



Original article

A study of the optical bandgap energy and Urbach tail of spray-deposited CdS:In thin films

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ABSTRACT

Cadmium sulfide (CdS) is an interesting material for applications in optoelectronic and photovoltaic devices. In particular, thin films of n-type CdS are widely used as a window layer in heterojunction solar cells. The optical bandgap energy is the most interesting parameter for these applications. For spray-deposited indium-doped cadmium sulfide (CdS:In) thin films prepared on glass substrates the transmittance measurements were used to estimate the optical bandgap energy. Tailing in the bandgap was observed and found to obey Urbach rule. The effects of film thickness and the substrate temperature on the bandgap energy and the width of the tail were investigated. A linear relation between bandgap energy and width of the tail was found.

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1. Introduction

Cadmium sulfide (CdS) is an interesting material for applications in optoelectronic, integrated optics and photovoltaic devices. In particular, thin films of n-type CdS are widely used as a window layer in heterojunction solar cells [1], because of the fact that CdS has intermediate energy bandgap, reasonable conversion efficiency, stability and low cost [2]. To take advantage of the optoelectronic properties of CdS by producing

n-type films, extrinsic doping is required. Several methods have been developed to grow n-type CdS films; i.e. the variation of the reagent precursors concentration in order to vary the Cd:S ratio, or the doping with silver or indium atoms [1]. There are different methods to prepare undoped and doped CdS films, such as rf sputtering [3] chemical bath deposition (CBD) [4–7], pulsed laser deposition (PLD) [1], and spray pyrolysis (SP) [8–18]. Spray pyrolysis was used in this study because it enables the low cost production of highly transparent, large area thin films with easy intentional doping.

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Many workers investigated the optical properties of CdS thin films, but few have studied the relation between bandgap energy and film thickness [19,20] and the tailing in the forbidden bandgap [20,21]. Sahay et al. [19] studied the optical properties of vacuum evaporated CdS thin films deposited at room temperature. They investigated the relation between the optical bandgap energy and the thickness of the films for films of thickness 250–1000 Å. Our group [20] studied the thickness dependence of the bandgap and Urbach tail for CdS thin films prepared by vacuum evaporation at the ambient temperature. In this study, indium-doped cadmium sulfide (CdS:In) thin films with thickness in the range 150–700 nm were prepared by the SP technique, the bandgap energy was estimated, and its dependence on film thickness and substrate temperature were studied. The Urbach tail width was also estimated and its relation with film thickness, substrate temperature and the bandgap energy was investigated.

2. Experimental part

The precursor solution of CdS thin films was prepared by dissolving 2.06×10^{-2} mol of extra pure $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ (MERCK Art. 2011) and 2.24×10^{-2} mol of thiourea $(\text{NH}_2)_2\text{CS}$ (>97% S) in 350 mL of distilled water. Indium chloride InCl_3 (MERCK Art.12471) was used as a doping compound. The ratio of the concentration of indium ions to that of cadmium ions in the solution which is not necessarily the same as their ratio in the films was 1.0×10^{-4} which is considered as the doping ratio. The solution was sprayed intermittently by using the spraying system described by Ikhmayies [8] on glass substrates that were ultrasonically cleaned with methanol at a substrate temperature $T_s = 490^\circ\text{C}$.

The transmittance of the films was measured at room temperature in the wavelength range 300–1100 nm by a double beam Shimadzu UV 1601 (PC) spectrophotometer. The films' thickness was in the range 150–700 nm, where it was estimated by using Lambert law for absorption in a semiconductor by making use of the relative transmittance through each film at a certain wavelength.

3. Results and discussion

Usually the deposition parameters affect the optical properties of thin films. The effect of the film thickness and deposition temperature on the optical properties of CdS:In thin films will be investigated.

Fig. 1 shows the transmittance against wavelength in the range 300–1100 nm for a set of CdS:In thin films of thickness in the range 150–700 nm deposited at a substrate temperature $T_s = 490^\circ\text{C}$. From the figure it is found that the transmittance has a minimum larger than 75% and a maximum close to 98%. The high value of the transmittance is suitable for solar cell applications where CdS can be used as a window material in heterojunction solar cells such as CdS/CdTe solar cell. As the figure shows, the transmittance of the films for wavelength values smaller than the cut-off wavelength (≈ 510 nm) is a function of film thickness; that is the transmittance decreases as the film thickness increases. Also a shift of the absorption

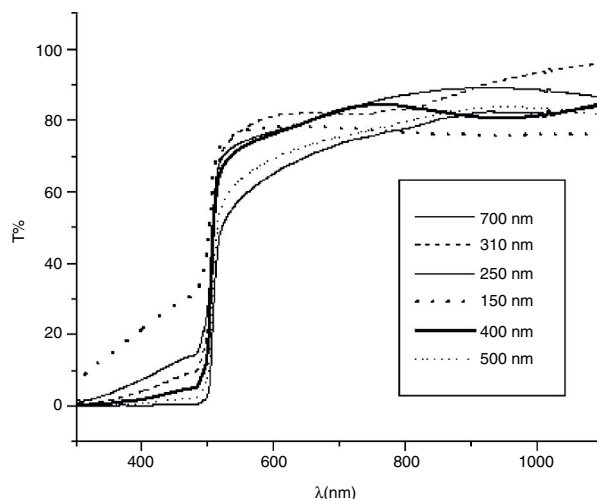


Fig. 1 – The transmittance curves of CdS:In thin films of different thickness deposited at 490°C .

tail toward longer wavelengths for thicker films was observed. These observations are in excellent agreement with Sahay et al. [19] and with our previous work on vacuum evaporated CdS thin films [20].

Fig. 2 displays the transmittance curves at different substrate temperatures for two films of thickness 180 nm deposited at two different substrate temperatures, 450°C and 490°C . Before the absorption edge the transmittance of the films is approximately unaffected with the substrate temperature. The change in transmittance after the absorption edge is related to the uniformity of the films where the one deposited at 490°C shows interference maxima and minima while the other one does not show them. This means that the quality of the films had improved at the higher substrate temperature.

Fig. 3 displays the relation between the absorption coefficient α and the photon energy $h\nu$, where h is Planck's constant, and ν is the frequency of the radiation. The inverse relation

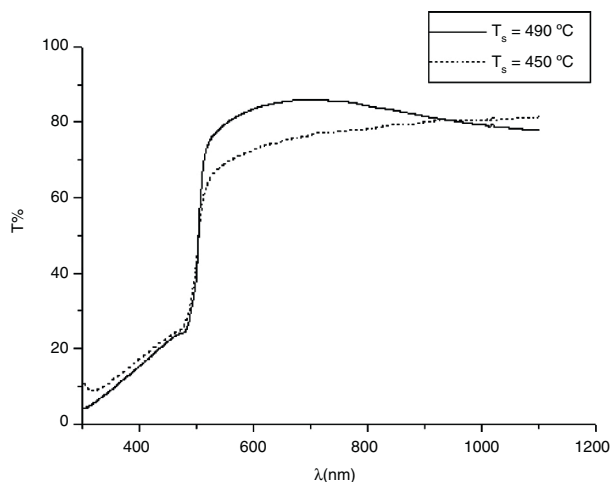


Fig. 2 – The transmittance of the films at different substrate temperatures as a function of wavelength for two films of thickness 180 nm.

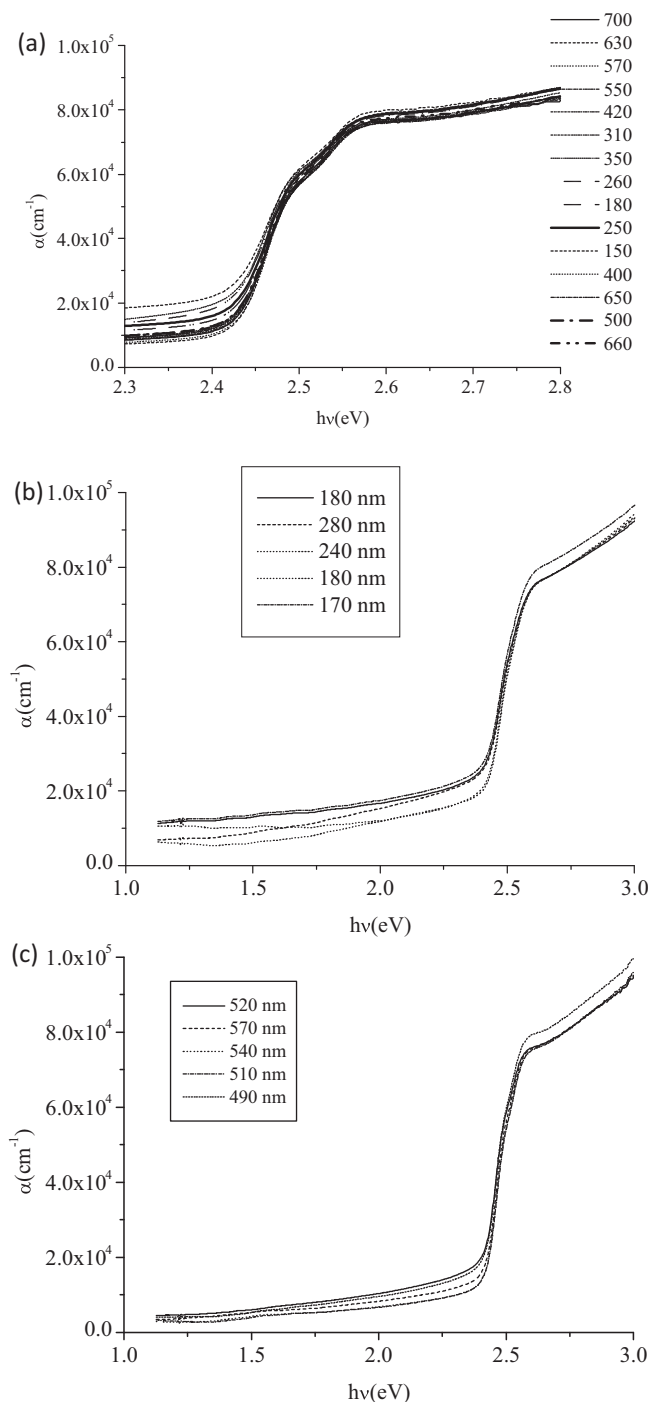


Fig. 3 – The relation between the absorption coefficient α and the photon energy $h\nu$ for CdS:In thin films with different thickness at different substrate temperatures: (a) 490 °C; (b) 450 °C; (c) 375 °C.

between the absorption coefficient and film thickness is obvious for wavelength values smaller than the cut off wavelength. Part (a) of this figure which represents the films deposited at 490 °C is different from the figure obtained by Perna et al. [1] for undoped and indium doped CdS thin films prepared by pulsed laser deposition, where two absorption edges appear her, but just one band edge appears in their plot.

Table 1 – The estimated values of the bandgap energy and width of Urbach tail with the corresponding values of film thickness for the substrate temperature 490 °C.

No.	t (nm)	E_g (eV)	E_e (meV)
1	700	2.443	38.1
2	660	2.442	42.2
3	650	2.441	41.5
4	630	2.445	39.2
5	570	2.444	37.6
6	550	2.443	41.4
7	500	2.441	45.2
8	420	2.442	41.0
9	400	2.443	41.1
10	350	2.441	54.7
11	310	2.441	44.2
12	260	2.436	47.4
13	250	2.440	50.1
14	180	2.439	56.4
15	150	2.431	64.9

Table 2 – The estimated values of the bandgap energy and width of Urbach tail with the corresponding values of film thickness for the substrate temperature 450 °C.

No.	t (nm)	E_g (eV)	E_e (meV)
1	180	2.418	107.5
2	280	2.421	103
3	240	2.433	81
4	180	2.429	83
5	170	2.418	105

Table 3 – The estimated values of the bandgap energy and width of Urbach tail with the corresponding values of film thickness for the substrate temperature 375 °C.

No.	t (nm)	E_g (eV)	E_e (meV)
1	520	2.429	68.9
2	570	2.435	59.3
3	540	2.438	55.0
4	510	2.438	57.2
5	490	2.432	62.2

Parts (b) and (c) represent the films deposited at substrate temperatures 450 °C and 375 °C, respectively. For these deposition temperatures there is a good agreement with Perna et al. [1] for undoped and indium doped CdS thin films. The presence of two absorption edges is most probably interpreted by the presence of two phases of CdS:In (cubic and hexagonal). As we see in the figure, the increase in the substrate temperature encourages the presence of the two absorption edges, which means at low substrate temperatures there is one phase (cubic) and for the higher substrate temperature the two phases are present.

To estimate the value of the bandgap energy a plot of $(\alpha h\nu)^2$ versus $h\nu$ was established assuming that the transition is a direct one and a linear fit was made. The bandgap energy E_g was obtained from the intercept with the energy axis and the results were inserted in Tables 1-3. As the tables show, there is a slight increase of the bandgap with film thickness in all cases, but it is more evident for $T_s = 490$ °C. Fig. 4 displays

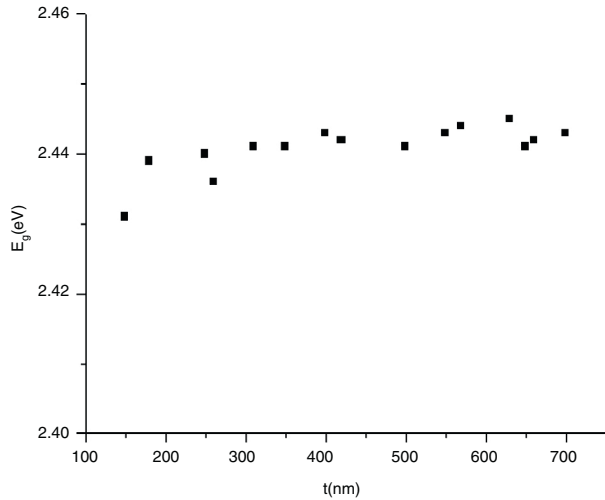


Fig. 4 – The relation between the bandgap energy and film's thickness for CdS:In thin films at $T_s = 490^\circ\text{C}$.

the relation between the bandgap energy with film thickness for this case. As the figure shows, the bandgap energy first increases, then becomes constant. The increase of E_g with film thickness was attributed to the improvement of the crystallinity of the films when they become thicker [12]. That is the grain size increases with film thickness in the beginning and then becomes constant.

The increase of E_g with film thickness that is in agreement with what was obtained for vacuum evaporated CdS thin films [20] for films' thickness 50–700 nm, but the bandgap energy of vacuum evaporated CdS films was increased from 2.347 to 2.500 eV for the increase of film thickness from 50 to 700 nm. Also the increase of bandgap energy with film thickness is consistent with what obtained by Shaaban et al. [22] for CdTe thin films prepared by thermal evaporation on glass substrates at 373 K. They interpreted this result by saying that the optical bandgap increases with the increase in film thickness because the crystallinity of the film also increases due to the increase in crystallite size.

Other authors got a decrease or no change of E_g with film thickness. For example Sahay et al. [19] studied the relation of E_g and film thickness for films of thickness in the range 25–100 nm, and got the smallest $E_g = 2.28$ eV for the thinner film, then they got a decrease of the bandgap energy with thickness. They interpreted this by saying that the lower value of E_g is attributed to the creation of allowed energy states in the bandgap at the time of film preparation, while the higher value of E_g is accounted to the very small grain size of the film. Metin and Esen [4] got a decrease of the bandgap energy with film thickness for CdS films of thickness 0.4–0.8 μm grown by chemical bath deposition (CBD). Albin et al. [23] found that the bandgap of CdS films prepared by chemical bath deposition (CBD) varies significantly with film thickness (decreases), while that of CdS films prepared by closed space sublimation (CSS) does not. They explained these results by saying that variations in the bandgap with thickness for CBD case are a result of the changing growth chemistry present during CBD deposition, and in contrast, the film

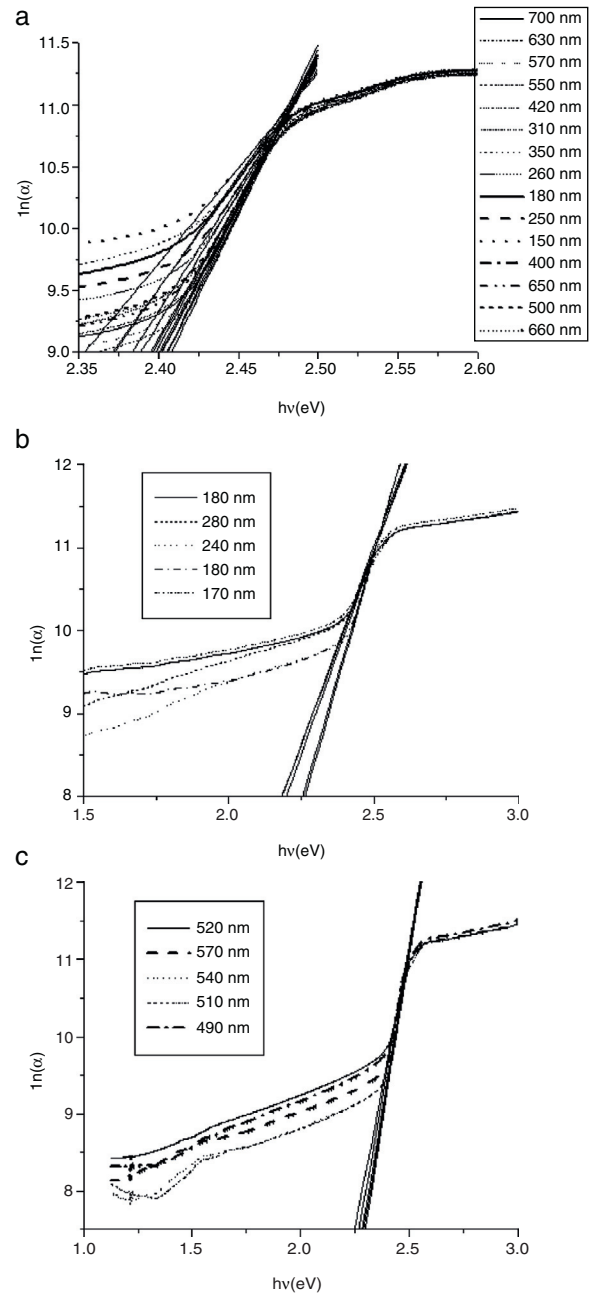


Fig. 5 – A plot and linear fit of $\ln(\alpha)$ against the photon energy $h\nu$ for CdS:In thin films with different thickness deposited at (a) 490°C ; (b) 450°C ; (c) 375°C .

growth mechanisms present during the CSS process are more invariant.

A slight increase of the bandgap with the substrate temperature is also observed. For the films with thickness 180 nm E_g (490°C) = 2.436 eV and E_g (450°C) = 2.418 eV for one film and 2.429 eV for the other. For two films of thickness 570 nm E_g (490°C) = 2.444 eV and E_g (375°C) = 2.435 eV. So the bandgap increased with substrate temperature, which is opposite to the behavior of bandgap energy with temperature known for semiconductors. Our explanation of this behavior is that the higher substrate temperature results in better

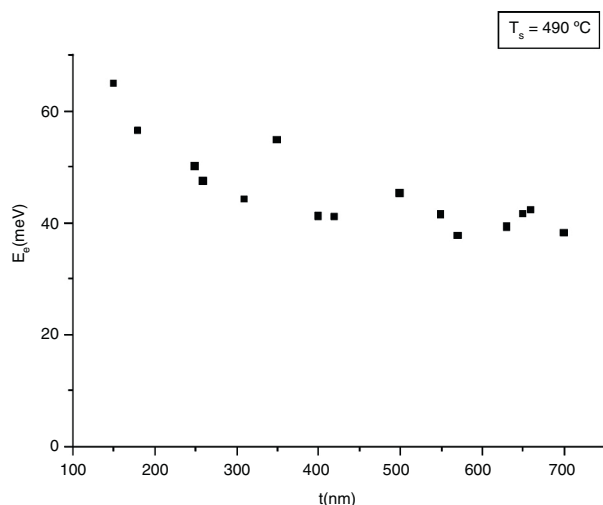


Fig. 6 – The relation between the width of the tail and film thickness of spray-deposited CdS:In thin films at T_s = 490 °C.

crystallization of the films as explained in our previous work [9] and hence more order and smaller density of localized states.

In the low photon energy range it is assumed that the spectral dependence of the absorption edge follows the empirical Urbach rule given by [21,24]

$$\alpha(\nu) = \alpha_0 \exp(h\nu/E_e) \tag{1}$$

where α_0 is a constant, E_e denotes an energy which is constant or weakly dependent on temperature and is often interpreted as the width of the tail of localized states in the bandgap. The exponential tail appears because disordered and amorphous materials produce localized states extended in the bandgap.

A plot of $\ln(\alpha)$ against the photon's energy was shown in Fig. 5 for the three substrate temperatures and a linear fit was established in the linear portions of the curves. The width of Urbach tail E_e was obtained from the fit and the results were inserted in Tables 1-3. The relation between E_e and film thickness for $T_s = 490^\circ\text{C}$ was displayed in Fig. 6, where a decrease of the width of Urbach tail with film thickness can be observed. For $T_s = 375^\circ\text{C}$ and 450°C the relation with film thickness is not apparent because the values of film thickness are close to each other in each case. The decrease with film thickness is due to the increase of order, because as it is mentioned earlier, the crystallization becomes better with film thickness. Also by taking a look to Tables 1 and 2 it is noticed that E_e decreases with the substrate temperature. For the films of thickness 180 nm E_e (490°C) = 56.4 meV but E_e (450°C) = 83 meV for one film and 107.5 meV for another one. The same conclusion could be obtained for other films of comparable thickness too. These results support our interpretation of the increase of bandgap with substrate temperature as mentioned before, since the decrease of E_e with temperature is an indication of the smaller density of localized states.

Bilgin et al. [21] got E_e values in the range 122–175 meV for ultrasonically spray CdS films of thickness 2.8–7.3 μm

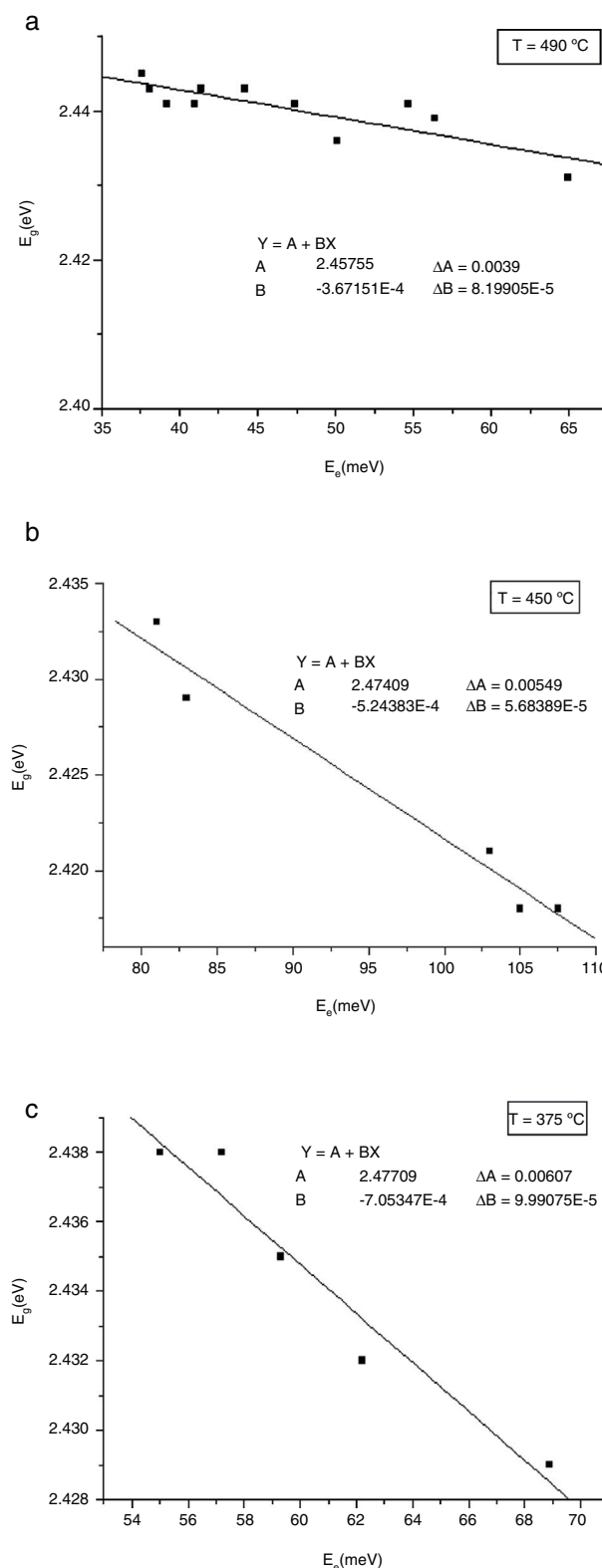


Fig. 7 – The relation between the bandgap energy and the width of Urbach tail for CdS:In thin films deposited at (a) 490 °C; (b) 450 °C; (c) 375 °C.

prepared at substrate temperatures in the range 623–473 K. Our values are smaller than their values despite the fact that their films are thicker than ours. They have a decrease in E_e and they attribute it to the increase in the substrate temperature which is consistent with our results. But the film thickness in their work is also varying so – in our opinion – this decrease in E_e is not only related to the substrate temperature, but also to film thickness.

The relation between the bandgap energy and the width of Urbach tail is shown in Fig. 7 for films deposited at $T_s = 490^\circ\text{C}$, 450°C and 375°C . It is noticed that as the value of E_e increases the bandgap decreases and there is a linear relation between them, so a linear fit was established in each case. The constant A obtained from the fit represents the bandgap energy at $E_e = 0$ or the bandgap in the case of the absence of tailing. The obtained values are 2.458, 2.474 and 2.477 eV for the substrate temperatures 490°C , 450°C and 375°C respectively. So the bandgap value in the case of no tailing decreases with the increase in the substrate temperature, in accordance with the known situation of semiconductors. This result supports our aforementioned explanation of the increase of bandgap energy with the substrate temperature; that is the higher substrate temperature results in films with more order and smaller density of localized states. The values of the slopes of the straight lines in the three fits (B) are -3.67×10^{-4} , -5.24×10^{-4} and 7.05×10^{-4} for the substrate temperatures 490°C , 450°C and 375°C , respectively. So they decrease with the increase in the substrate temperature in accordance with the bandgap energy. This means that as the substrate temperature increases the influence of tailing on the bandgap energy becomes less.

This linear relation between bandgap energy and the width of Urbach tail is similar to that obtained by Melsheimer and Ziegler [25] for tin dioxide thin films, where they have a decrease in the band tail on going from the amorphous to the polycrystalline structure. In this case the width of Urbach tail decreases on going from the thinner to the thicker films which means that from disorder to order in agreement with Melsheimer and Ziegler [25].

4. Conclusions

CdS:In thin films were produced by the spray pyrolysis technique on glass substrates at three different temperatures 375°C , 450°C and 490°C . The transmittance measurements were taken at room temperature in the wavelength range 300–1100 nm. The optical bandgap energy was estimated by assuming a direct transition and found to be slightly increasing with film thickness and substrate temperature. The absorption coefficient was deduced from the transmittance measurements and tailing in the low energy side was observed. From the plot of the natural logarithm of the absorption coefficient against the photon energy it was found that this tailing follows Urbach rule. The width of the tail was estimated and found to decrease with film thickness and substrate temperature due to the increase of order. A linear relationship was found between the bandgap energy and the width of Urbach tail.

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