will be TE-polarized since the index in the normal direction is too low to support TM-polarized modes.

Our measurements of the refractive index of OC_1C_{10}–PPV films are similar to, but not identical to, previously published results obtained with spectroscopic ellipsometry.[9] However, this is most likely due to difference in molecular weight or deposition conditions. For when a parameter, such as the solvent used to cast the film, is varied, different values for the refractive index are obtained. For example, when the solvent is changed from dichlorobenzene to *p*-xylenes, the refractive index versus photon energy curve shifts by 0.03 eV. A similar shift occurs in the absorption spectrum. This observation highlights the need for making refractive index measurements using exactly the same processing conditions used to make the device that is to be modeled.

In summary, we have described a simple method for measuring the dielectric properties of anisotropic polymer films over the emissive region of the spectrum. The information gained from these measurements will be useful in improving the performance of optical devices made from these materials and in studying the degree of anisotropy in polymer films.

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