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Preparation of cadmium oxide films by spray pyrolysis and its conversion into cadmium chalcogenide films

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Thin films of cadmium oxide were prepared on to glass substrates by a spray pyrolysis technique from an aqueous solution of cadmium chloride. Cadmium oxide films are further converted into cadmium chalcogenide films by using simple chemical displacement method. The cadmium oxide films were dipped into sodium sulphide and sodiumseleno sulphate solution to convert into CdS and CdSe films respectively. The XRD studies show that the films of CdO and CdSe are microcrystalline, however films of CdS are polycrystalline. The optical absorption studies gives the bandgap energies as 2.45, 2.30 and 1.9 eV for the CdO, CdS and CdSe films respectively.

1 Introduction

In recent years, there has been growing interest in II-VI materials because of their potential applications in electronics and optoelectronics devices[1-4]. Cadmium sulphide and cadmium selenide compounds belongs to II-VI group and are used in the variety of semiconductor devices such as solar cells, transistors, photoconductors and recently in light activated values for large screen liquid crystal displays[5,6]. Extensive studies have been made on CdS both in single crystal and thin film form. Films of CdS and CdSe were prepared by various chemical and physical methods and their characteristics have been studied. Recently Lokhande *et al.*[7,8] have reported chemical conversion of SnS_2 in Ag_2S film by ion displacement method. This is a simple and inexpensive technique as compared with chemical methods.

In the present investigation, thin films of CdO are spray deposited from cadmium chloride solution at 400°C and then converted into CdS and CdSe by using chemical conversion method at room temperature (27°C). The structural, optical, electrical properties of such films are studied.

2 Experimental Procedure

Thin film of cadmium oxide were prepared by spray pyrolysis method by using 0.1 M aqueous solution of cadmium chloride. The glass substrates used are ultrasonically cleaned. Solutions of cadmium chloride was sprayed through a glass nozzle onto hot glass substrates kept at 400°C. The spray rate was maintained as 4 cc /min. by using air as a carrier gas. For the chemical conversion of CdO films into CdS films, the CdO films were dipped in a (1 M) Na_2S solution (pH = 10) for ten minutes. Similarly CdO films were dipped into Na_2SeSO_3 solution (pH = 9.3) for 2 hours to convert into CdSe films. The conversion was carried out at room temperature (27°C). The X-ray diffraction analyses were performed for films by using Philips (PW-1710) diffractometer to study the crystals structure of the films. The optical absorption was studied with in the wavelength range 300 to 900 nm by using a Hitachi, Japan spectrophotometer (UV-VIS-NIR) model 300. A two probe method was used for the resistivity measurement. Thermoelectric power study was carried out to determine the type of conductivity of the films.

3 Results and Discussion

3.1 Film formation mechanism

Aqueous solution of (01.1 M) cadmium chloride, was sprayed over the hot substrates kept at 400°C, cadmium chloride decomposes at 400°C substrate temperature and results into formation of cadmium oxide films on glass substrates. The possible reaction that took place is as follows.

$$CdCl_2 \xrightarrow[air]{\Delta} CdO + Cl_2$$

The CdO films are yellowish, uniform and adherent to the substrates. The thickness of the fill was in the range of 0.4 to 0.5 micron.

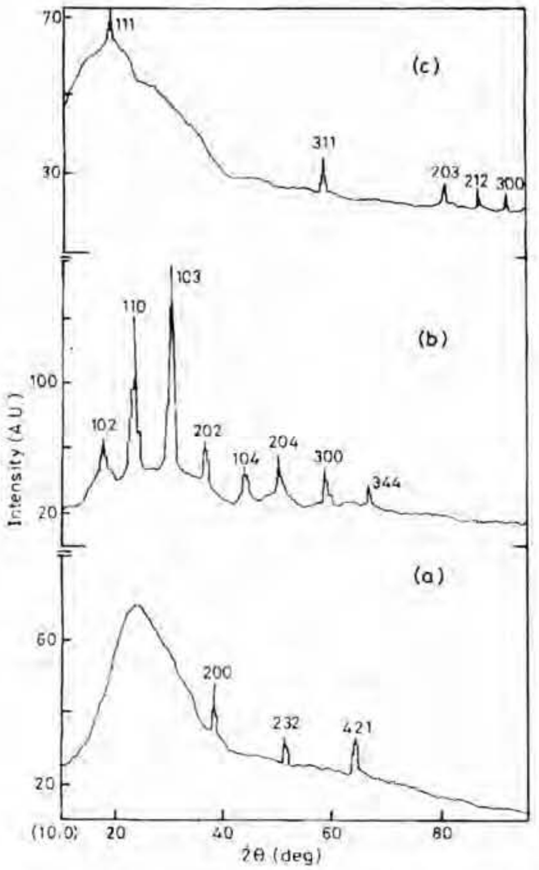

Fig. 1 — XRD patterns of (a) CdO and chemically converted (b) and (c) CdSe thin films

Chemical conversion is a process which can be defined by the following reaction

$$\text{Sub/MY} \xrightarrow{X^{n-}} \text{Sub/MX}$$

Using above method, in the present investigation,

$$\text{Sub/CdO} \xrightarrow{S^{2-}} \text{Sub/CdS, and}$$

$$\text{Sub/CdO} \xrightarrow{S^{-2}} \text{Sub/CdSe}$$

A oxygen ion is displaced by S and Se ions, converting the films of CdO into CdS and CdSe respectively.

3.2 X-ray diffraction

Structural analyse of as deposited CdO, and chemically converted CdS and CdSe films was carried out by using CuK_α radiation source having wavelength of 1.5406A. Data were collected for the variation in diffracting angle 2θ from 10° to 100° with a step width of 0.02 Fig. 1(1, b, c) shows X-ray diffraction patterns of CdO and chemically converted CdS and CdSe thin films. From the figures, it is seen that CdO films chemically converted CdSe films are amorphous or consist of fine grains however, converted CdS films are nanocrystalline. The observed *d* values of CdO, CdSe and CdS are in good agreement with standard *d* values of ASTM data and are compared in Table 1. The XRD patterns of chemically converted CdS and CdSe films do not show the presence of CdO peak indicating complete conversion of CdO into CdS and CdSe.

Table 1 — Comparison of observed *d* values with standard *d* values of CdO, and chemically converted CdS and CdSe for CdO

Sample	Observed *d* values	Standard *d* values	Planes
	2.3232	2.34	200
CdO	1.7449	1.738	232
	1.4702	1.471	421
	2.4679	2.450	102
	1.0659	2.068	110
	1.8944	1.898	103
CdS	1.5859	1.581	202
	1.5087	1.520	104
	1.4249	1.453	204
	1.2235	1.2247	300
	1.1846	1.1860	344
	3.510	3.510	111
	1.840	1.833	311
CdSe	1.470	1.450	203
	1.27	1.300	212
	1.259	1.241	300

3.3 Optical absorption

The optical absorption spectra of the CdO, CdS and CdSe films were studied. It is observed that absorption coefficient (∝) decreases with increase in wavelength and sharp cutoff is observed near the absorption edge. The optical absorption data were further analysed by plotting the graph $(\propto h\nu)^2$ vs hv and are shown in Fig. 2. The band gap energies of CdO, CdS and CdSe films were estimated by extrapolating the linear part of these plots to energy axis. The estimated band gaps of CdO and chemically converted CdS and CdSe are 2.45, 2.3 and 1.9 eV respectively. These results are well agreement with the results reported by other workers[7,9] for chemically deposited films. This change in the band gap

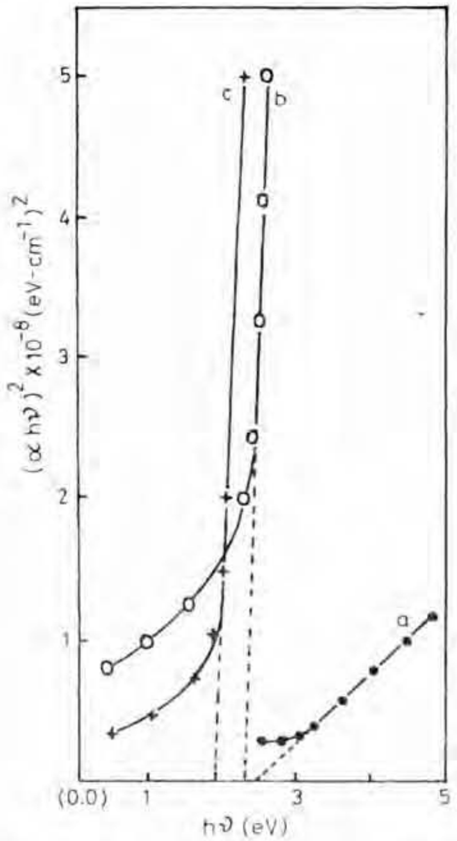

Fig. 2 — Variation of $(\alpha h\nu)^2$ versus $h\nu$ of (a) CdO and chemically converted (b) CdS, and (c) CdSe films

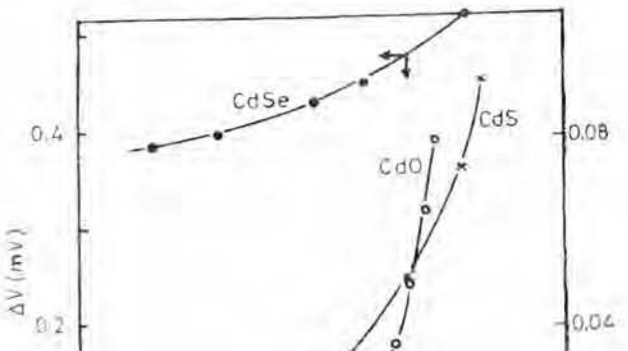

Fig. 3 — Dark electrical resistivity variation (ρ) with temperature for (a) CdO, and chemically converted (b) CdS and (c) CdSe films

values of CdO films also confirms the formation of CdS and CdSe by the present chemical conversion method.

3.4 Thermoelectric power

Thermoelectric power was measured as a function of temperature with in the temperature range 300-500 K. The thermoemf varies exponentially with respect to temperature for all the samples indicating semiconducting behaviour of the films. Fig. 3 shows the variation of thermoemf ΔV vs change in temperature ΔT for CdO, CdS and CdSe films. The polarity of the thermoemf at the hot end was positive which shows that the films of CdO, CdS and CdSe films have n-type electrical conductivity which is in good agreement with the results reported by others[10,11].

3.5 Electrical properties

The dark electrical resistivity of CdO and chemically converted CdS and CdSe films was measured as a function of temperature. It is interesting to note that resistivity of the film was increased after chemical conversion is higher for CdSe than CdS films. Fig. 4 shows the variation of dark electrical resistivity with reciprocal of temperature. It is found that the resistivity decreases linearly with increase in temperature indicating semiconducting behaviour of the CdO, CdS and CdSe. The data were further analysis to determine the activation energy by using the relation,

$$\rho = \rho \exp^{\Delta E/KT}$$

where ΔE is the activation energy and other terms have their usual meanings. The graph shows two distinct regions corresponding to low and high temperatures, for CdS and CdSe films which indicates the presence of shallow and deep trap levels, however, only one shape was found in case of CdO films. The activation energies in low and high temperature regions are calculated and are listed in Table 2.

Table 2 — Estimated activities for the plot of log ρ versus $1/T$

Sample	High temp. region eV	Low temp. region eV
CdO	0.29	
CdS	0.25	0.07
CdSe	0.17	0.14

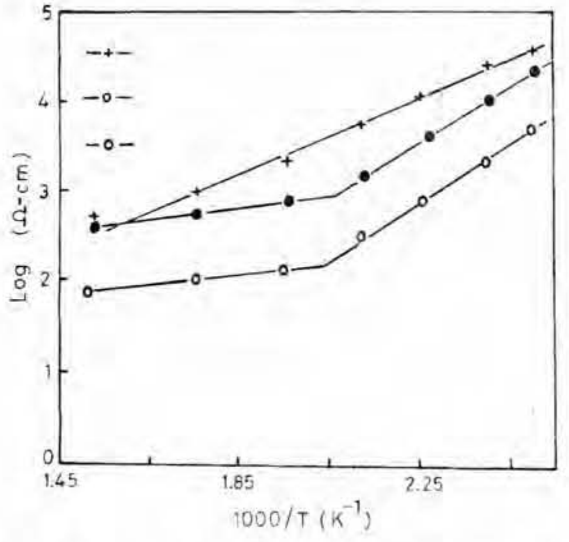

Fig. 4 — Thermo emf (Δv) versus temperature difference (ΔT) of (a) CdO and chemically converted (b) CdS and (c) CdSe thin films

3.6 Scanning electron microscopy

SEM micrographs of as deposited CdO and chemically converted CdS and CdSe films on glass substrates are shown in Fig. 5 (a-c). Cadmium oxide films consists of fine grains and show full coverage to the substrate. When CdO films were chemically converted into CdS and CdSe films, the surface becomes smooth with the presence of some loosely bound particles. These changes took place during the conversion of CdO films into CdS and CdSe films.

4 Conclusion

Deposition of CdO films was made by spray pyrolysis method and these films can be chemically converted into CdS and CdSe by chemically conversion methods. The CdO and converted CdSe films are amorphous and consist of fine grains and CdS films are nanocrystalline. The conversion of CdO films into CdS and CdSe was confirmed by optical absorption and XRD and it was concluded that such conversion is possible by chemical conversion method.

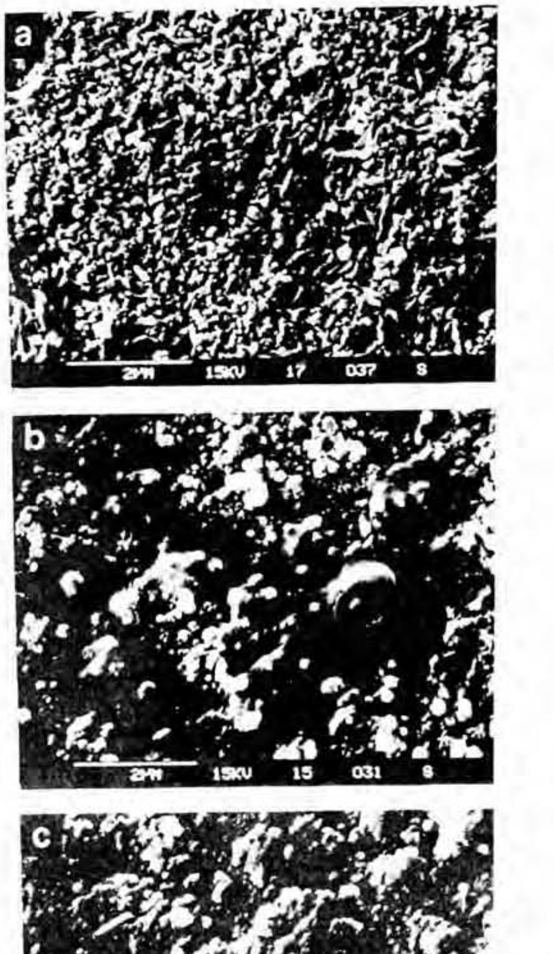

Fig. 5 — Scanning electron micrographs of (a) CdO and chemically converted (b) CdS and (c) CdSe films magnifications.

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