

Research Article

Optical and Morphological Studies of Thermally Evaporated PTCDI-C8 Thin Films for Organic Solar Cell Applications

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PTCDI-C8 due to its relatively high photosensitivity and high electron mobility has attracted much attention in organic semiconductor devices. In this work, thin films of PTCDI-C8 with different thicknesses were deposited on silicon substrates with native silicon dioxide using a vacuum thermal evaporator. Several material characterization techniques have been utilized to evaluate the structure, morphology, and optical properties of these films. Their optical constants (refractive index and extinction coefficient) have been extracted from the spectroscopic ellipsometry (SE). X-ray reflectivity (XRR) and atomic force microscopy (AFM) were employed to determine the morphology and structure as well as the thickness and roughness of the PTCDI-C8 thin films. These films revealed a high degree of structural ordering within the layers. All the experimental measurements were performed under ambient conditions. PTCDI-C8 films have shown to endure ambient condition which allows post-deposition characterization.

1. Introduction

Small organic molecules represent a remarkable group of materials that exhibit alterable physical, optical, and electrical properties. Furthermore, charge transport and optical properties of organic thin films are strongly dependent on the overlap between the molecular orbitals of the neighboring molecules [1]. Hence, determination of the molecular packing of the organic thin films is an essential input for a comprehensive understanding of the correlation between the material structure and the device optical and electrical properties. Perylene Tetracarboxylic Diimide derivatives are among the most promising small organic molecules to fabricate organic thin film transistors (OTFTs) and organic solar cells (OSCs) [2–5]. Their optical and electrical properties can be modified by attaching different functional groups at specific molecular positions [6, 7]. PTCDI-C8 (N,N' -Diocetyl-3,4,9,10 perylenedicarboximide) is a compound belonging to the perylenes family that shows high photosensitivity (~20%) [8] and high electron mobility (~0.6–1.7 cm^2/Vs) [9, 10]. Since structural properties of thin films are defining parameters of the device optical and electrical characteristics,

a detailed study of the morphological properties of PTCDI-C8 thin films is essential to optimize the performance of the devices based on this material. Although investigation of the structure of the PTCDI-C8 on different substrates has been reported before [11], the importance of the material effects on the device performance is the main reason for the continuing research in this area. In this work, optical properties and molecular structure of PTCDI-C8 thin films have been investigated combining several material characterization techniques such as ellipsometry, AFM, and XRR. The obtained results revealed a high degree of structural ordering that explains the superior electrical and optical properties of these films.

2. Experimental

Several sets of PTCDI-C8 films with thicknesses ranging from 20 to 45 nm were deposited on p-type boron-doped Si (111) substrates with native oxide using a vacuum thermal evaporator system. These films were deposited under high vacuum condition with a base pressure of about 4×10^{-7} Torr at a rate of 1 \AA/sec at room temperature. Topographic

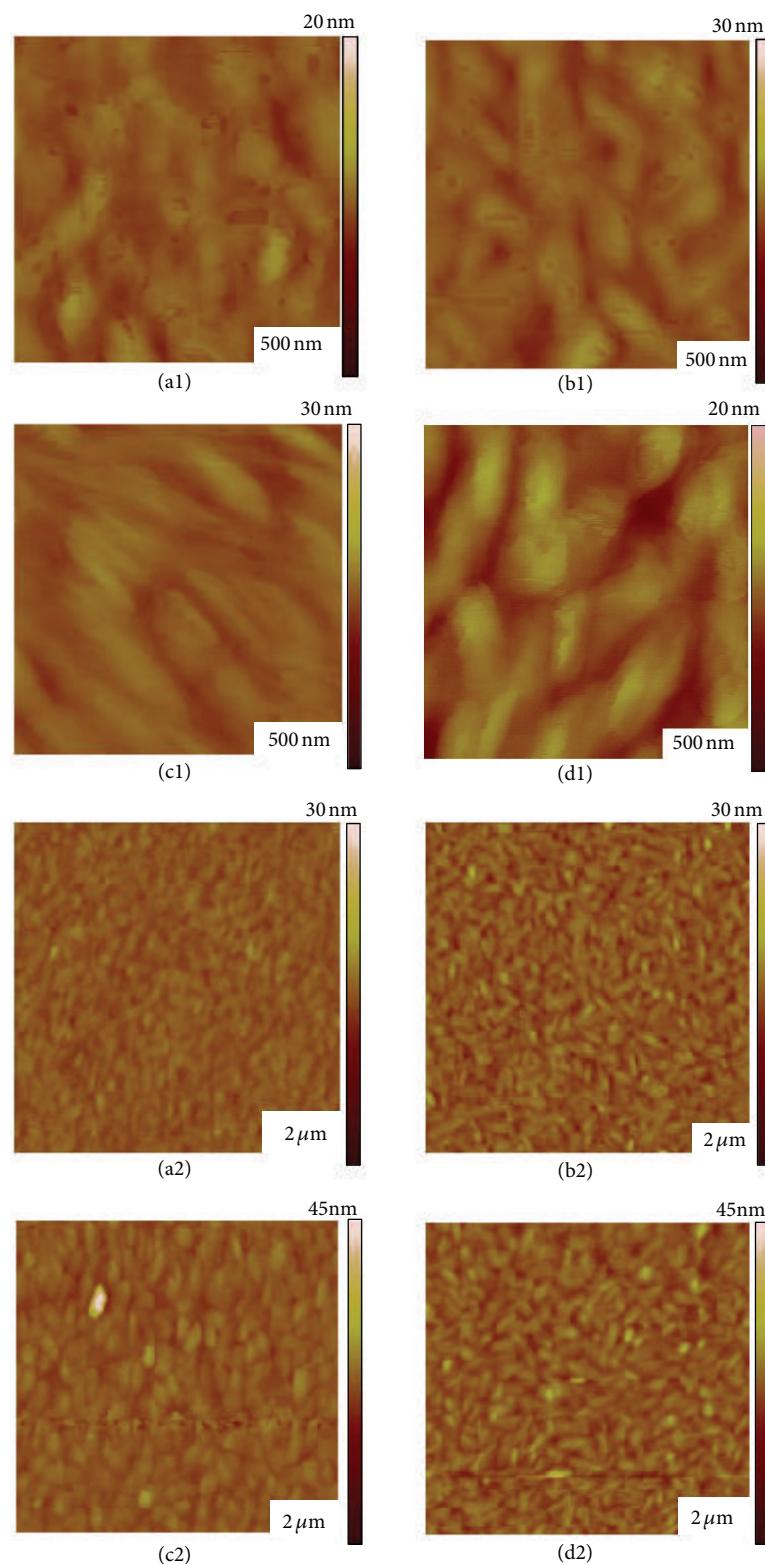


FIGURE 1: AFM images for PTCDI-C8 films with (a) 20, (b) 27, (c) 33, and (d) 45 nm thickness deposited on Si substrate at room temperature for scan sizes of $500 \times 500 \text{ nm}^2$ and $2 \times 2 \mu\text{m}^2$.

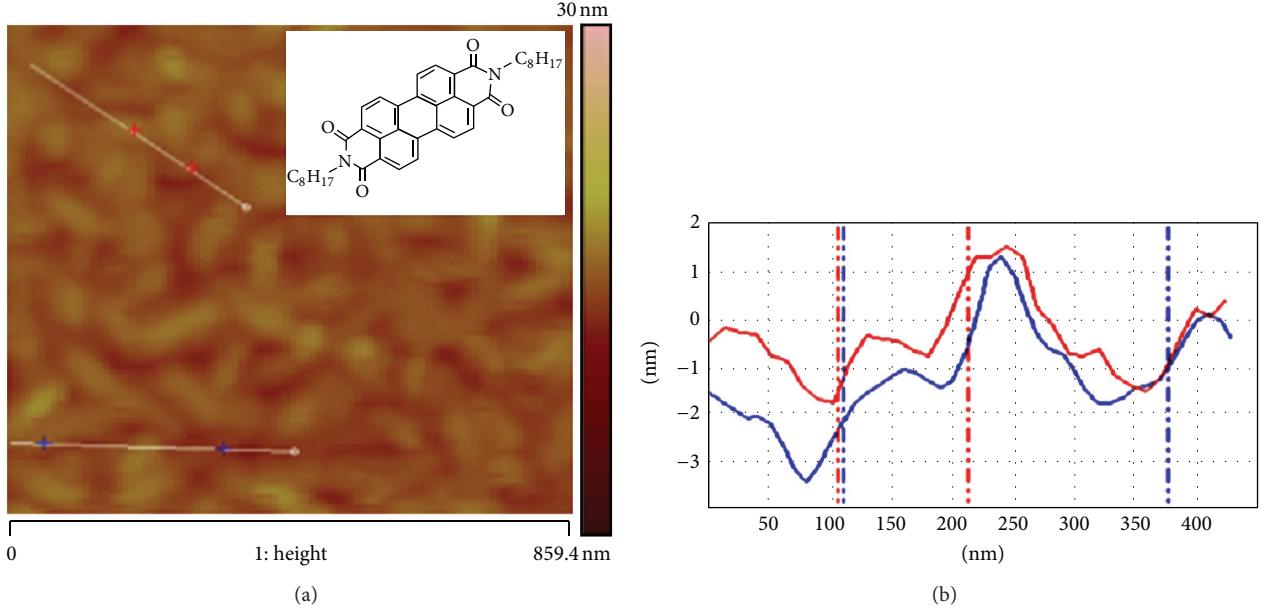


FIGURE 2: Line scans of the terraces which show monomolecular steps of 2 nm for 27 nm of PTCDI-C8 on Si. The inset presents the chemical structure of PTCDI-C8.

images were taken using a Veeco Multimode Scanning Probe Microscope AFM operated in tapping mode. X-ray reflectivity was performed using a Bruker-AXS D8-Discover high resolution X-ray diffractometer. This system utilizes a horizontal goniometer, fixed X-ray tube with a Cu anode ($\text{CuK}\alpha$ radiation, $\lambda = 0.15418 \text{ nm}$), Göbel mirrors, Cu rotary absorber, 4-bounce Ge (022) monochromator, and Lynx Eye position sensitive detector (PSD) with automated Iris. The reflectivity data were analyzed using the Parratt formalism which takes into account multiple scattering effects [12]. Spectroscopic ellipsometry measurements were performed using a variable-incidence-angle ellipsometer from Woollam Company in the photon energy range of 1.4 to 3.5 eV and at the incident angles of 65, 70, and 75 degrees. All the experiments were carried out in the ambient condition. Summary of the material characterization is presented in the next section.

3. Results and Discussion

Figure 1 displays the typical topographical AFM images of 20, 27, 33, and 45 nm thick PTCDI-C8 films deposited on Si substrate at room temperature. PTCDI-C8 films display a relatively smooth surface morphology with needle-like features. These features which are randomly oriented in the film have a length of about several hundred nanometers. Planar terraces on the needles can be seen in the AFM images. The line scan of the terraces (Figure 2) reveals monomolecular steps of about 2 nm which is close to the film periodicity determined by the XRR data. The line scan has been performed over the area with the largest differences between the heights of the features. A summary of the roughness of the films with different thicknesses has been presented in Figure 3. As can be seen in this figure, the root mean square roughness

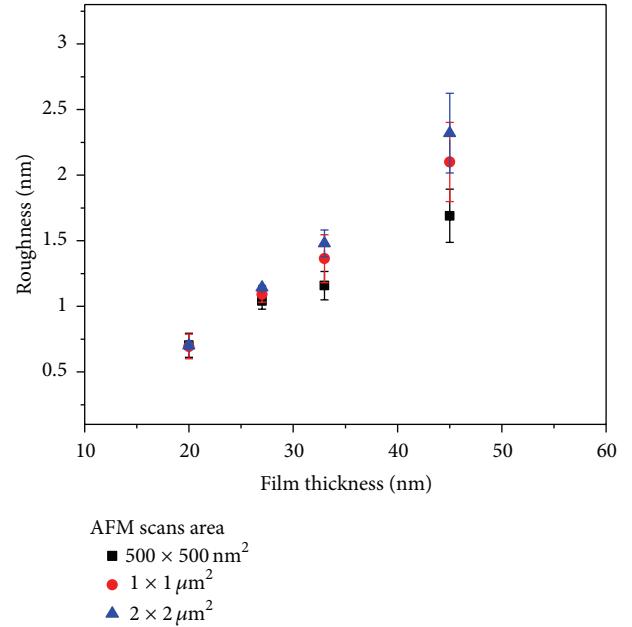


FIGURE 3: Plot of the surface roughness versus thickness of the PTCDI-C8 films deposited on Si substrates.

increases from 0.7 nm to 1.7 nm as the film thickness increases from 20 nm to 45 nm. Having a relatively smooth surface for thicker films suggests that the films display a wetting behavior on the Si substrates [13].

Furthermore, X-ray reflectivity was performed to evaluate the structural properties of PTCDI-C8 films. The results of the XRR studies are presented in Figure 4(a) and have been offset deliberately for better presentation. These reflectivity curves were analyzed using the Parratt formalism. In this

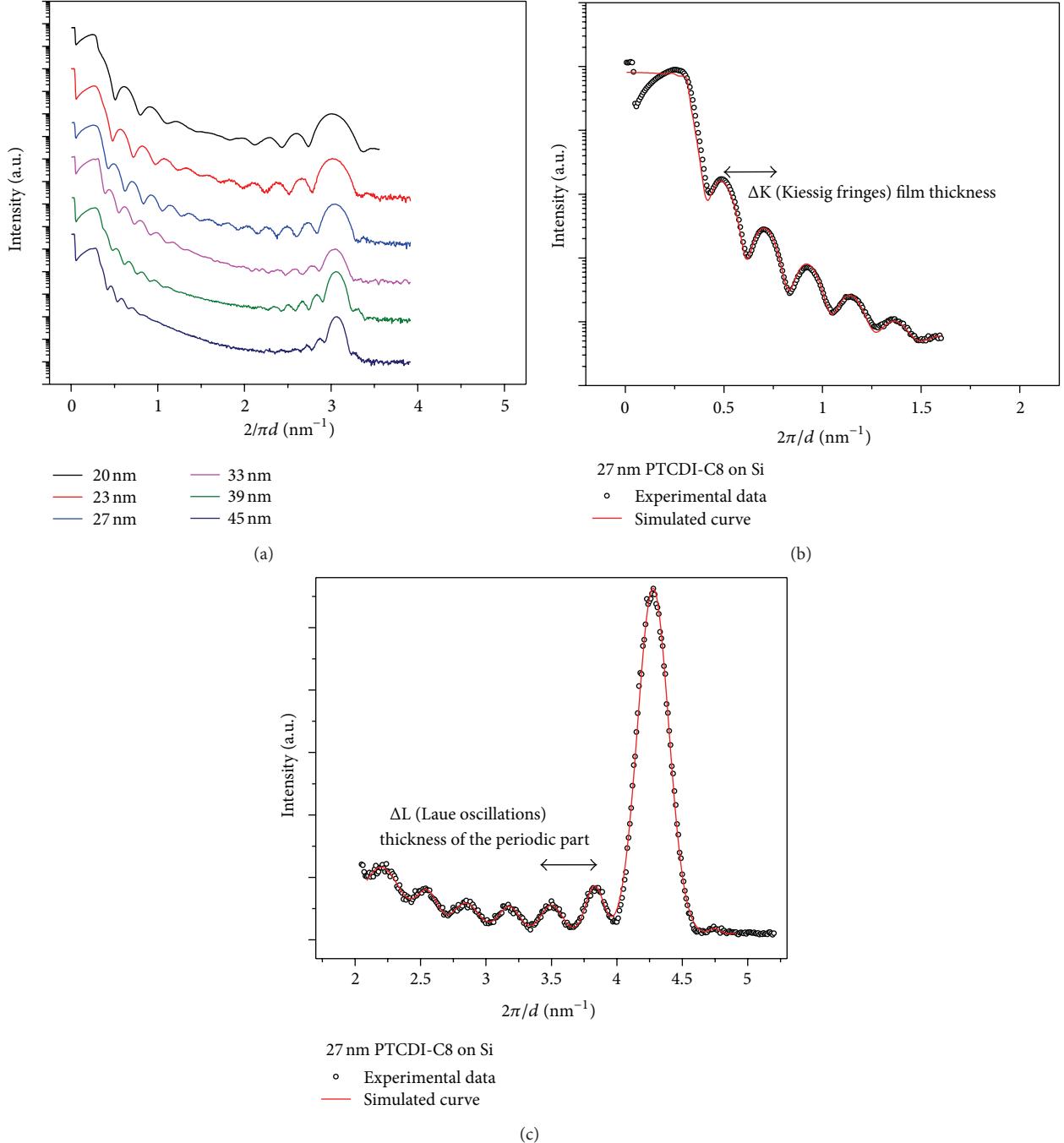


FIGURE 4: X-ray reflectivity curves for (a) different thicknesses of PTCDI-C8 films as well as the measured and simulated reflectivity data for (b) Kiessig fringes and (c) Laue oscillations for PTCDI-C8 film with 27 nm thickness.

model, the transmitted X-ray in the top-most layer serves as a new source for the scattering at the next lower interface [14]. Kiessig fringes at low angles as well as the Bragg peak with un-damped Laue oscillations indicate formation of films with a highly ordered structure. The low angle Kiessig fringes are related to the total film thickness and the Laue oscillations around the Bragg peak are related to the coherently ordered film thickness. Figures 4(b) and 4(c) show the measured and simulated reflectivity data for a 27 nm thick film of PTCDI-C8. Similarity of the widths of the Kiessig fringes with

the Laue oscillations around the Bragg peak suggests that PTCDI-C8 films are coherently ordered across their entire thickness.

The roughness and the thickness of the deposited films have been determined by a combination of techniques including AFM, ellipsometry, and XRR. A summary of the roughness analysis from AFM and XRR has been shown in Figure 5(a). Thickness data from ellipsometry and XRR is also summarized in Figure 5(b). As presented in these figures, the results of characterization from different techniques are

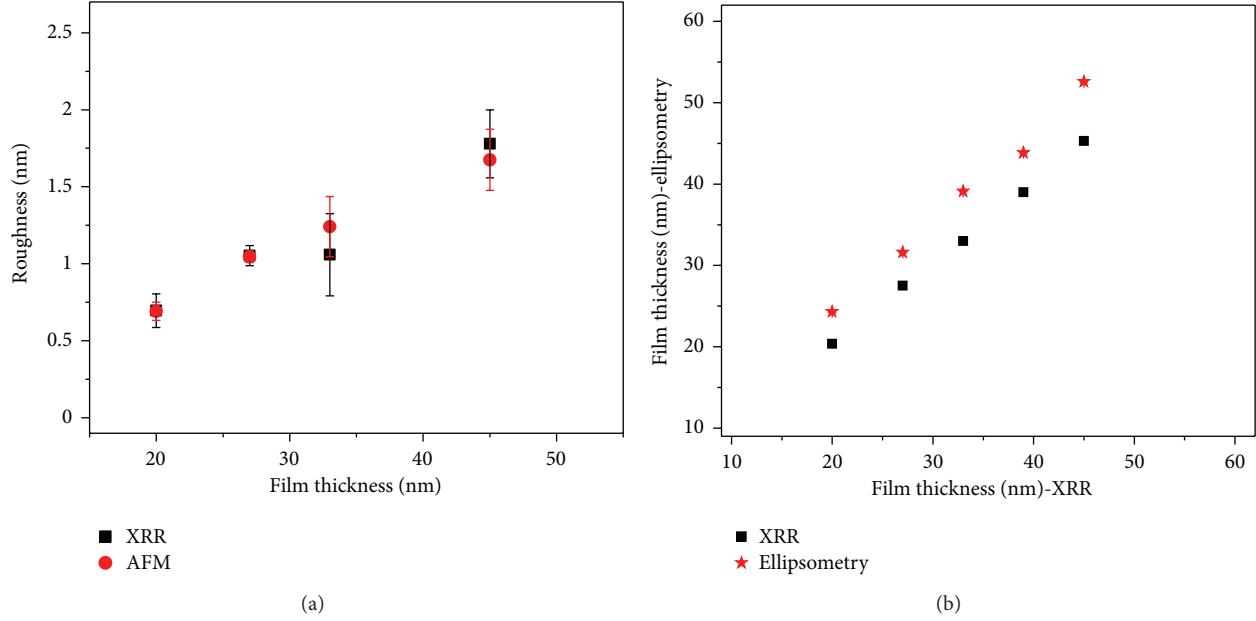


FIGURE 5: Comparing the measured and calculated (a) roughness from AFM and XRR data and (b) thickness from ellipsometry and XRR data. As can be seen in these figures, results from different methods match.

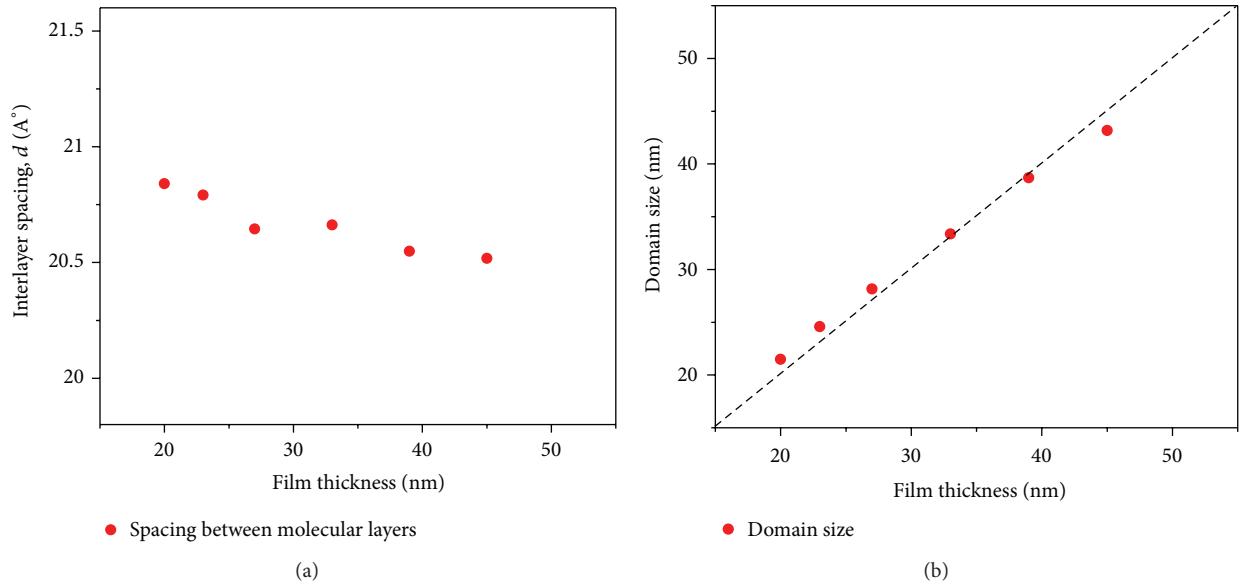


FIGURE 6: Calculated (a) interlayer spacing and (b) domain size for PTCDI-C8 films with different thicknesses.

similar. Among these techniques, XRR is the best method to characterize the structure of the materials in a thin film since it provides detailed information about the film roughness and thickness as well as molecular ordering and film morphology.

Moreover, the interlayer spacing (d) can be determined from the diffraction peaks according to Bragg's equation, $n\lambda = 2d \sin \theta$, where n is the order of the diffraction peak and θ is the scattering angle. A summary of the calculated values for PTCDI-C8 films with different thicknesses is presented in Figure 6(a). Calculated values for interlayer spacing are in good agreement with the height of the molecular terraces measured from AFM topographical images. In a simplified

way, considering negligible contribution from the strain, the mean size of the crystalline domains can be estimated from the inverse of the full width at half maximum (FWHM) of the Bragg peak using equation $D \approx K\lambda/\beta \cos \theta$, where K is the Scherrer constant, λ the wavelength, β the FWHM, and 2θ is the Bragg peak angular position. The domain sizes calculated for the different thicknesses of PTCDI-C8 films are presented in Figure 6(b). As can be seen in this plot, thicker films possess larger domain size and therefore sharper peaks compared to the thinner films. The size of the crystalline domains estimated from the X-ray reflectivity measurements is in the range of 20 to 40 nm for different thicknesses.

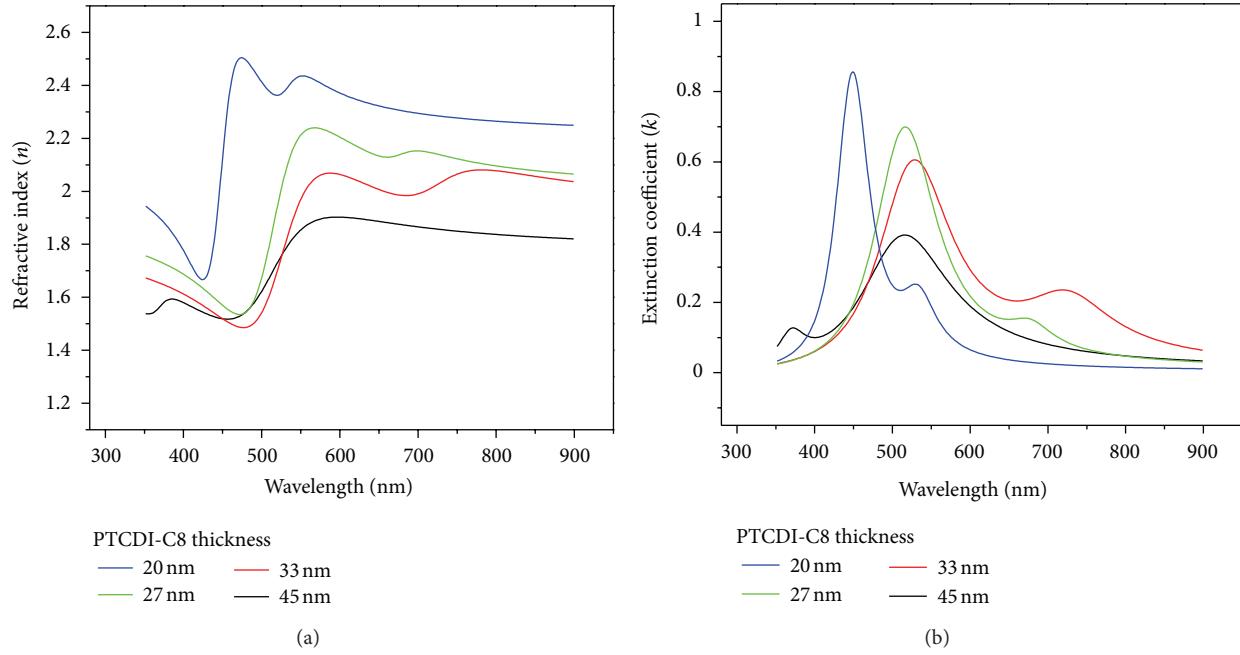


FIGURE 7: The (a) refractive indices (n) and (b) extinction coefficients (k) for PTCDI-C8 films with different thicknesses.

The fact that these values are considerably smaller than the grains size (needle-like features) observed in the AFM images indicates that the deposited films possess polycrystalline structure.

The refractive indices (n) and extinction coefficients (k) were extracted from the ellipsometry spectra of PTCDI-C8 thin films using Lorentz model. Figure 7 shows the ellipsometry results for different thicknesses of PTCDI-C8 films. Optical constants of some derivatives of perylenes family such as PTCDA and PTCDI-C13 have been reported previously in the literature [15]. However, the authors believe that their attempt to model optical spectra of PTCDI-C8 may be one of the only reported ones. As can be seen in these figures, for both n and k spectra, increasing the thickness of the film decrease the intensity of the peaks and shifts their position toward lower energies. The effects of thickness variation on the optical constants can be attributed to the change in the density of the defects in the films [16]. XRR studies revealed that thicker films possess larger crystalline domains, which modify the formation and the density of the defects inside the deposited films. Therefore, the differences in the optical properties of these films can be attributed to the thickness variation.

4. Conclusions

In summary, in order to study the structural properties of PTCDI-C8 thin films, different thicknesses of this material have been deposited on SiO_2/Si substrates by vacuum thermal evaporator at room temperature. The effect of the thickness variation on the structural and optical properties of these films has been investigated performing AFM, XRR, and ellipsometry. The results of this study verify the existence of a very high internal molecular ordering within the PTCDI-C8 films

regardless of the thickness variation. The average sizes of the crystalline domains which have been extracted from the XRR analysis coincide with the film thickness. This implies the presence of a 3D crystalline structure across the entire thickness of the layered film. Therefore, the reported outstanding optical and electrical properties of organic semiconductor devices based on PTCDI-C8 can be attributed to the high degree of molecular packing observed for these films.

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