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Short Communication

Physical Properties of Spray Pyrolysed Cadmium Sulfide Thin Films Deposited on Different Polymer Substrates

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This paper investigates the properties of 80 nm cadmium sulfide (CdS) thin films prepared by chemical spray pyrolysis technique on polyethylene terephthalate (PET) and polyimide (PI) plastic substrates at 250 ^{0}C for application as window layer in thin film solar cells. The influences of the type of substrate on the films' structural and optical features were studied. The patterns of diffraction of high resolution X-ray show formation of hexagonal CdS structure. AFM reveals smooth surface morphologies of the films deposited on PET and PI substrates with root mean square (RMS) roughness of below 10 nm. Optical transmittance exhibits values exceeding 70% in the visible and infrared (IR) regions on the two substrates. CdS deposited on PET records 2.48 eV and CdS deposited on PI obtains 2.47 eV of optical band gap (E_g) from Tauc plot. Hall measurements show that the CdS film is an n-type semiconducting material. The electrical resistivity , charge carrier mobility and carrier concentration of the CdS films deposited on PET and PI plastic substrates are 32.2 and 44.1 Ω.cm, 26.85 and 31.08 $cm^2v^{-1}s^{-1}$ well as $5.2X10^{17}$ and $6.78\ X10^{17}\ cm^{-3}$ respectively.

Keywords: Semiconductors; Thin films; Optical properties; X-ray diffraction; Raman spectroscopy

1. INTRODUCTION

Cadmium sulfide (CdS) is an important semiconductor material in optoelectronic devices such as optical sensors, light-emitting diodes, transistors and photovoltaic cells [1]. In solar cells, CdS is used as a window layer because it has high optical transmittance in the visible region, high optical

band gap (E_g ~ 2.4 eV) at room temperature, homogeneity, compactness, crystallinity, photoconductivity as well as natural n-type electrical conductivity [2-4]. CdS is a II-VI semiconductor material that has two crystalline forms: the hexagonal wurtzite structure, which has greater stability, and the metastable cubic zinc blende structure [5, 6].

Regarding the fabrication of CdS thin films, different physical and chemical deposition methods are adopted, such as electrodeposition [7], chemical bath deposition [8, 9], thermal evaporation [10], femtosecond pulsed laser deposition [11], molecular beam epitaxy [12], successive ironic layer adsorption and reaction [13], screen printing [14], close spaced sublimation [15], radio frequency (RF) sputtering [16], metal organic chemical vapor deposition [17], pulsed-laser deposition [18] and spray deposition [19]. Spray pyrolysis is widely employed for depositing CdS thin films due to its simplicity in fabrication process, low-cost and suitability for deposition of large area thin films [19, 20]. Besides, this technique can be carried out at low temperature, which allows the use of low-cost flexible polymer substrates, including polyethylene terephthalate (PET) and polyimide (PI). The use of flexible plastic substrates for optical applications, particularly for energy production devices used as solar cells, is attracting a great amount of interest [21–23] since they are light in weight and have high shock resistance. The aim of this paper is to assess the suitability of employing flexible CdS as window layer in solar cell by using chemical spray pyrolysis technique.

In this paper, the fabrication of CdS thin films was via chemical spray pyrolysis technique on PET and PI plastic substrates. The films were then characterized to analyze the effect of the polymeric substrate type on the optical, structural and electrical features of the CdS thin films.

2. EXPERIMENTAL DETAILS

2.1. Substrates Cleaning

In this work, PET plastic substrate from PenfibreSdn. Bhd. and PI plastic substrate from DuPont Corporation were used. Both substrates were first cleaned using alcohol for 10 minutes to get rid of contamination, rinsed with deionized (DI) water and dried with nitrogen (N_2) gas.

2.2. Materials

The materials used for preparation of the CdS thin films included cadmium chloride ($CdCl_2$, 99.99%) and thiourea ($CS(NH_2)_2$) ≥ 99.0%, from Sigma Aldrich. The materials were used as received.

2.3. Preparation of CdS Solution

Appropriate volumes of 0.1 M solutions of cadmium chloride ($CdCl_2$) and thiourea ($CS(NH_2)_2$) were mixed with DI water with the aid of a magnetic stirrer for 30 minutes. Then, the solution of $CdCl_2$ and $CS(NH_2)_2$ were mixed to obtain cadmium sulfide (CdS) and ammonium chloride (NH_4Cl), according to the equation below [24, 25]:

$$CdCl_2 + CS(NH_2)_2 + 3H_2O \longrightarrow CdS + 2NH_4Cl + CO_2\uparrow + H_2O$$

The resulting solution was sprayed using chemical spray pyrolysis onto PET and PI plastic substrates at substrate temperature of 250 ^{0}C. The ammonium chloride (NH_4Cl) was decomposed with heating into ammonia gas and hydrogen chloride gas, as shown in the reaction equation **[26]**.

$$CdS + 2NH_4Cl + H_2O \xrightarrow{\triangle} CdS\,(s) + 2NH_3\uparrow + 2\,HCL\uparrow$$

To obtain uniform thin films, all depositions were performed for 25 min while keeping the source to substrate distance at 27 cm. The solution was sprayed at a flow rate of 5 ml/min using compressed air at a pressure of 6 N/cm^2 as carrier gas. The thickness of CdS thin films deposited on PET and PI plastic substrates were both 80 nm, as measuredusing an optical reflectometer (Model: Filmetrics F20). The structural features of the CdS films were determined using a high-resolution X-ray diffractometer system (Model: Panalytical Empyrean) with CuKα radiation (λ) of 0.154 nm. The surface morphology of the films was studied by atomic force microscope (AFM) (Model: ULTRA1Objective). Raman measurement was carried out at room temperature using a JobinYvon HR800UV system. An argon-ion laser (514.5 nm) was used as an excitation source for Raman measurement. The optical features of the films were determined with the aid of ultraviolet–visible-near infrared (UV–Vis-NIR) spectrophotometer (Hitachi U-2000). Photoluminescence (PL) was recorded using a JobineYvon HR 800 UV system at an excitation wavelength of 325 nm. The Hall measurement was implemented with HL5500PC system.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

Fig. 1 displays the patterns of X-ray diffraction (XRD) for the CdS thin films prepared on PET as well as PI plastic substrates. From Fig. 1 a, the main peak corresponding to the PET substrate was observed at angle $2\Theta = 26^0$ and shows an extremely high intensity. This suggests that the CdS has a peak at an identical position as the peak of the same position. This behavior is in agreement with other published works [31–33]. Besides, CdS with (110) peaks (hexagonal structure) were observed at angle 43.69. For the CdS thin film deposited on the PI plastic substrate, the main peak corresponding to the PI plastic substrate was observed at angle $2\theta = 22.08°$, as shown in Fig. 1b. This value is in accordance with previously reported data [34]. All CdS films had hexagonal structure in agreement with standard XRD data, JCPD6-314 [35]. The XRD patterns of all the CdS films showed a sharp (002) peak beside a minor peak corresponding to the (110) plane.

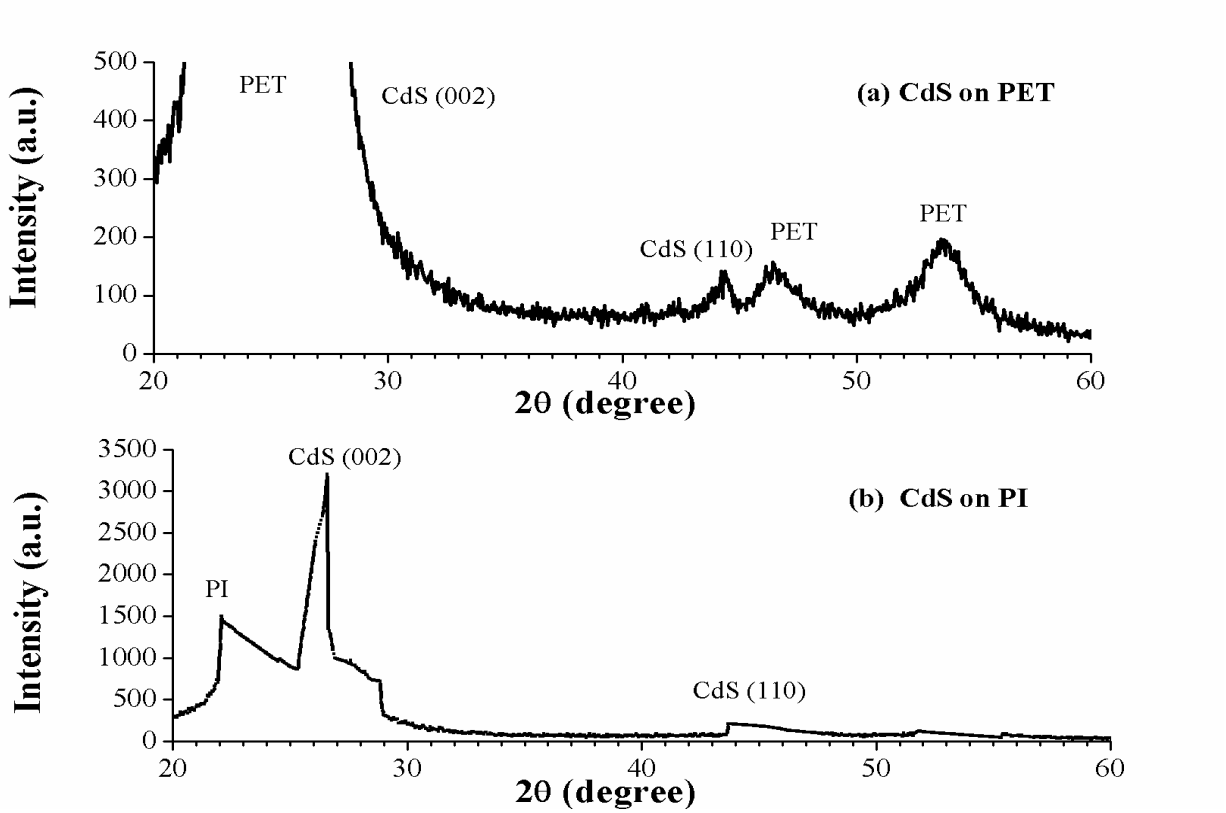

Figure 1. XRD patterns of CdS thin films deposited on (a) PET substrate and (b) PI substrate.

The AFM images of the CdS thin films prepared on PET and PI plastic substrates are shown in Fig. 2. The root mean square (RMS) roughness for the film deposited on PET is 7.62 nm, while the RMS for PI substrate is 8.21 nm. From the figure, smooth surface morphologies are evident on both substrates.

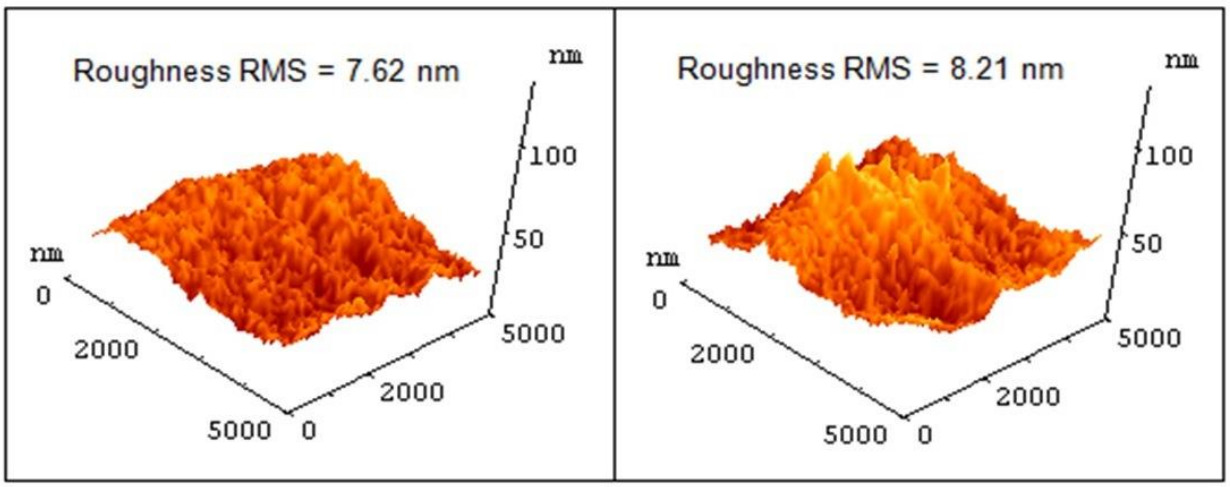

Figure 2.AFM analysis of CdS thin films prepared on PET (left) and PI substrate (right).

The Raman spectrum of the CdS thin films prepared onto PET and PI plastic substrates are illustrated in **Fig. 3 (a, b)**. Strong fundamental and weak overtone modes are observed. The fundamental and overtone modes show correspondence to the longitudinal optical 1LO and 2LO peaks and are the results of phonon vibration [36, 37]. For the CdS thin film deposited on the PET substrate, the two peaks are detected at 295.93 cm^{-1} and 592.28 cm^{-1}, as shown in Fig. 3a. On the other hand, for the CdS thin film deposited on PI plastic substrate, the two peaks are identified at 302.033 cm^{-1} and 600.246 cm^{-1}, as shown in Fig. 3b. This corresponds to the similarities within the nearest neighbor arrangement of the hexagonal structures of CdS, which is the same behavior reported by previous studies [38, 39].

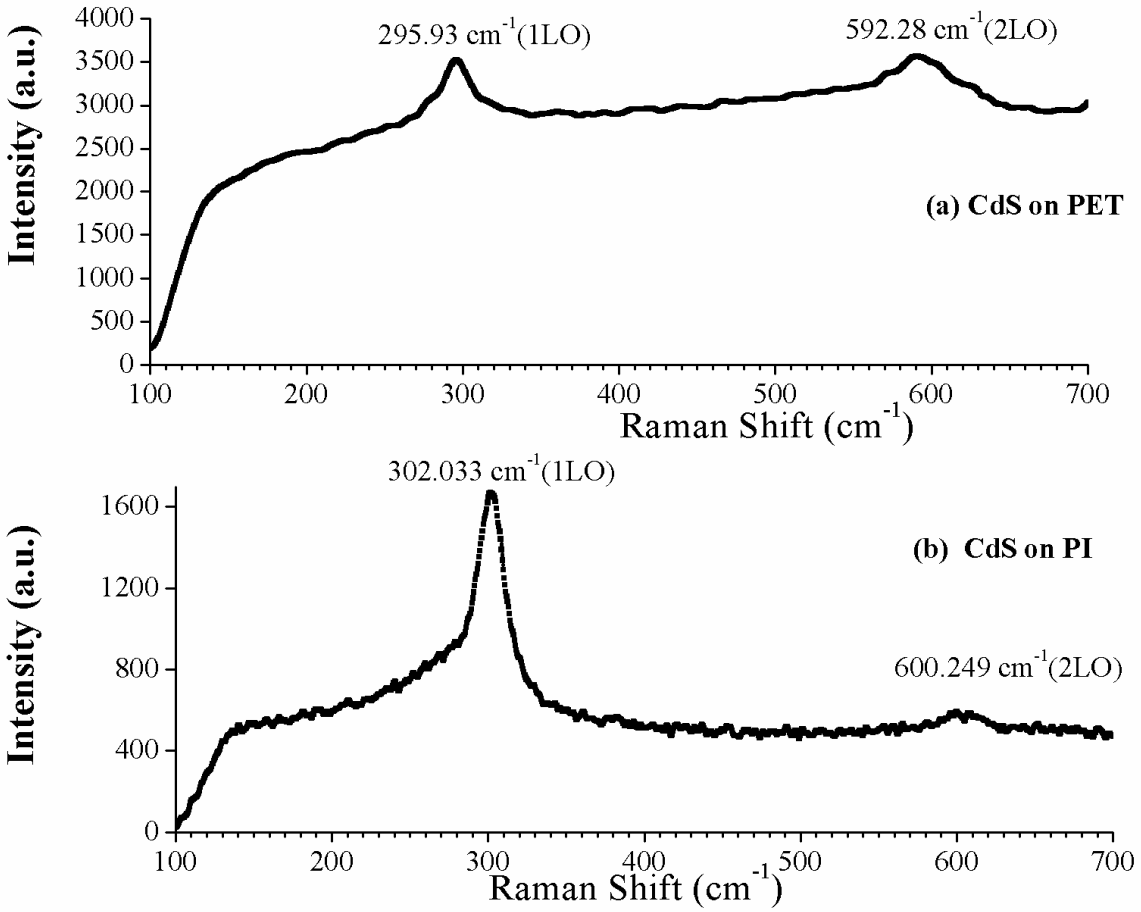

Figure 3. Raman spectra of the CdS thin films prepared on (a) PET substrate and (b) PI substrate.

3.2 Optical Properties

Fig. 4 depicts the optical transmittance curve of the CdS thin films prepared on PET and PI substrates measured in the spectral region of 300 - 1000 nm by the UV-Vis-NIR spectrophotometer system. From this figure, it is ascertained that the CdS films show high optical transmittance, slightly more than 70% in the visible region. The transmittance of the CdS thin film deposited on PET substrate is higher than that of PI substrate, particularly at wavelengths >600 nm. The average

transmittance of the film deposited on PET plastic is about 79%, while that of the PI plastic substrate is about 70%. In thin film solar cells, high transmittance within the 300-1100 nm wavelength region is highly desirable in a window layer in order to ensure that most of the incident light is transmitted to the absorber layer for carrier (electron-hole pairs) generation process [40].

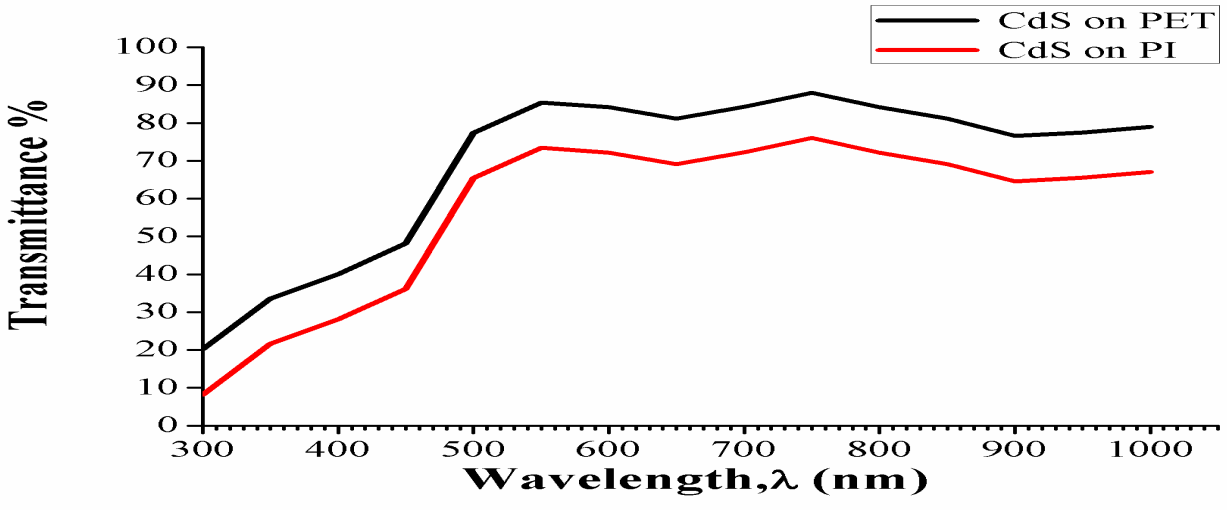

Figure 4. Optical transmittance of CdS thin films deposited on PET and PI plastic substrates.

It is well known that CdS is a direct-band-gap semiconductor. Thus, the absorption coefficient within the region of strong absorption obeys the subsequent equation [41].

$$\alpha = \frac{k}{h\nu}\left(h\nu - E_g\right)^{\frac{1}{2}} \quad (3.1)$$

where k is a constant, h is Planck constant, ν is the radiation frequency, and E_g is the band gap energy.

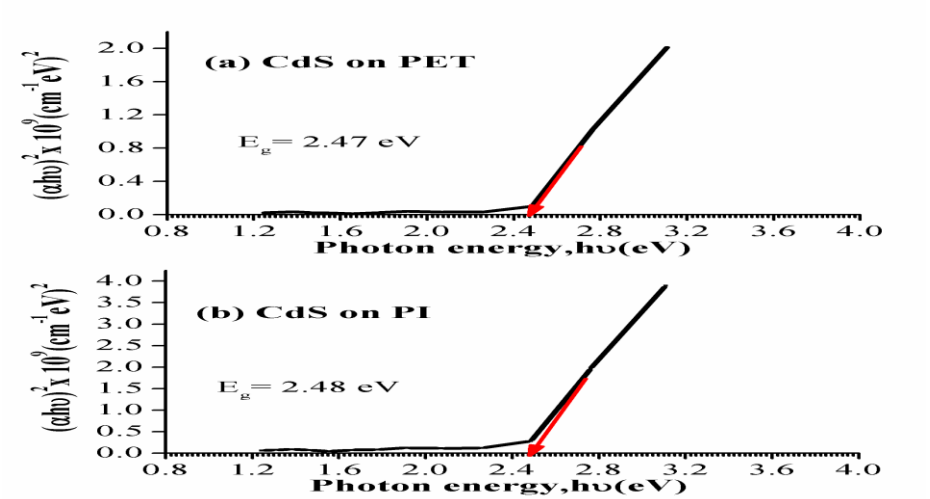

Figure 5. A plot of $(\alpha h\nu)^2$ vs photon energy for CdS thin films deposited on (a) PET substrate and (b) PI substrate.

The band gap energy can then be calculated from the straight line of the plot of $(\alpha h\nu)^2$ vs. photon energy for CdS thin films, as shown in Fig. 5. From the linear extrapolation, the E_g of the CdS thin films are determined to be 2.47 eV for CdS deposited on PET and 2.48 eV for CdS deposited on PI substrate. These values deviate from the standard bulk value of 2.42 eV [42].

Fig. 6 shows the photoluminescence spectra of CdS thin films deposited on PET and PI plastic substrates. According to Fig. 6a, the CdS thin film deposited on the PET substrate is found to exhibit an emission peak at 501 nm (2.47 eV), which is ascribed to the band-to-band transition. The emission band at 501 nm is known because of the green emission band of CdS [43]. On other hand, according to Fig. 6 b, the CdS thin film prepared on PI plastic substrate is found to exhibit an emission peak at about 500 nm (2.48 eV). The above values are very similar to those obtained from the optical transmittance studies previously presented in Fig. 5.

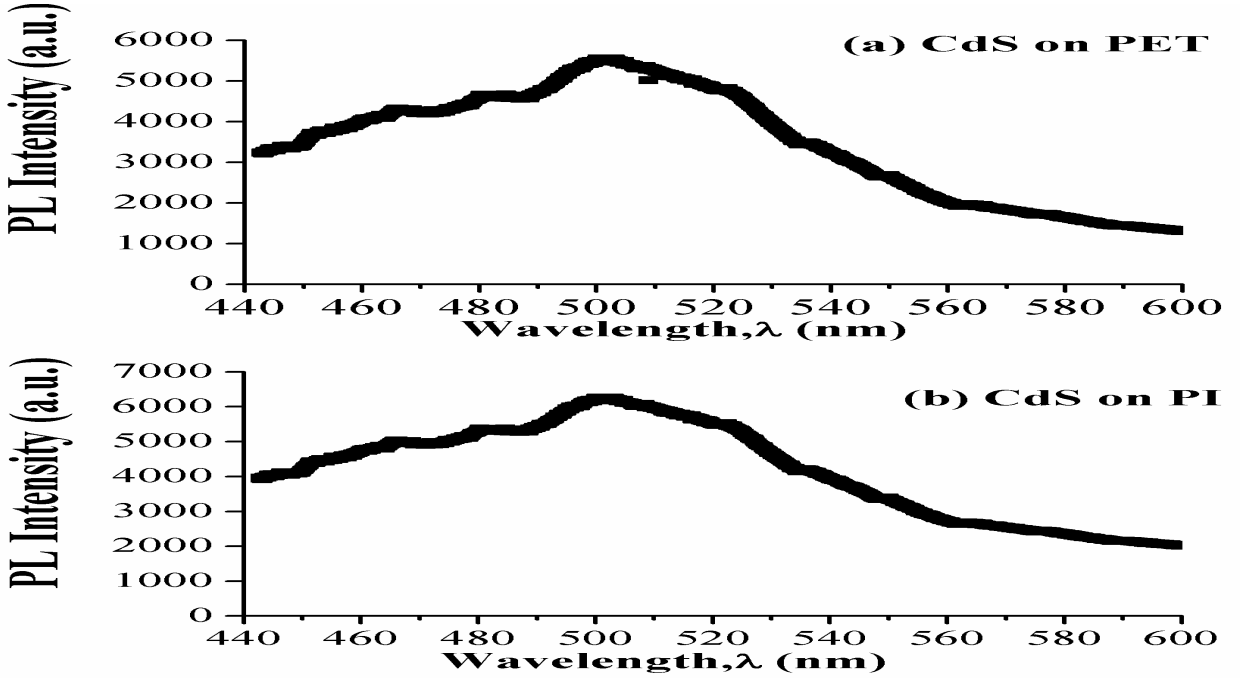

Figure 6. Photoluminescence spectra of CdS thin films prepared on (a) PET substrate and (b) PI substrate.

3.2 Electrical Properties

The Hall measurements results indicate that CdS films show n-type conductivity. The values of resistivity for CdS prepared on PET and PI plastic substrates are 32.2 and 44.1 Ω.cm respectively. This is in agreement with previous works [44]. The charge carrier mobility for CdS prepared on PET and PI plastic substrates are 26.85 and 31.08 $cm^2v^{-1}s^{-1}$ respectively. This behavior is in agreement with the findings of other studies [45]. The carrier concentration of the CdS deposited on PET and PI plastic substrates are $5.2X10^{17}$ and $6.78\ X10^{17}\ cm^{-3}$ respectively. This is in agreement with previous works [46].

4. CONCLUSIONS

CdS thin films with a nominal 80 nm thickness were prepared on PET and PI substrates at 250 ^{0}C with chemical spray pyrolysis technique. The patterns of diffraction of X-ray proves the proper phase formation of the CdS. AFM reveals smooth surface morphologies on both substrates with RMS roughness of below 10 nm. CdS deposited on PET records 2.48 eV and CdS deposited on PI measures 2.47 eV of optical band gap (E_g) from Tauc plot. Analysis of the electrical results indicates that the CdS thin film is an n-type semiconducting material. The optical features of the films deposited onto PET and PI substrates show (70–79%) visible transmission, making the films suitable for optoelectronic devices. Based on this study, it can be concluded that CdS thin films prepared on the two substrates can be suitably applied in solar cells.

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