Optical and Electrical Properties of $CdIn_2S_4$ Thin Films for different Substrate Temperature

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Abstract

Semiconducting $CdIn_2S_4$ thin films have been deposited by spray pyrolysis technique onto glass substrates of varied temperatures from $340°C$ to $420°C$. Using van-der Pauw method, the variation of the electrical resistivity $[(1.6 * 10^{3} - 0.36 * 10^{3})\Omega.cm]$ was found for different substrate temperatures. The as-grown layers were optically characterized in order to evaluate the optical band gaps.Optical investigations show an indirect transition $(E_g^i)$of (2.29-2.20)eV and an optical direct gap (E_g^d) of (2.75-2.61)eV .

Introduction

Spray pyrolysis is one of the most convenient, economical, inexpensive and simple method for preparation of large area of semiconductor thin films.Films manufactured by chemical spray pyrolysis technique, are of promising future applications. To deal with chemical spray pyrolysis technique, one has to deal with different affecting factors: substrate-nozzle distance, substrate temperature, solvent used and solute's concentration, to mention some. Consequently, a study of preparation conditions of these films and their effects on the films properties is a necessity.

Indium-doped-CdS thin films prepared by chemical spray pyrolysis have been investigated by different authors [A.Palafox , et.al;1998, K.S.Ramaiah,et.al;1999]. It has been found that with increasing indium concentration in the sprayed solution there is an increase tendency of the formation of such compounds as $CdIn_2S_4$ and In_2O_3 in the film. It was suggested that the substrate temperature plays some role in the final product's composition and properties. Apparently at high temperatures, the thermal energy provided for the formation reaction is enough to promote the synthesis of such compounds.

Cadmium indium sulphide ($CdIn_2S_4$)is one of the indirect ternary semiconductors chalcogenide compound of the class$A^{II}B^{III}C^{VI}$ (where A=Zn, Cd and Hg; B=Ga, In; and C=S, Se and Te) [R.R.Sawant,et.al;2010, M.Fuentes,et.al;2000]. They are potential materials for applications in solar cells, optoelectronic and photochemical devices, light emitting diodes, non linear optics, photoconductor optical sensing, etc.[R.R.Sawant,et.al;2007,G.F.Epps and R.S.Backer;1982, K.Y.Rajpure, et.al;1999].$CdIn_2S_4$ compound is indirect band gap energy E_g^i which found to be 2.29eV while, the inter-band gap of the direct transition E_g^d has a value of 2.62ev at Room Temperature [H Nakanishi ;1980].

The films of $CdIn_2S_4$ can be synthesized by multimethods as for example: hot wall epitaxy [S.H You,et.al;2004], vacuum evaporation on glass and sapphire substrate [S.Fafard and E.Fortin;1990,A.Bhirud,et.al;2011], chemical sprayed pyrolysis [R.R.Sawant,et.al;2010, R.R.Sawant,et.al;2007, G.F.Epps and R.S.Backer;1982 , R.R.Sawant and C.H.Bhosale ;2006]. The films show a poly-crystalline structure [K.Y.Rajpure, et.al;1999 , R.R.Sawant and C.H.Bhosale ;2006]. Unfortunately, due to complexity of heavily Indium –doped- Cadmium Sulphide films formed by chemical spray pyrolysis the results published by different workers of the physical properties are not always in a good agreement [K.Y.Rajpure, et.al;1999 , R.R.Sawant and C.H.Bhosale ; 2006 , A . N . Georgobiani , et.al ; 1984 , S.N.Baek,et.al;2004, P.PHankare,et.al;2006, A.V.Kokate,et.al; 2006, A.V.Kokate,et.al;2006].

In this article, we report the results on an investigation of the optical and electrical resistivity of chemical spray pyrolysis $CdIn_2S_4$ films under different substrate temperature. The Cd:In:S ratio used in the sprayed solution is 1:2:4. The study shows the role-plays by the substrate temperature on the properties of the prepared films.

Experimental Technique

The sprayed is achieved by mixing 0.05M aqueous solution, of $CdCl_2$, $CS(NH_2)_2$, and $In(NO_3)_3$. The Cd:In:S ratio in the solution was 1:2:4. The obtained solution is immediately sprayed onto temperature-controlled glass substrate. The substrate is heated at the required temperature for 20min previous to the spraying. The spraying was carried out on and off periodically (10sec on and 20sec off). The sprayed rate is 1ml/min. By this procedure; the substrate is kept at the required temperature. It also gives enough time for the solution droplets to evaporate and the compound to settle down. The diameter of the spray nozzle is about 0.3mm. The nozzle to substrate distance was 30cm. More details of the spray set-up and the preparation technique have been described elsewhere [O.P.Agnihotri, et.al;1983].

In this work, the spraying set-up is kept constant except the substrate temperature (T_S) has changed from 340-420$°C$. The thickness of the prepared films was in the range (0.12-0.26)μm.The films obtained were clear, transparent, and yellow in color, with good adhesive to the substrate and exhibit smooth surfaces free from pinholes.

The optical absorbance measurements are carried out using Pye-Unicom SP-800 UV/VIS spectrophotometer. It covers the range from 200-900nm. The resistivity was measured using Van-der Pauw method [J.L.van-der Pauw; 1958]. Ohmic contacts were prepared by evaporation of Aluminum electrodes. All measurements (optical and electrical) were carried out at room temperature. Hot probe measurements proved that the films were P-type.

Results and Discussion

The absorption data was analyzed in accordance with the theory of Bardeen et al [J.Bardeen,et.al;1956], which gives for direct transition:

$$\alpha = \alpha_o\left(h\nu - E_g^d\right)^{1/2}$$

(1)

WhereE_g^d, is the direct allowed transition, and α_o is a constant dependant on the probability of the transition. The plot of α^2 versus $h\nu$ is shown in Fig.(1) for films deposited at different substrate temperatures. The extrapolation of the linear region of $\alpha^2 = 0,$ gives according to the equation the direct allowed band gap.

To obtain information concerning the indirect band gap transition and phonon involvement, the low absorption region data was analyzed again in the frame of the same model which gave the equation [E.A.davis and N. F.Mott; 1970]:

$$\alpha h\nu = \alpha_o\left(h\nu - E_g^i \pm E_{Ph}\right)^2$$

(2)

WhereE_g^i, is the indirect allowed transition, and E_{Ph} is the absorbed (+) or emitted (-) phonon energy. Fig.(2), shows the relation between $(\alpha h\nu)^{1/2}$ versus $h\nu$ for the case of substrate temperature ($T_S = 390°C$). The plot shows, two straight line portions, the lower energy line corresponds to phonon absorption term having energy intercept at$E_g^i - E_{Ph}$, while the other line portion corresponds to phonon emission term having energy intercept at $E_g^i + E_{Ph}$. By adding the two results together, one can evaluate $E_g^i\ and\ E_P$. Fig.(3) shows the calculated phonon energy(E_{Ph}), direct energy gap(E_g^d), and indirect band gap (E_g^i)as a function of substrate temperature (T_S).

It is well known that CdS thin films have a direct optical band gap 0f 2.38eV [A.Palafox,et.al;2010]. For CdS:In the optical direct band gap ranges from 2.5-2.9eV [A.Palafox,et.al;2010]. To compare these results with the values obtained by this work. The indirect optical energy gap (E_g^i) is clearly due to the presence of $CdIn_2S_4$ compound. The variation of (E_g^d) with the substrate temperature may be correlated to the presence of other phases of Cd or In compounds.

Table (1) below shows a summery of some experimental values for (E_g^d) and (E_g^i) for $CdIn_2S_4$films and crystal compared with this work.

Table 1: The experimental data for the direct and indirect energy gaps for $CdIn_2S_4$ compound for different techniques.

	Direct Energy gap	Indirect energy gap	Reference	remarks
Thin films				
Spray pyrolysis	2.16 -2.22	2.14 – 2.15	13,20,22	N - type
Electro-chem.	2.16 – 2.17		4,5,19	N - type
Chemical	2.3 – 2.42		14, 29	N - type
Hot wall epitxy method	2.62		25	P - type
Crystal	2.62	2.29	8 ,26	

From the above table; this work is in accordance with films grown by hot wall epitaxy method [S.H You,et.al;2004]. Same results were obtaind in ref [H Nakanishi ;1980, S.N.Baek,et.al;2004].

One can mention here, some times S- atoms play some role as point defect (acceptor) in preparing $CdIn_2S_4$ films which coverts the films into the optical p-type [S.H You,et.al;2004].

Fig.(4) shows the resistivity (ρ) as a function of substrate temperature. It can be seen that the resistivity decreases steeply with increasing the substrate temperature up to $390°C$ and then increases slightly. The lowest value of the electrical resistivity $(0.36*10^{3})\Omega.cm$ is achieved for films prepared at substrate temperature around $390°C$. This value is of two orders of magnitude less than $10^5\Omega.cm$ reported for $CdIn_2S_4$ thin films [S.Fafard and E.Fortin;1990] and far less than $10^6-10^7\Omega.cm$ reported for $CdIn_2S_4$ single crystal [A.N. Georogobiani,et.al; 1984].

Conclusion

The picture arises from the investigation is the following: The condition of the technique used (considering the high percentage of indium plus the high substrate temperature), apparently promotes the formation of $CdIn_2S_4$ thin films. It is to be understood that the films prepared for our investigation have in fact a polycrystalline structure of a mixture of compounds: such as CdS, CdS:In, In_2O_3, besides $CdIn_2S_4$. The dominant (if not the major) factor in the optical absorption is controlled by the $CdIn_2S_4$ parameters. These parameters (and may be via interacting with other factors) are a function of substrate temperature. In this work a direct allowed transition (2.75 to 2.61)eV and indirect transition (2.29 to 2.20)eV with phonon energy (0.15 to 0.07)eV depending on the substrate'stemperature. These values are comparable with those of$CdIn_2S_4$ crystals reported in the literature [H Nakanishi ;1980, S.N.Baek,et.al;2004]. These results are in accordance with the idea that the $CdIn_2S_4$ is the dominant compound in the present films.The fact that the films are P-type suggests that (E_g^i) corresponds to the acceptor levels for $CdIn_2S_4$ single crystals [A.N.Georgobiani,etal;1984]. The reported donor levels due to deep-seated traps [A.N.Georgobiani,etal;1984] or those with Gaussian distribution from the bottom of the conductivity band [S.Charbonneau,et.al;1985] did not show up in our investigation. These localized levels within the gap are usually related to structure defects, which in turn are due to preparation condition [A.N.Georgobiani,etal;1984, S.Charbonneau,et.al;1985]. Besides, there is some evidence of self composition mechanism of donor state in indium doped CdS [U.V.Desnica,et.al;1999].

The variation of the optical gap (and consequently the indirect transition or acceptor level) with the substrate temperature can be divided into two regions. The first region where there is a strong dependence on the temperature, the second one is nearly temperature independent. An increase in the disorder/order ratio would expect to narrow the gap [J.M. Zimen; 1979]. Consequently, the behavior of the gap may be explained by increasing this ratio of disorder/order ratio by increasing substrate temperature, which would attain a saturation value beyond $390°C$.

Before any conclusion can be drawn from the above results, further studies are needed for the possibilities of using such technique and such films in device application.

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<u>Figure Captions</u>

Fig. (1): α^2 versus $(h\nu)$ for films deposited at different substrate temperature.

Fig. (2): $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ for film deposited at $T_S = 390°C$.

Fig. (3): The variation of direct band gap E_g^d , indirect band gap E_g^i , and

Phonon energy E_{ph} as a function of substrate temperature (T_S).

Fig. (4): The resistivity (ρ) as a function of substrate temperature (T_S).

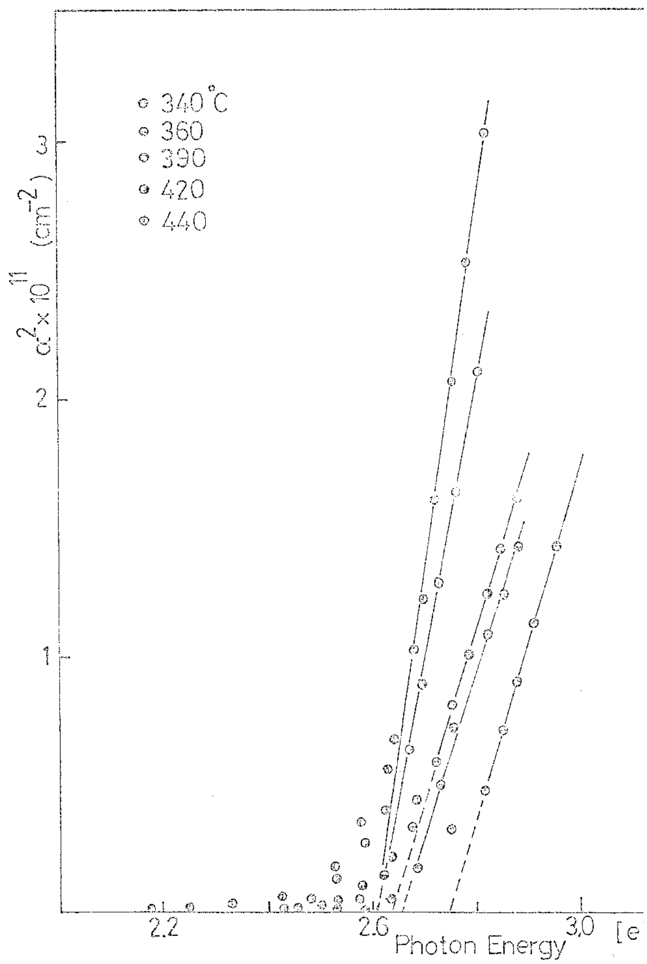

Fig. (1): α^2 versus (hv) for films deposited at different substrate temp

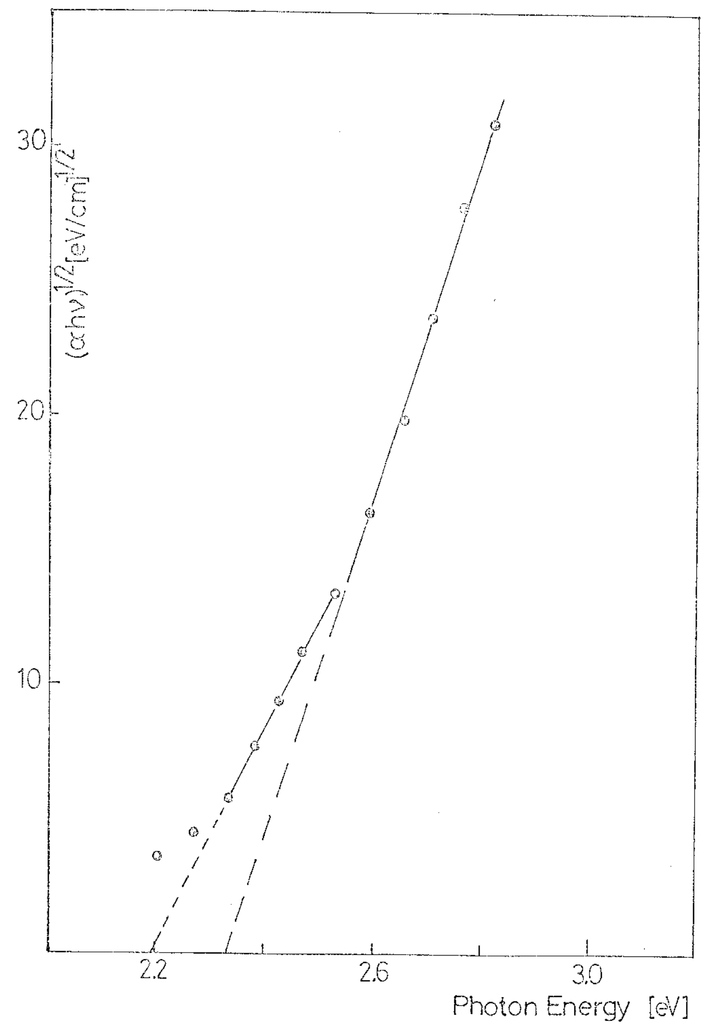

Fig. (2): $(\alpha h\nu)^{1/2}$ versus (hν) for films at T_s= 390°C.

From the intercepts, it is found that Eg^i =(2.22+0.02) eV, and E_p=(0.07+0.005) eV.

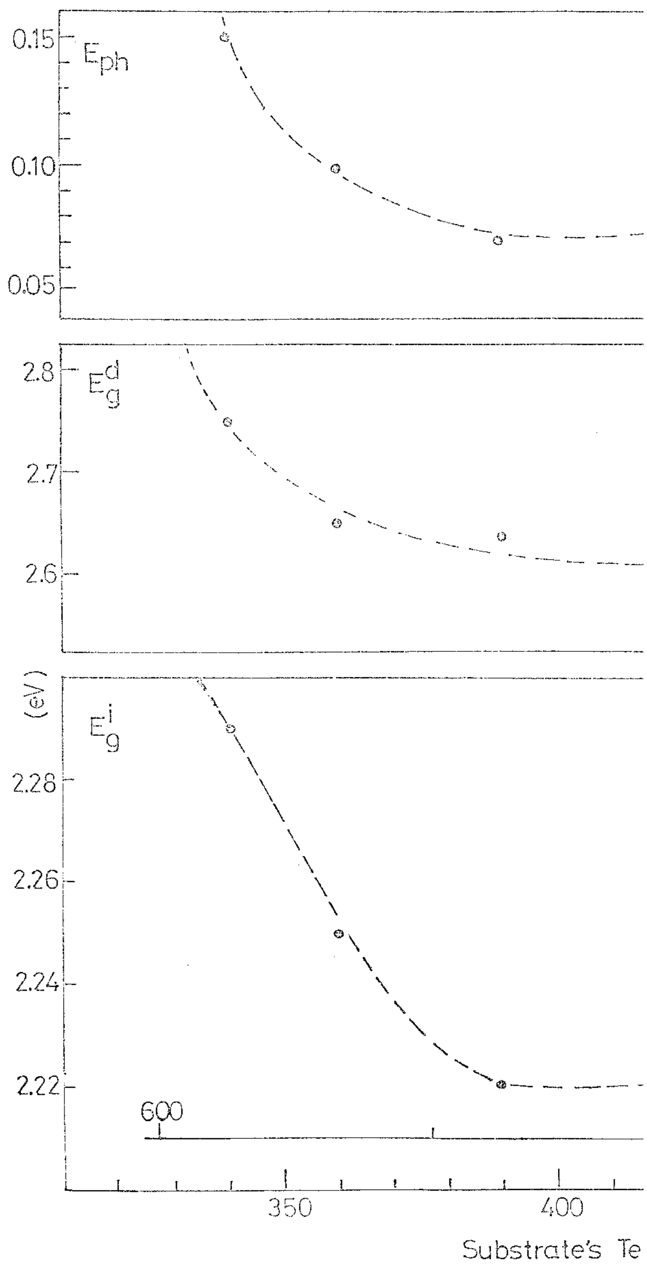

Fig. (3): The variation of direct band gap E_g^d , indirect ba

phonon energy E_{ph} as a function of substrate ten

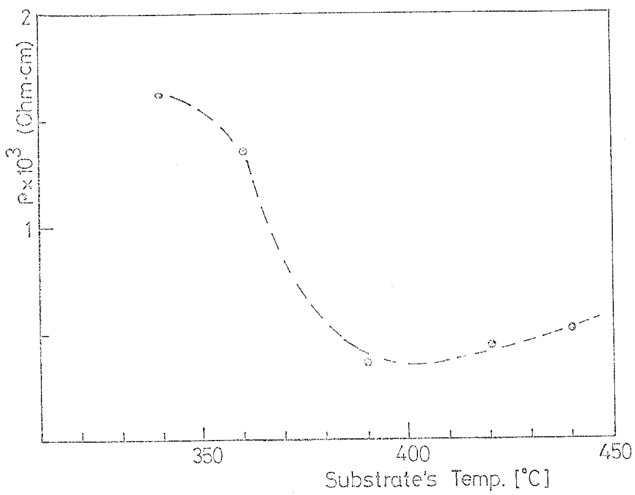

Fig. (4): The resistivity (ρ) as a function of substrate temperature (T_s).

الخواص الضوئية والكهربائية لاغشية المركب $CdIn_2S_4$ المحضرة بدرجات حرارية مختلفة

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المستخلص

حضرت الاغشية الرقيقة شبة الموصلة للمركب $CdIn_2S_4$ بطريقة الرش الكيميائي الحراري على قواعد زجاجية لدرجات حرارية مختلفة تتراوح من $340\ ^OC$ الى $420\ ^OC$.

باستعمال طريقة فاندر باو لقياس المقاومة الكهربائية وجد ان تغير المقاومية الكهربائية ضمن المدى $[(1.6x10^{+3}$ - $0.36x10^{+3})\Omega.cm$ عند درجات حرارية مختلفة للقاعدة . من تشخيص الخواص الضوئية للنماذج اتضح وجود انتقالات غير مباشرة بفجوة طاقة غير مباشرة E^i_g ضمن المدى $(2.29\text{-}2.20)eV$ وبفجوة طاقة مباشرة E_g^d ضمن المدى $eV\ (2.6 - 2.75)$.