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Optical and electrical properties of thermally treated hybrid blend ZnPc/CdS thin films

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Abstract

Spin coating technique used to prepared ZnPc, CdS and ZnPc/CdS blend thin films, these films annealed at 423K for 1h, 2h and 3h. Optical behavior of these films was examined using UV-Vis. and PL. The absorption spectrum of ZnPc shows a decreasing in absorption with the increase of annealing time while CdS spectrum give a clearly absorption peak at~510 nm. Energy gap of ZnPc increases from 1.41 to 1.52 eV by increasing the annealing time. E_g of CdS decrease by increasing annealing time, from 2.3 eV to 2.2 eV. Pl spectra showed that the intensity of the peak increases by increasing the time of annealing. D.C. conductivity measurement showed that all the thin films have two different activation energies in the temperature range 303–473K.

Key words

Zinc Phthalocyanine, Cds Nps, Hybrid blend.

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الخصائص البصرية و الكهربائية لأغشية المزيج الهجين ZnPc/CdS الرقيقة المعاملة حراريا

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الخلاصـــة

استخدمت تقنية البرم الطلائي لتحضير ZnPc و CdS و المزيج الهجين وتم تلدين هذه الاغشية عند درجة حرارة 423 كلفن لمدة ساعة وساعتين و ثلاث ساعات. ان السلوك البصري لهذه الاغشية تم دراسته باستخدام مطياف الاشعة فوق البنفسجية - المرئية و اللمعانية الضوئية. اظهر طيف امتصاص ZnPc تناقصا بزيادة وقت التلدين بينما اظهر طيف CdS وجود قمة امتصاص عند الطول الموجي 510 نانومتر. ان فجوة الطاقة لاغشية ZnPc تزداد من 1.41 الى 1.52 الكترون فولت و من 3.02 الى 3.08 الكترون فولت وذلك بزيادة زمن التلدين و ان فجوة الطاقة لأغشية CdS تقل مع زيادة وقت التلدين من 2.3 الى 2.2 الكترون. وضح طيف PL ان شدة القمم للاغشية تزداد بزيادة زمن التلدين. أظهرت قياسات التوصيلية الكهربائية المتناوبة ان كل الاغشية تمتلك طاقتي تنشيط وبمدى درجات الحرارة يتراوح بين 303 كلفن الى 473 كلفن.

Introduction

The hybrid system is a unique way to generating and designing new materials with useful physical or chemical properties by combining inorganic and organic components at the molecular level. The organic block offer structural flexibility, tunable electronic properties, photoconductivity and efficient luminescence, while, the inorganic block form the basis for magnetic or electric properties, and confer good thermal and mechanical stability [1].

Nanostructure materials preparation and characterization has got researchers attention during many years ago has because of their exciting electronic, optical and chemical properties [2]. A smaller dimensions of a materials make the detected physical and optical properties changing; such as the absorption spectra of the specimens [3]. Quantum confinement of materials have involved a good interest as a light absorbing material for high efficient and low cost device preparation [4].

CdS is one of the best main classes of materials, it is a n-type semiconductor. CdS nanocrystals which appear a properties lying between the bulk confines and molecular [5].

Organic semiconductors are a kind of materials that linked the electronic benefits of semiconducting materials with the mechanical and chemical profits of organic compounds. Thus, the capability to conduct electricity, absorb light and emit light is united with a material construction to reformed by chemical synthesis [6]. Phthalocyanines are one group of organic semiconductors materials, of which optical, electronic and photo electronic behaviors are being broadly studied. ZnPc, is a metal phthalocyanine ,it is a p-type organic material, it keeps high absorption in the visible region, great thermal stability and optimal optical energy gap [7]. Because of their ring structure all of phthalocyanine organic molecules and their derivatives appear an optical properties [8]. The aim of this work is to manufacture the CdS nanoparticles (CdS Nps) to study the size effect on the optical spectrum due to annealing time at 423 K and estimate their energy gap.

Among different techniques of deposition, ZnPc, CdS and blended films of these two compounds are formed by spin coating, which is a simple and clean technique. In this work the energy gaps of hybrid blend ZnPc/CdS thin films using different techniques such as UV–Vis absorption spectrum and photoluminescence, and then compare the results obtained with the ZnPc and CdS compounds. The activation energy got from D.C. conductivity confirms the behavior of energy gaps.

Experimental

CdS nanoparticles prepared by chemical method using cadmium chloride ($CdCl_2$), sulfur (S), paraffin oil, and oleic acid. The preparation of the S-paraffin oil solution be first, then Cd complex solution prepared by dissolving $CdCl_2$ in Paraffin:Oleic acid solution. The mixture of S-Paraffin solution and Cd-Paraffin:Oleic acid complex heated up to 300 °C then cooled down and adding a large amount of absolute ethanol (500-750 ml) to the reaction. The CdS nanoparticles colloidal then washed many times by ethanol and centrifuge, the last treatment is washing by toluene and and centrifuged then with ethanol and using ultrasonic, the precipitate dried at T=60 °C for 30 minutes to get CdS nanoparticles powder.

Zinc phthalocyanine (ZnPc) which purchase from sigma Aldrich without more purification was dissolved in chloroform, and putted on a hot plate stirrer for (36) hours with temperature of 50 ^{o}C, then the solutions is filtered using 0.45μm filter and placing again on stirrer for 10 hours, then placing the solutions in ultrasonic for 5 hours to get homogenous solution. The same solvent using to dissolved CdS and the same steps following to get CdS solution. Then ZnPc and CdS solutions was mixing together and following the same steps to get a blend solution, prepared thin films from these solutions by spin coating method on pre-cleaned substrates of glass. The prepared samples leaved in R.T for one day then putted in an oven at 50^{o}C for 10 min to remove the residual solvent may be stay inside the film. This paper treats with the optical and electrical characterizations of deposited CdS, ZnPc and ZnPc/CdS blend thin films and annealed thin films at 423 K for 1, 2 and 3 hours.

Measurements

The electrical properties and optical one for prepared and annealed CdS, ZnPc and ZnPc/CdS thin films were examined using UV-Vis Spectroscopy, PL measurements and D.C. conductivity.

Results and discussion

1. UV-Vis. Spectrometer analysis

1.1 Absorption spectrum

UV–Vis. is a good and simple technique of the energy gap determination for semiconductors. The energy gap can be estimated from tauc equation [9]:

$$(\alpha h\gamma)^{1/2} = B(h\gamma - E_g)$$

Absorption spectrum of the prepared and annealed ZnPc thin films for 1h, 2h and 3h at 423 K are shown in Fig.1(a). Organic molecules of ZnPc appears an optical characteristics because of their ring structure (this agreement with Stillman) [10]. ZnPc appear a three chief absorption peaks, B band at 305 nm in the UV region and Q bands at 694 nm and 690 nm in visible region [10], the intense visible absorption and ultraviolet B band is due to the electronic transitions from π to π^*. The peak around 305 nm of the B-band of as-deposited ZnPc film (this single peak is similar to that noticed in many Pcs [11, 12] was shifted to 307, 309 and 310 nm for 1h, 2h and 3h annealing films respectively [13].

The Q1-band of the 611 nm peak had been shifted to 620, 613 and 615 nm for 1h, 2h and 3h annealing films respectively, while the Q2-band shows a maximum peak at 694 nm, the peak was shifted to 698, 692 and 690 nm respectively by increasing the time of annealing, this may be due to that the splitting structure of this peak could be affected by the orbital overlapping of Pc ring with the chief metal (Zn), therefore the optical absorption was dependent directly on crystal distributions [13-16].

Generally, the absorption decreases by increasing the annealing time for (RT, 2h, 3h) except (1h) increases with annealing time 1h, this may be attributed to transformation of the phase from metastable α-ZnPc to stable β-ZnPc [16].

On the other hand, the optical behavior is clearly affected by heat treatment for CdS thin films. Fig.1(b) shows several absorbance spectra for different annealing times (1h, 2h and 3h at 423K) for as-deposited and annealed CdS nanoparticles films. The absorbance spectra for CdS films show that the absorbance value for all samples is low (in the range of 500 to 800 nm). The spectrum shows a definite absorption peak at ~510 nm, which is noticeably blue-shifted (indicating quantum confinement of the particles) [17, 18]. This peak refers to the optical transition of the first excitonic state quantum Generally, this wavelength of the maximum exciton absorption decreases as the particle size decreases as a result of quantum confinement of the photo generated electron-hole pairs [19, 20]. Fig.1(b) also shows that the band-edge shifts to higher wavelength (316, 320, 328 and 336) nm because of the increasing of the particle size during the heat treatment [21]. Optical behavior of thermal treated CdS films is in good agreement with other studies [22-24].

The spectra of ZnPc/CdS blend thin films display a properties absorption of MPcs with Q-band followed by a smaller shoulder and a weak broad Soret band around at 300–310 nm as shown in Fig.1(c), also it shows an absorption peaks around 300–690 nm, and the beginning set λ is at 700 nm conforming the energy gap of 1.7 eV for CdS which is in aggrement with the last studies [4, 25-27].

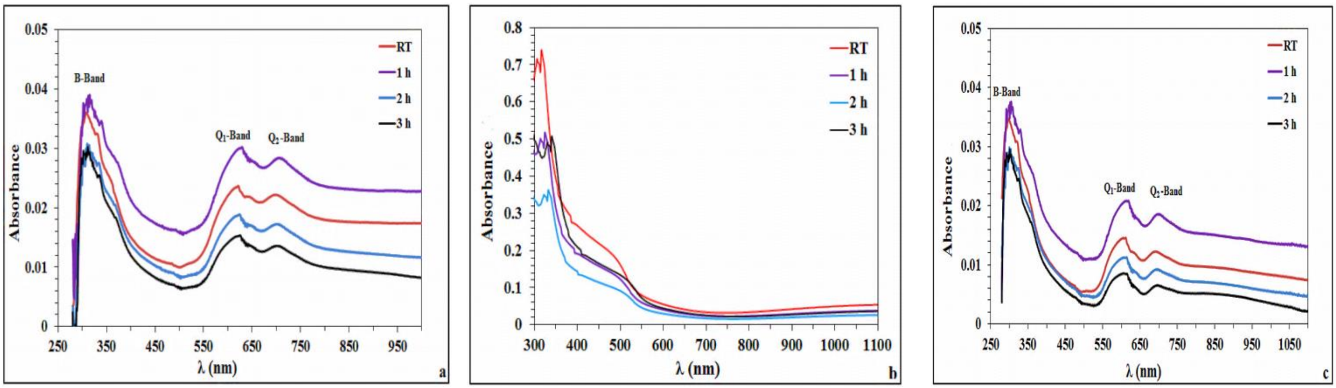

Fig.1: The variation of $(\alpha h\gamma)^2$ versus the photon energy ($h\gamma$) for as-deposited and annealed a: ZnPc, b: CdS and c: ZnPc/CdS blend films at different annealing time.

1.2 Energy gap

The optical absorption spectra give a good indication about the energy gaps of as-deposited an annealed ZnPc films were specified by the energy peak at low-energy maxima. In the Fig.2(a) the plot of α^2 versus phonon energy was charted, it's concluded that as-deposited and annealed ZnPc thin films exhibits only the direct allowed transition and the estimated band gap energy values increases from 1.41 to 1.52 eV for Q-band and from 3.02 to 3.08 eV for B-band by increasing the annealing time this result agreement with K. Hamam [16].

The energy gap of CdS has been determined from UV-Vis. Spectra as shown in Fig.2(b). It was noticed that when the annealing time increasing, the absorbance spectrum below the energy gap (Eg) decreased and this may be belong to the trap state reduction that occurred in CdS Nps [28, 29, 23, 21]. As the size of CdS particles decrease to nanoscale, the band gap of the film increases, producing a blue shift in UV-Visible spectra ,so CdS film exhibit a band gap 2.3 eV for prepared CdS thin film and decrease to 2.18 eV by increase annealing time, this result in good agreement with Duchaniya [20]. Energy gap behavior of the blended films has the same behavior of ZnPc energy gap, it increases from 1.48 eV to 1.66 eV for Q-band and from 3.04 eV to 3.08 eV. Table 1 illustrate the values of E_g for as-deposited and annealed ZnPc, CdS and ZnPc/CdS blend films for 423 K at different annealing time.

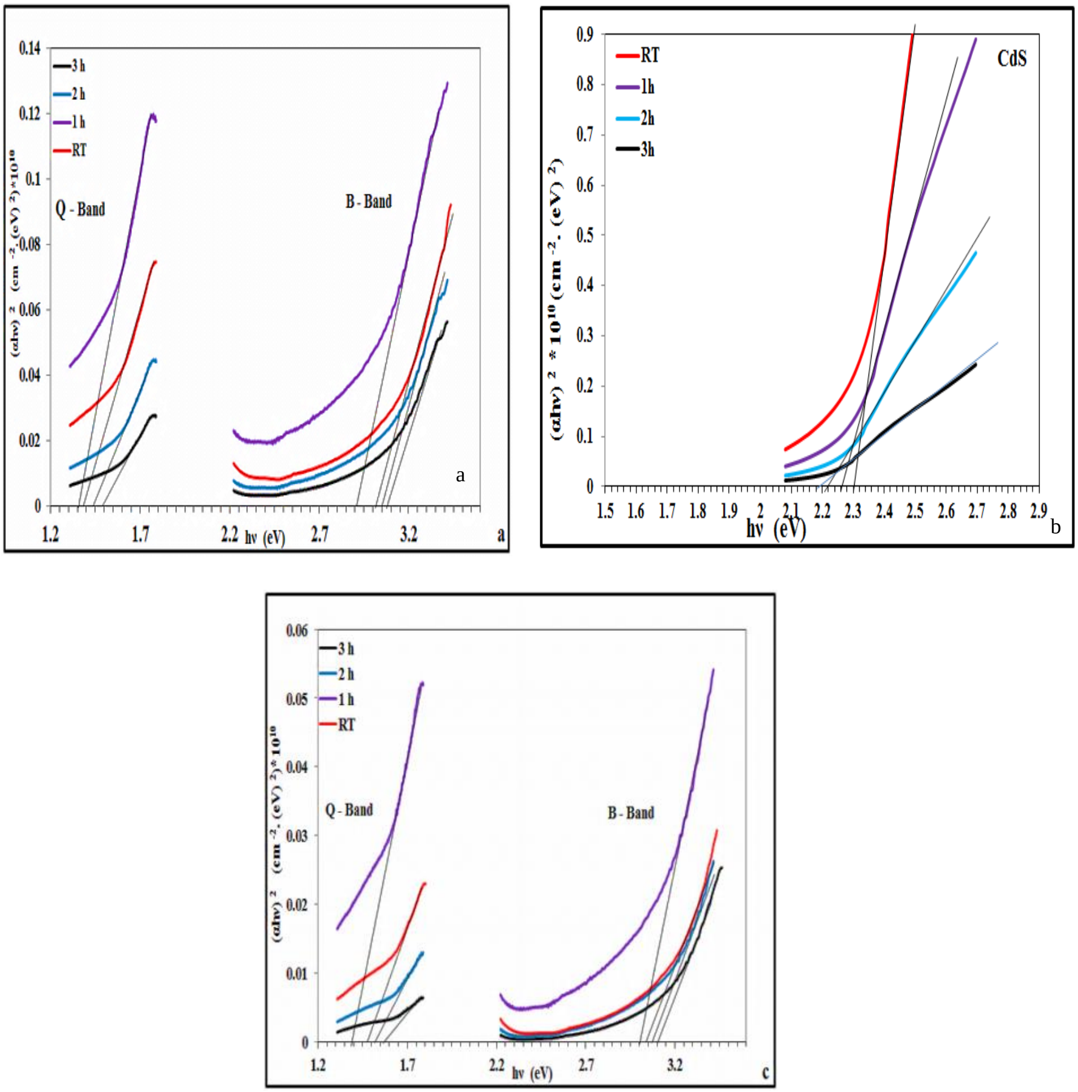

Fig.2: $(\alpha h\upsilon)^2$ variation versus $(h\upsilon)$ for a:ZnPc, b:CdS and c:ZnPc/CdS blended films at different annealing time at 423 K.

Table 1: The values of E_g for as-deposited and annealed ZnPc, CdS and ZnPc/CdS blend films for 423K at different annealing time.

Sample	Time of annealing	E_g (eV)	
		Q-band	B-band
ZnPc	RT	1.41	3.02
	1h	1.37	2.91
	2h	1.47	3.05
	3h	1.52	3.08
CdS	RT	2.30	
	1h	2.27	
	2h	2.22	
	3h	2.18	
ZnPc/CdS blend	RT	1.48	3.04
	1h	1.4	3.00
	2h	1.56	3.06
	3h	1.66	3.08

2. Photoluminescence (PL)

PL spectra were illustrated in Fig.3 for blended films. The prepared films treated by heat at 423K for different annealing time. Feature of broadening in the annealed films for 2h demonstrated on the PL spectrum. A low energy spectra represented by the as-deposited film.

The main PL peak centered at 2.94 eV, at 2.93, 2.96 and 2.97 for the blended films prepared at RT, 1h, 2h and 3h. The peak intensities were strongly dependent on annealing time. Generally, the intensity of the peak increases by increasing the time of annealing. Table 2 show a comparison between the values of E_g for prepared and heat treated blended films obtained from UV data and PL data.

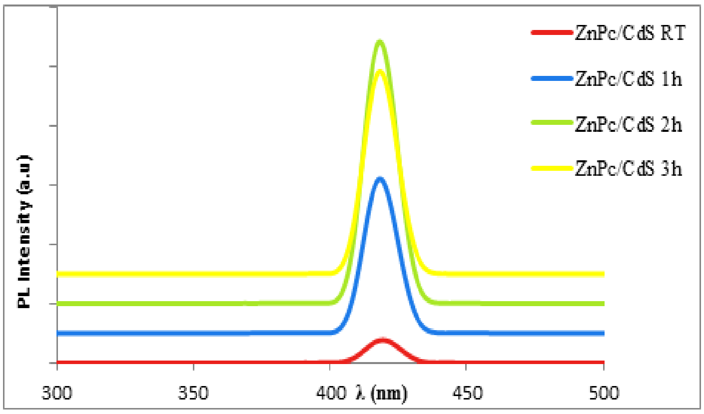

Fig.3: PL spectrum of ZnPc/CdS blended films.

Table 2: Comparison between the values of E_g for prepared and heat treated ZnPc/CdS blended films obtained from UV data and PL data.

Sample	E_g (UV) Q-band	E_g (PL) Q-band
ZnPc/CdS RT	3.04	2.94
ZnPc/CdS 1h	3.00	2.93
ZnPc/CdS 2h	3.06	2.96
ZnPc/CdS 3h	3.08	2.97

3. D.C Conductivity

To estimate the activation energy and study the annealing time effect on the activation energy, the electrical conductivity must be study the prepared and annealed thin films.

The variation of $\ln\sigma_{d.c}$ versus $10^3/T$ for as-deposited and annealed ZnPc, CdS and ZnPc/CdS blended films for 423K at 1h, 2h and 3h shown in Fig.4. From this figure the activation energies were calculated according to equation [30]:

$$\sigma = \sigma_o \exp(-E_a/k_B T)$$

and listed in Table 3, this table illustrate the values of σ, Ea_1 and Ea_2 for as-deposited and annealed ZnPc, CdS and ZnPc/CdS blended films. All prepared and annealed thin films have two different activation energies in the temperature range 303–473 K, hence there are two transport mechanism. For all films, the E_1 conformable to the lower temperature variation is related with the resonant energy, while E_2 is related with a short-lived charge (due to carrier's excitation into the extended states beyond the mobility edge) and the impurity. That means E_1 associated with an intrinsic generation procedure while E_2 related with impurity conduction (due to carrier's excitation into localized state at the edge) [31].

There are two activation energy shown in Fig.4(a) (Ea_1 and Ea_2) for ZnPc thin films. They show a large decreasing in resistivity (increase in conductivity) related with air and this is may be due to oxygen adsorption, it is acting as electron acceptors when they be in the form of surface complexes and thus refer to creating a p-type film by decreasing the electrons concentration (the penetration of oxygen of atmospher in the material is accountable for p-type attitude of MPcs (here ZnPc) [32]. This result are improving the results found by XRD pattern of ZnPc [33].

Prepared and annealed CdS thin films appear a variation of dc electrical conductivity as a function of $10^3/T$ and that illustrates in Fig.4(b). E_2 estimated from the resistivity plot and equal to 0.83 eV for as-deposited CdS thin film and decreased to 0.19 E_2 eV by increasing annealing time. Generally, the rsistivity of the films increases with decrease the time of annealing, this result disagreement with S.A. Jassim et al. [34], that refers to increasing in the conductivity.

Fig.4(c) shows that the prepared and annealed blended thin films have two dissimilar activation energies also in the range 303–473 K. The values of Ea_2 equal to 0.22 eV at RT. Generally, Ea_2 increased to 0.68 eV by increasing the annealing time of the films for 1h, 2h and 3h, these result agreements with the behavior of energy gap.

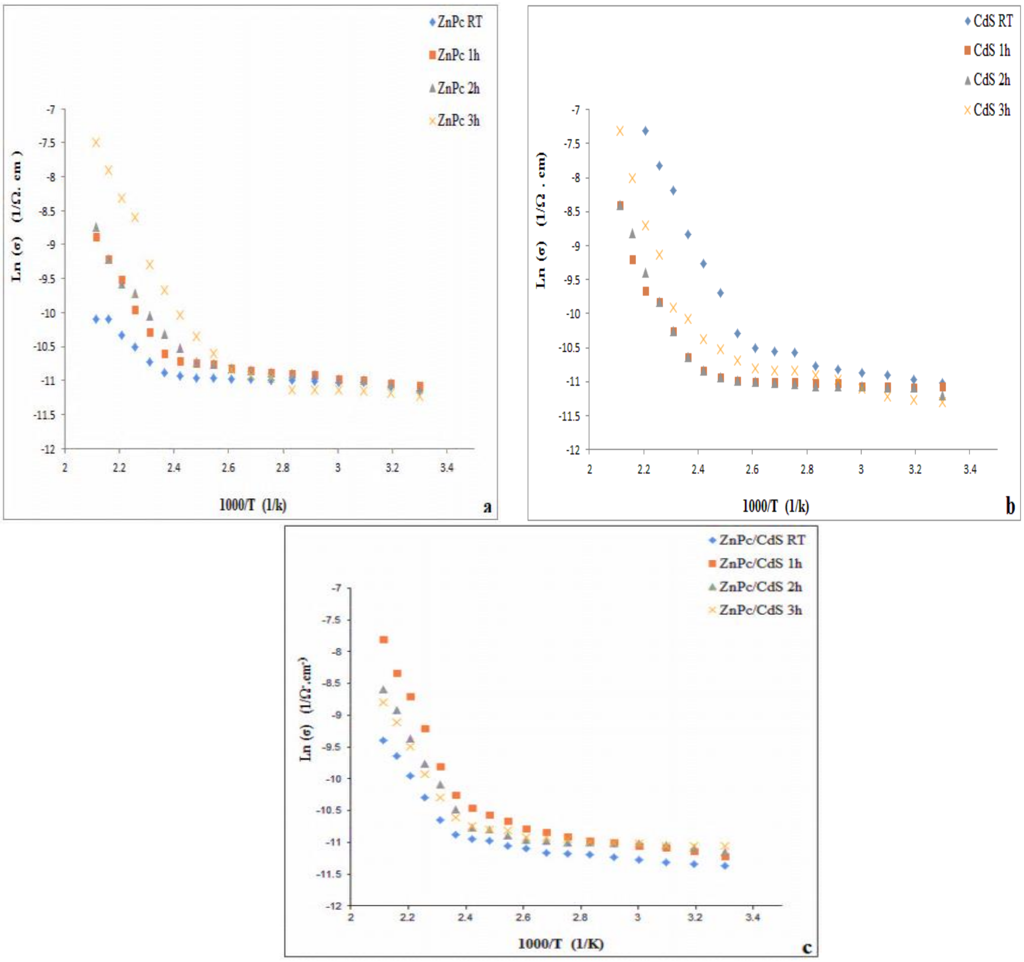

Fig.4: The relation between Ln (σ) versus reciprocal of temperature for s-deposited and annealed a:ZnPc, b:CdS and c:blended films for 423K at different annealing time.

Table 3: The values of E_{a1} and E_{a2} and these ranges for as-deposited and annealed ZnPc, CdS and ZnPc/CdS blend films for 423K with different annealing time.

Sample	Time of annealing	$(\Omega.cm)^{-1}*10^{-5}$	Ea_1 (eV)	Temperature range (K)	Ea_2 (eV)	Temperature range (K)
ZnPc	RT	1.344	0.0225	303-413	0.2971	413-473
	1h	1.55	0.0340	303-413	0.5867	413-473
	2h	1.48	0.0360	303-413	0.5438	423-473
	3h	1.32	0.0424	303-413	0.6082	413-473
CdS	RT	1.56	0.0450	303-413	0.8351	413-473
	1h	1.55	0.0654	303-413	0.7058	413-473
	2h	1.37	0.0351	303-413	0.6202	413-473
	3h	1.23	0.0711	303-413	0.1942	413-473
ZnPc/CdS blend	RT	1.14	0.0234	303-413	0.2273	413-473
	1h	1.33	0.0465	303-413	0.5033	413-473
	2h	1.44	0.0442	303-413	0.5511	413-473
	3h	1.57	0.0482	303-413	0.6832	413-473

Conclusion

CdS absorption spectrum exhibits a definite and clear absorption peak at ~510 nm, while the absorption spectrum of ZnPc shows a decreasing with the increase of annealing time. UV-Vis. plot indicates that ZnPc and blended films have the same behavior; they have a direct allowed transition and their energy gap values increased by increasing the annealing time, this result in contrary with CdS Eg behavior. Generally, D.C. conductivity measurements confirms the results obtained from UV-Vis. analysis, as well as the results obtained from Pl data.

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