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1 October 2001

OPTICS
COMMUNICATIONS

Optics Communications 197 (2001) 355–361

www.elsevier.com/locate/optcom

Optical properties of doped polycarbonate layers

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Received 14 May 2001; accepted 25 July 2001

Abstract

Optical properties of polycarbonate layers doped with triphenylamine and chlorotricarbonyl diimine rhenium complex have been investigated. The samples have been prepared by spin coating on quartz glass and indium tin oxide (ITO) coated glass substrates. Root mean square surface roughness of the films obtained by atomic force microscopy is low (~ 3 Å). Optical functions of ITO and doped polymer layer for two different dopant concentrations have been determined by spectroscopic ellipsometry in the spectral range from 1.55 to 4.1 eV. The absorption spectra of the chlorotricarbonyl diimine rhenium complex dissolved in chloroform and toluene have also been measured. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Spectroscopic ellipsometry; Optical constants; Organic thin films

1. Introduction

Optical properties of organic materials have been receiving lots of attention recently for potential applications in optoelectronic devices. Due to low cost and relatively simple fabrication, applications of organic materials in photovoltaic devices are still being considered, although typical power conversion efficiency in organic solar cells rarely exceeds 1%. Organic optoelectronic devices can be fabricated either by thermal evaporation (for small molecules) or spin coating (for polymers

and small molecule doped polymers). For phthalocyanine based solar cells, it has been shown that spin coating of a phthalocyanine in a polymer has advantages over evaporation of phthalocyanine films [1], while the use of polar polymers leads to higher efficiencies. Polymer host materials are often doped with organic compounds to enhance charge transport or to enhance photogeneration. Doping polycarbonate (PC) with triphenylamine is known to enhance hole transport [2], and photogeneration efficiencies of triphenylamine doped PC have been measured [3]. The quantum yields calculated from Onsager's theory were increasing with triphenylamine concentration from about 0.01 to about 0.03 [3]. In order to further enhance quantum yield, triphenylamine doped PC can be

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doped with various photosensitizers. Diimine complexes of some transition metals such as rhenium are potential candidates for photosensitizers [4,5]. They exhibit a relatively long-lived metal-to-ligand charge transfer (MLCT) excited state based on the $d\pi(\text{Re})-\pi^*(\text{diimine})$ electronic transition. Previously reported trifunctional rhenium complexes could serve as hole transport, electron transport, and light emitting molecules [6]. The charge transport properties of these complexes were found to be dependent on the nature of the metal center and structure of the ligand [7]. In this paper, we report the spectroscopic ellipsometry study of PC doped with triphenylamine and another chlorotricarbonyl rhenium complex based on 1,4-diazabutadiene ligand. The synthesis [8] and detailed study of photogeneration of this complex doped in PC will be reported elsewhere.

In order to design optoelectronic devices more efficiently, the optical functions of each layer should be known. While the data on the refractive index of pure PC have been reported previously [9–11], to our knowledge no data on the optical functions of triphenylamine and chlorotricarbonyl diimine rhenium complex have been published up to date. The chemical formulae for PC, triphenylamine and chlorotricarbonyl diimine rhenium complex are shown in Fig. 1. In this work, we have determined the optical functions of PC doped with triphenylamine and chlorotricarbonyl diimine rhenium complex for different concentrations of the rhenium complex. The optical functions in the spectral range from 1.55 to 4.1 eV have been determined by spectroscopic ellipsometry. The optical functions have been extracted by point-to-point fit, and modeled using Lorentz oscillator model (LOM).

2. Experimental results

The samples have been prepared by spin coating on ITO glass substrates and quartz glass substrates. Quartz glass substrates have rough backside to suppress reflections from the back surface of the substrate. All samples exhibit pale yellow color, with color intensity dependent on the concentration of chlorotricarbonyl diimine rhenium complex. All samples exhibited low surface

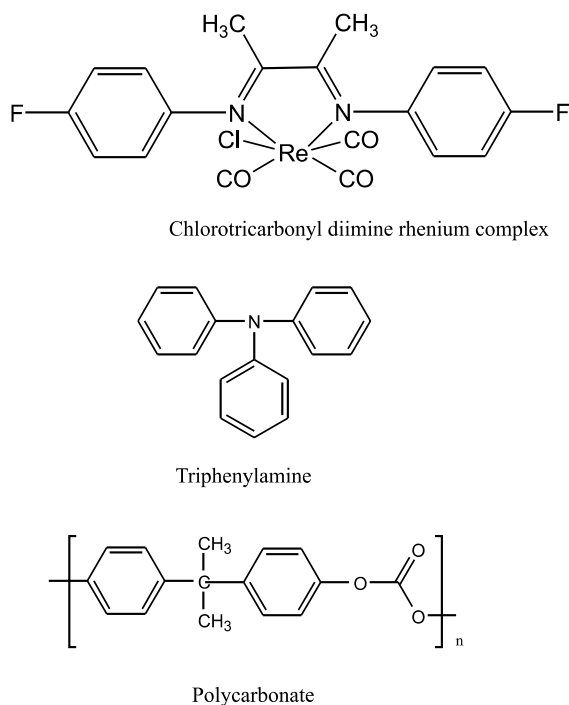


Fig. 1. Chemical formulae for PC, triphenylamine and chlorotricarbonyl diimine rhenium complex.

roughness (root mean square surface roughness $rms \approx 3 \text{ \AA}$), which is lower than the surface roughness of the ITO substrate ($rms \approx 7 \text{ \AA}$). Atomic force microscopy (AFM) images of 1 PC:0.9 triphenylamine:0.1 chlorotricarbonyl diimine rhenium complex film on ITO substrate and ITO substrate are shown in Fig. 2(a) and (b), respectively.

We have measured the absorption spectrum of the chlorotricarbonyl diimine rhenium complex in a solution. Fig. 3 shows the absorption spectrum of chlorotricarbonyl diimine rhenium complex in chloroform denoted with dashed line, while solid line denotes the absorption spectrum of the chlorotricarbonyl diimine rhenium complex in toluene. The absorption band at 450–470 nm is assigned to the MLCT transition. It can be observed that this MLCT transition energy is dependent on the polarity of the solvent, which strongly suggests that the electronic transition is charge transfer in nature.

Spectroscopic ellipsometry spectra were measured in the spectral range from 1.55 to 4.1 eV. We

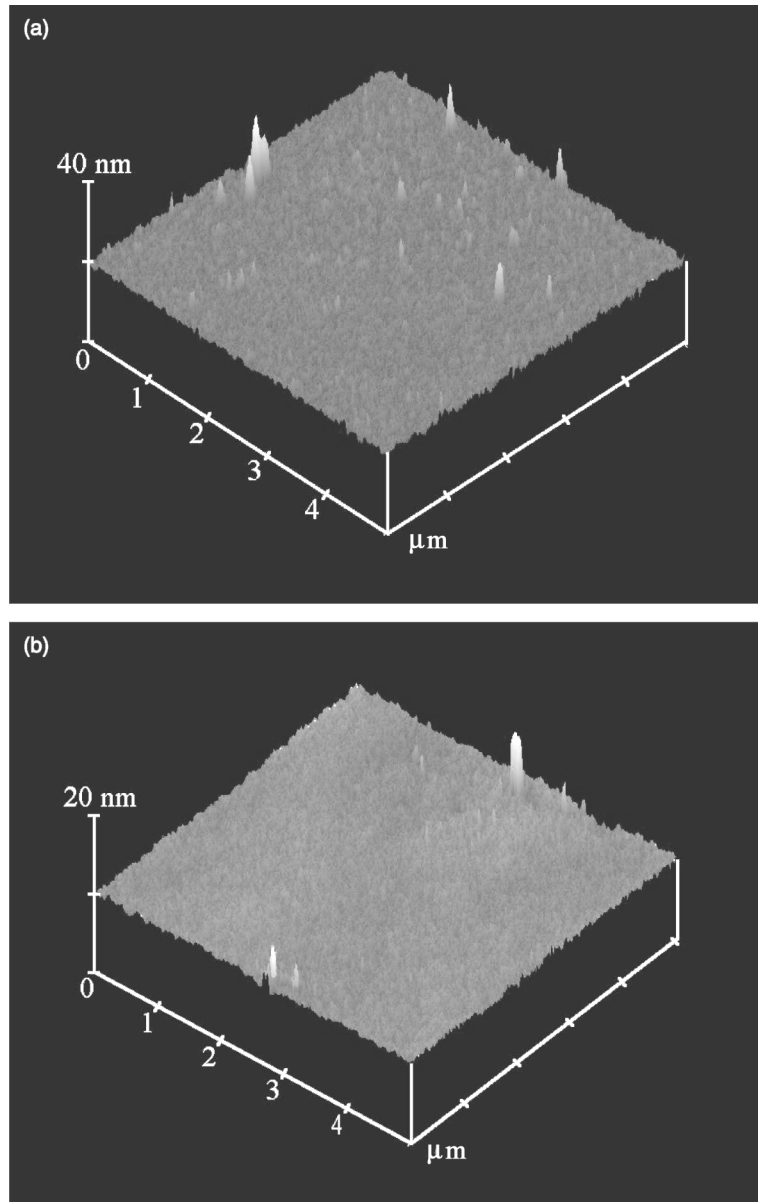


Fig. 2. (a) AFM image of ITO substrate (rms surface roughness 6.8 Å), (b) AFM image of PC film doped with triphenylamine and chlorotricarbonyl diimine rhenium complex spin coated on ITO glass substrate (rms surface roughness 3.3 Å).

have used simulated annealing algorithm to fit the data [12], and the objective function employed was

$$F = \sum \left[(\tan(\Psi)_{\text{exp}} - \tan(\Psi)_{\text{cal}})^2 + (\cos(\Delta)_{\text{exp}} - \cos(\Delta)_{\text{cal}})^2 \right], \quad (1)$$

where subscript exp denotes experimental values, while subscript cal denotes calculated values. The choice of unbiased objective function is in our experience more appropriate for the optimization algorithm used in the fitting procedure. We have investigated both point-to-point fitting and

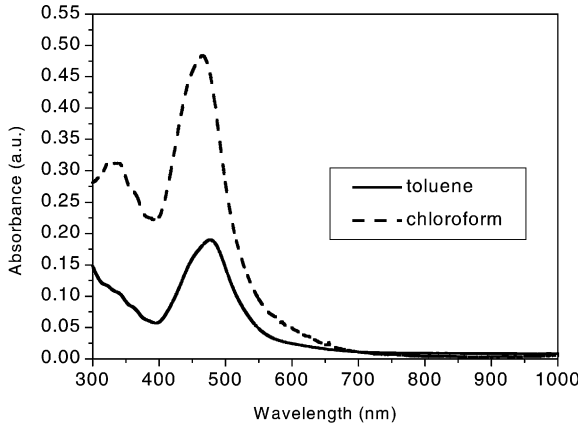


Fig. 3. Absorption spectrum of chlorotricarbonyl diimine rhodium complex in toluene (—) and chloroform (---).

modeling to determine the optical functions from the measured ellipsometry data. Point-to-point fitting for weakly absorbing films on a transparent substrate results in optical functions having oscillatory character. Therefore, it is necessary to assume a model for the optical functions of an investigated material. The optical functions for all investigated samples have been modeled using LOM. In LOM, the real and imaginary parts of the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ are given by

$$\varepsilon_1(\omega) = \varepsilon_{1\infty} + \sum_{j=1}^m \frac{F_j(\omega_j^2 - \omega^2)}{(\omega_j^2 - \omega^2)^2 + (\omega\Gamma_j)^2}, \quad (2)$$

$$\varepsilon_2(\omega) = \sum_{j=1}^m \frac{F_j\omega\Gamma_j}{(\omega_j^2 - \omega^2)^2 + (\omega\Gamma_j)^2}, \quad (3)$$

where m is the total number of oscillators with frequency ω_j broadening Γ_j and oscillator strength $F_j = f_j\omega_j^2$. When the dielectric function is known, the real and imaginary parts of the index of refraction are readily calculated from the formulae

$$n = \left[0.5(\varepsilon_1 + (\varepsilon_1^2 + \varepsilon_2^2)^{1/2}) \right]^{1/2}, \quad (4)$$

$$k = \left[0.5(-\varepsilon_1 + (\varepsilon_1^2 + \varepsilon_2^2)^{1/2}) \right]^{1/2}.$$

LOM has been employed for modeling the optical functions of both ITO and doped PC layers.

In the case of ITO, inclusion of the Drude term $\omega_p^2 f_0 / \omega(\omega + i\Gamma_0)$, where ω_p is the plasma frequency, may be necessary if the optical functions below 1.55 eV are analyzed. In the spectral region considered in this work, inclusion of Drude term did not yield any improvement of the fit. Three oscillators have been employed for all samples. Initial estimate for the film thickness has been obtained by Talistep profile measurements. In order to refine the initial guess for the thickness of the film, the data in the transparent spectral region have been fitted to the Cauchy formula for the refractive index $n = A + B/\lambda^2 + C/\lambda^4$. The initial thickness guess was used to define narrow boundaries for the possible thickness value but we did not fix the thickness in the final fitting stage. This is because the films are not fully transparent, and hence fixing thickness to a value determined from Cauchy fit may result in slightly inferior fit.

Fig. 4 shows the $\tan(\Psi)$ and $\cos(\Delta)$ spectra of the ITO substrate, while the inset shows the obtained real and imaginary parts of the index of refraction of ITO. The obtained optical functions are in good agreement with the previous studies of the optical properties of ITO [13–15]. However, it should be pointed out that the properties of ITO, including the optical functions, are highly dependent on the deposition conditions. Also, the index of refraction changes with the depth of the film so that the optical constants at the bottom are dif-

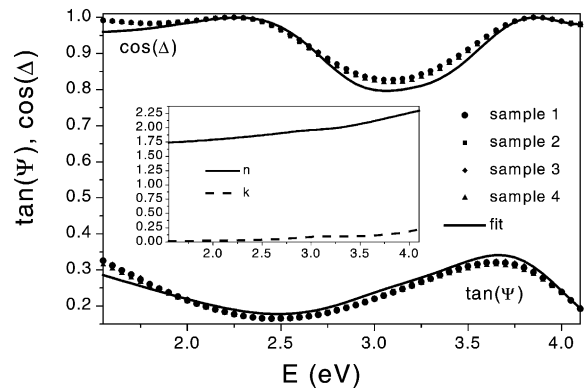


Fig. 4. $\tan(\Psi)$ and $\cos(\Delta)$ spectra of ITO coated glass substrate. The circles, squares, triangles, and diamonds denote experimental data for four samples, while solid line denotes the fit. The inset shows the real and imaginary parts of the refractive index of ITO.

ferent from those at the top [15]. Furthermore, the extinction coefficient obtained from spectroscopic ellipsometry measurements of ITO film on transparent substrate may be overestimated. It has been shown that the extinction coefficient values of low refractive index transparent thin films on transparent substrates follow both sign and magnitude of the spectral noise [16]. This is mostly due to inherent low reflectivity of such a structure which leads to high noise levels in reflectance spectroscopic ellipsometry. It has also been demonstrated that surface roughness of the glass yields increase in the determined coefficient of extinction of transparent glasses [17]. Although this can be reduced by surface roughness correction, the obtained values are still too high. This would indicate that the material is opaque for typical thickness in the order of mm. As a consequence, the coefficient of extinction of transparent films on transparent substrates determined from spectroscopic ellipsometry is likely to be slightly overestimated, and should not be regarded as true coefficient of extinction. We have not performed surface roughness correction since the roughness of ITO/glass interface in commercially available ITO coated glass substrates is unknown, and roughness of both glass/ITO and ITO/air interfaces should be taken into account.

Our samples consist of either one or two weakly absorbing layers with low refractive index on a transparent substrate. In order to investigate our ability to extract optical function values from the measured ellipsometry spectra for such samples, we have generated synthetic data, with and without random noise (noise has been added to simulate experimental errors) for the structures glass/ITO/PC and quartz glass/PC. We have assumed that PC is fully transparent in the spectral region of interest, and we have generated n values according to $n = 1.564 + 5538.02 \times \lambda^{-2} + 6.23 \times 10^8 \lambda^{-4}$ which represents a fit to the refractive index data reported in Ref. [7]. In the former case, algorithm did not converge at all, except when the initial values have been chosen close to the values used in generating test data and effective temperature in simulated annealing algorithm set to a low value so that algorithm operated in practically downhill only mode. This indicates that it would be

difficult, if possible at all, to characterize two transparent films on transparent substrate using spectroscopic ellipsometry only. It has been shown that optical constants of tungsten oxide on ITO coated glass can be determined from combination of spectroscopic ellipsometry and reflectance and transmittance measurements, although fit to the ellipsometry data is relatively poor [18]. In the latter case (quartz glass/PC structure), point-to-point fit gave noisy optical functions, while fit to a Cauchy model was able to extract accurate values of the refractive index even with the random noise with magnitude up to 0.05 in $\tan(\Psi)$ and $\cos(\Delta)$. This is illustrated in Fig. 5, which shows $\tan(\Psi)$ and $\cos(\Delta)$ spectra of the computer generated data for the structure quartz glass/PC. Solid line denotes test data, dashed line denotes test data with added random noise, while dotted line denotes fit to the test data, and dash dot line denotes fit to the test data with noise. It can be clearly observed that in spite of large magnitude of noise, it is possible to obtain good agreement between the fit and original data.

In the determination of the optical functions of doped PC, point-to-point fit, as expected, yielded noisy and oscillatory optical functions. We have assumed that the optical constants of the doped PC films can be described by the LOM (to account for the absorption at lower wavelengths). Three

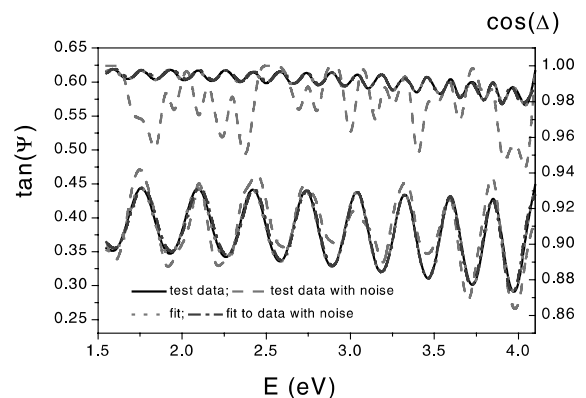


Fig. 5. $\tan(\Psi)$ and $\cos(\Delta)$ spectra of the computer generated data for the structure quartz glass/PC. Solid line denotes test data, dashed line denotes test data with added random noise, while dotted line denotes fit to the test data, and dash dot line denotes fit to the test data with noise.

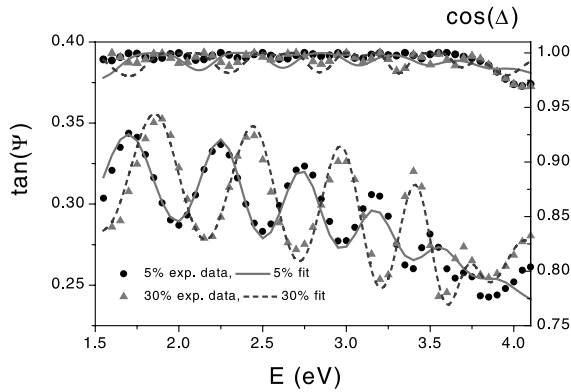


Fig. 6. $\tan(\Psi)$ and $\cos(\Delta)$ spectra of the doped PC films for two different concentrations of chlorotricarbonyl diimine rhenium complex. The circles and solid line correspond to measured and calculated values, respectively, for 5% concentration of the chlorotricarbonyl diimine rhenium complex, and triangles and dashed line denote 30%.

oscillators have been sufficient to obtain good fit. Since surface roughness of PC films is very low (see Fig. 2(b)), surface roughness correction has not been performed. Fig. 6 shows $\tan(\Psi)$ and $\cos(\Delta)$ spectra of the doped PC films for two different concentrations of chlorotricarbonyl diimine rhenium complex (ratio of concentrations of PC: triphenylamine:chlorotricarbonyl diimine rhenium complex is 1:0.9:0.1 for the first sample and 1:0.6:0.4 for the second sample). The circles and solid line correspond to measured and calculated values, respectively, for 5% concentration of the chlorotricarbonyl diimine rhenium complex, and triangles and dashed line denote 30%.

The obtained real and imaginary parts of the index of refraction for different concentrations of the chlorotricarbonyl diimine rhenium complex are shown in Fig. 7. The inset shows the refractive index of pure PC [9–11]. It can be observed that concentration of chlorotricarbonyl diimine rhenium complex at concentrations lower or equal 30% does not influence significantly the optical functions of the doped polymer. This may indicate that the refractive index values of chlorotricarbonyl diimine rhenium complex and triphenylamine are similar, especially at lower energies. Slight shift of the first absorption band to lower energies with higher concentration of the chlorotricarbonyl diimine rhenium complex can be ob-

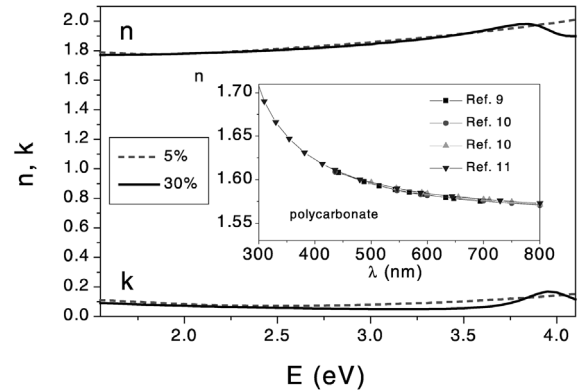


Fig. 7. The real and imaginary parts of the index of refraction for different concentrations of the chlorotricarbonyl diimine rhenium complex (5% (---), 30% (—)). The inset shows the refractive index of pure PC from the literature [9–11].

served, which is to be expected from the absorption spectra of the rhenium complex in the solution. The obtained refractive index values are higher than the pure PC, which is most likely due to triphenylamine component of the polymer blend.

3. Conclusions

Optical properties of the PC layers doped with triphenylamine and chlorotricarbonyl diimine rhenium complex have been investigated. The samples have been prepared by spin coating on quartz glass and ITO coated glass substrates. We have generated test data (with and without noise) and demonstrated that the optical functions of a weakly absorbing layer on a transparent substrate can be successfully determined if appropriate model for the optical functions of the layer is adopted, even though difference between refractive index of film and substrate is small. However, no convergence is obtained in fitting the structure consisting of two transparent layers on a transparent substrate. Optical functions of ITO and doped polymer layer for two different dopant concentrations have been determined by spectroscopic ellipsometry in the spectral range from 1.55 to 4.1 eV.

Acknowledgements

This work has been supported by the RGC earmarked grant of Hong Kong, RGC research grant (project no. HKU 7096/00P), the University of Hong Kong CRCG research grant, and RGC CRC grant of Hong Kong University of Science and Technology. EHL acknowledges support by Visiting Scholar Foundation of Key Lab. in University, China.

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