

Abstract

(Topic-Deposition Techniques)

PREPARATION OF ANTIMONY - DOPED TIN-OXIDE FILMS BY DIPPING PROCESS

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Sb-doped SnO₂ films have been prepared by dipping process, where substrates were withdrawn at a controlled speed from a solution of SnCl₂ in alcohol with requisite amount of SbCl₃ as dopant, and dried in a desiccator and finally baked at a temperature of 600°C. Films were obtained in the thickness range 400 Å - 3000 Å and are smooth and quite uniform. The sheet resistance of the films lie in the range 10⁵ - 10⁷ Ω/□ . This high value of sheet resistance, compared to SnO₂ films made by other method is possibly due to the amorphous nature of the film.

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CADMIUM SULPHIDE THIN FILMS BY THE DIP TECHNIQUE

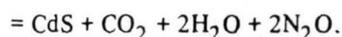
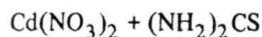
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Cadmium sulphide is one of the most studied materials useful for the fabrication of various solid-state devices such as photoconductive and solar cells. In this communication we report a new simple and low cost method for depositing cadmium sulphide thin films by the dip technique.

Traditionally, the dip technique has been used for the deposition of oxide films [1]. For depositing cadmium sulphide, the substrate is withdrawn vertically from a solution of cadmium nitrate and thiourea in methanol at a controlled speed of ≈ 1 mm/s, when a liquid film adheres to the substrate. It is then subjected to a high-temperature treatment at 250 to 400°C. This results in a solid film of cadmium sulphide according to the well-known reaction



By varying the speed of withdrawal of the sub-

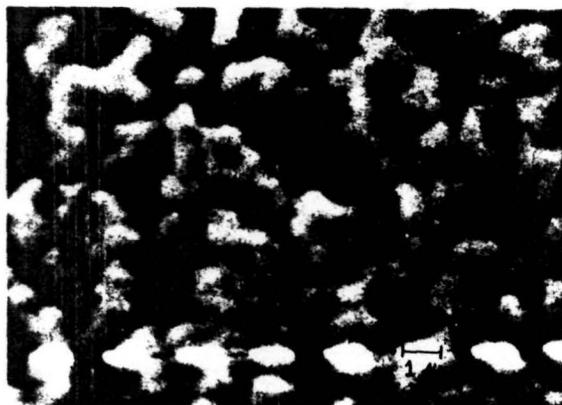


Fig. 1. SEM photograph of CdS film prepared by the dip technique.

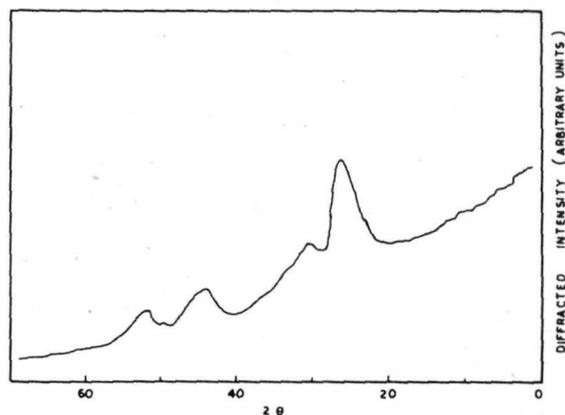


Fig. 2. X-ray diffractogram of CdS film.

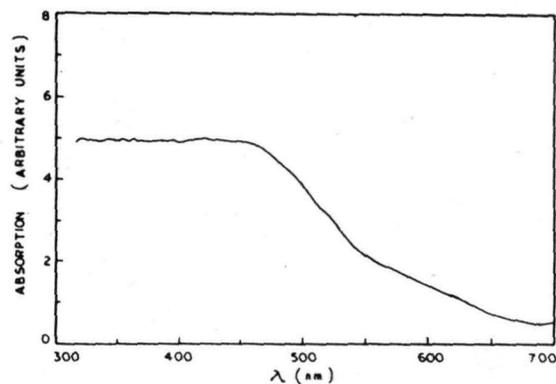


Fig. 3. Optical transmission curve of CdS film.

strate and concentration of the reactants, films having thicknesses 500 Å to 1 μm could be obtained. Films that were produced were smooth and uniform at low thicknesses (≈3000 Å), but tended to be rough and grainy when the thickness was higher (≈1 μm). It was not possible to measure the thickness of the thicker films by interferometry.

The surface topography of the samples, as studied by SEM showed that films with grain size ≈1 μm can be obtained (fig. 1).

From the X-ray diffractometer data (fig. 2), the films appeared to have a predominantly zinc blende structure. Optical transmission data correspond to that of cadmium sulphide films prepared by other methods (fig. 3).

The dip technique for sulphide films is essentially a variant of the familiar spray pyrolysis process. The difference here is that the substrate and the reactants are initially at room temperature and, being in contact, rise in temperature at the same rate. The relative ease and simplicity of the dip technique should make it attractive for the deposition of sulphide films.

Reference

- [1] H. Schroeder, in: *Physics of thin films*, Vol. 5, eds. G. Hass and R.E. Thun (Academic Press, New York, 1969) pp. 87-141.

PREPARATION AND STUDY OF SULPHIDE THIN FILMS DEPOSITED BY THE DIP TECHNIQUE

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Cadmium, zinc and Cd–Zn mixed sulphide films were prepared by the dip technique. In this method, the substrate is withdrawn from a methanol solution of the relevant nitrate(s) and thiourea and baked at a high temperature to form the film. The maximum film thickness obtainable per dipping (deposition cycle) is about 5000 Å. CdS films show a zinc blende structure, whereas ZnS films are completely amorphous. Cd–Zn mixed sulphide films consist of an aggregate of amorphous zinc sulphide and partially crystalline CdS phases. The grain size, typically 1 µm, is found to increase with number of dippings.

1. INTRODUCTION

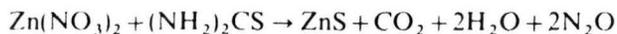
Sulphide thin films find extensive use in the fabrication of a number of solid state devices such as photoconductive and solar cells, thin film transistors and electroluminescent cells. A large variety of deposition techniques, which include vacuum evaporation, spray pyrolysis, sputtering, molecular beam epitaxy, vapour phase epitaxy, chemical vapour deposition, solution growth, screen printing and electrophoresis have been used for the preparation of these films. In recent years, a large amount of effort has been put into developing simple and low-cost methods for the deposition of these films suitable for device applications¹.

The dip technique for the preparation of oxide thin films was quite popular before the widespread use of the vacuum evaporation technique². It is very rarely used at present, the main reason being that it is limited to oxide films only. The method involves the dipping of the substrate in a solution of the corresponding metal nitrate in an organic solvent, withdrawal at a controlled speed and subsequent high temperature baking, when the nitrate decomposes to yield the oxide. It has been found that, by adding a suitable sulphur-containing compound, sulphide films can also be deposited by this technique³.

In this paper, we report the preparation of cadmium, zinc and mixed Cd–Zn sulphide films by the dip technique and the properties of these films obtained under various deposition conditions.

2. EXPERIMENTAL DETAILS

The experimental arrangement is shown in Fig. 1. The substrate was withdrawn vertically from a methanol solution of (1) cadmium nitrate, zinc nitrate or a mixture of the two and (2) thiourea in the requisite amounts at a controlled speed of about 1 mm s^{-1} with the help of a pulley and a geared motor. The substrate together with its adhering liquid film is transferred to a furnace at a temperature of 200–400 °C and baked in air for 5 min. The reaction that takes place is typically (for ZnS)



Since the emphasis was on the deposition of films that were as thick as possible, methanol was chosen as the solvent because of the high solubility of thiourea and the metal nitrate in it and also because of its good wetting property.

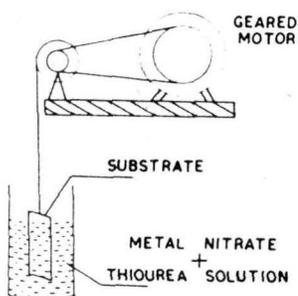


Fig. 1. Experimental arrangement for thin film deposition by the dip technique.

Preparation and study of CdS films were carried out for different baking temperatures, Cd:S ratios, types of substrate and numbers of dippings (in the following, the term "dipping" is used to mean one complete dipping-withdrawal-baking cycle). ZnS and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ films were prepared for a fixed M:S ($M \equiv \text{metal}$) ratio (1:1) and at a 400 °C baking temperature only. Except for CdS films on aluminium sheet, mica and transparent conducting SnO_2 , all films were prepared on soda-glass microslides.

Optical transmission measurements for the films were made over the wavelength range 320–600 nm with a Shimadzu UV 240 double-beam spectrophotometer with a bare soda-glass substrate placed in the reference beam.

3. RESULTS AND DISCUSSION

The films were uniform except for a vertical region about 2 mm wide (in the orientation in which the substrate was withdrawn) on the sides of the substrate and a horizontal region about 1 cm wide at the bottom. The thicker layer at the sides is caused by edge non-uniformities, as may be expected. The "trouble zone" at the bottom is produced because an extra amount of liquid adheres owing to surface tension. Studies were carried out on the uniform central part of the films. By varying the concentration of the starting solution and the speed of withdrawal, films having a

thickness of about 500–5000 Å could be obtained per dipping. The films were smooth at low thicknesses (no more than 3000 Å) but were rough and grainy at higher thicknesses (about 10000 Å). The thickness of these rough films was estimated gravimetrically, as standard optical interferometric techniques could not be used.

Adhesion of CdS films to the substrate was found to be dependent on the Cd:S ratio in the starting solution. Films with Cd:S = 2:1 and 1:1 are strongly adherent, whereas those with Cd:S = 1:2 have very poor adhesion properties. It is presumed that for Cd:S \geq 1:1 a certain amount of CdO is formed, which bonds strongly with the substrate surface. ZnS and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ films with M:S = 1:1 also show good adhesion.

3.1. CdS films

The surface morphologies of the CdS films prepared under various deposition conditions are shown in Fig. 2. It is seen that the grain size does not depend significantly on the baking temperature. It is, however, found that the grain size increases rapidly with the number of dippings but levels off after about five to six dippings. Except for the film produced by a single dipping, all subsequent films are really deposited on the underlying CdS layer, and it is clear that this exerts a substantial influence on the growth of the subsequent layer formed. This is also corroborated by the fact that the rate of increase in thickness per dipping is lower for the first dipping compared with the subsequent dippings (Fig. 3).

It was also found that the smoothness of the films as observed visually increases with the number of dippings, which is probably connected with the increase in grain size mentioned earlier. Films produced by more than five dippings also show evidence of dendrite-like growth.

There is no significant difference between films produced on glass, aluminium, mica or transparent conducting tin oxide substrates (Figs. 2(d) and 4).

X-ray diffractograms for typical films with Cd:S ratios of 1:1, 2:1 and 1:2 are shown in Fig. 5. The films show a predominantly zinc blende structure. In addition, the films with a Cd:S ratio of 2:1 show peaks corresponding to CdO as may be expected. The films with 1:1 stoichiometry gave the best diffraction peaks.

From optical transmission measurements (Fig. 6), the absorption edge is seen to occur at approximately 520 nm, corresponding to a band gap of 2.38 eV.

3.2. ZnS films

ZnS films show a grainy structure essentially similar to those of CdS (Fig. 7(a)). X-ray diffractometry shows, however, that the films are completely amorphous (Fig. 8). The optical absorption data in Fig. 6 show an absorption edge at approximately 340 nm (3.64 eV).

3.3. $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ films

Mixed Cd–Zn sulphide films having the composition $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ are important for the fabrication of Cu_2S solar cells. Figures 6, 7(b) and 8 show the optical absorption data, surface topography and X-ray diffractogram respectively for a typical film. It is seen that the diffraction peaks for this material occur at the same

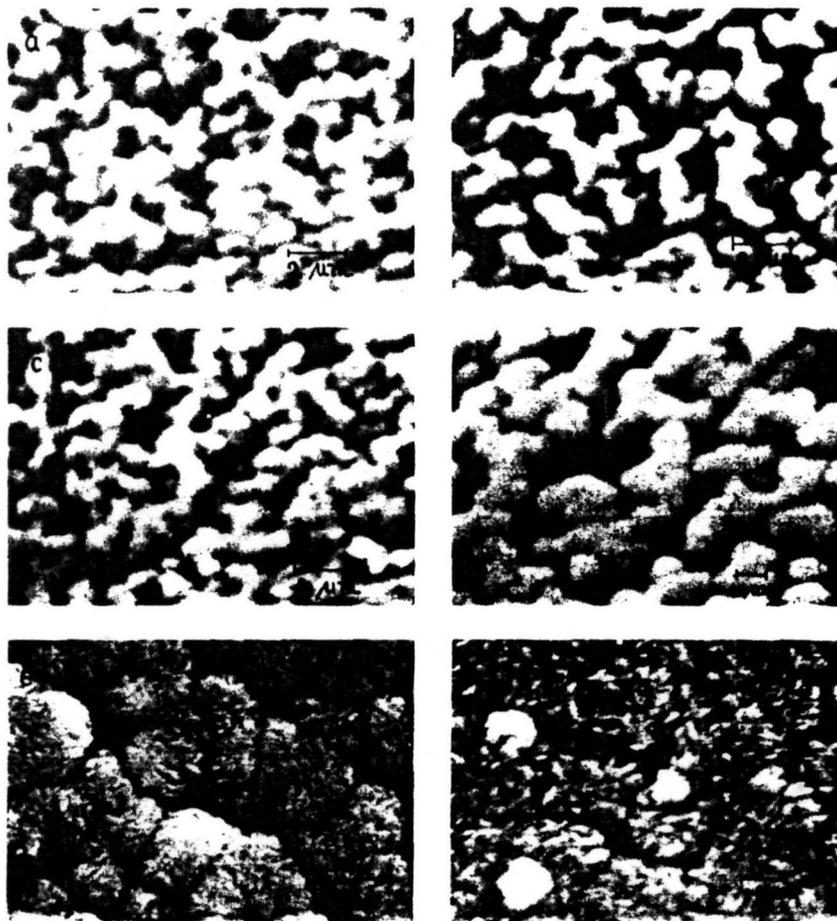


Fig. 2. Electron micrographs of CdS thin films on glass substrates for various deposition conditions (Cd:S = 1:1): (a) baking temperature $T_B = 200$ C, single dipping; (b) $T_B = 300$ C, single dipping; (c) $T_B = 400$ C, single dipping; (d) $T_B = 400$ C, double dipping; (e) $T_B = 400$ C, five dippings; (f) $T_B = 400$ C, ten dippings.

positions as those for pure CdS, but with much reduced heights, even allowing for the lower proportion of CdS. In addition, a broad peak, characteristic of amorphous materials, is present. Optical absorption measurements show the presence of two absorption edges, approximately coinciding in position with those for CdS and ZnS. This leads to the conclusion that the material formed consists of a mixture of CdS and ZnS phases, with the ZnS totally amorphous and the CdS partially crystalline. Similar results have been obtained by Banerjee *et al.*⁴ who found that the introduction of antimony as dopant in CdS reduces its crystallinity and, at 3 mol. % doping, the structure is completely amorphous.

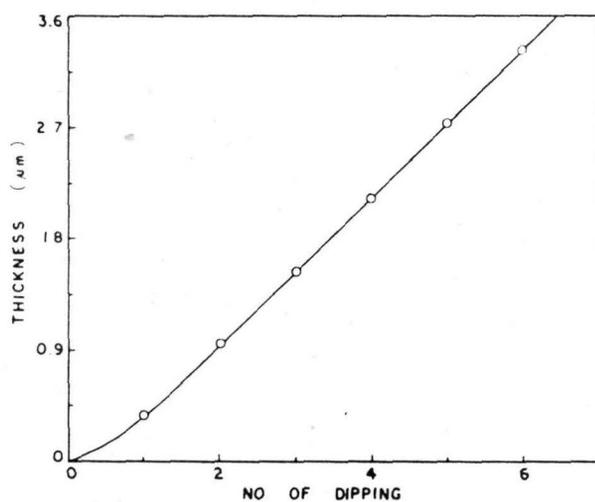


Fig. 3. Variation in thickness of CdS films on glass substrate with number of dippings ($T_B = 400^\circ\text{C}$).

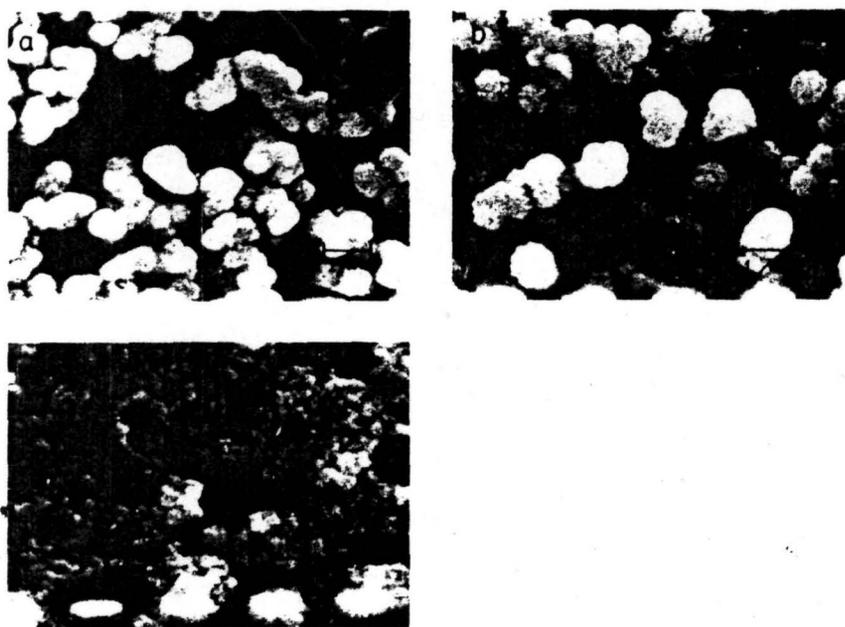


Fig. 4. Electron micrographs of CdS thin films on different substrates (double dipping; Cd:S = 1:1; $T_B = 400^\circ\text{C}$): (a) on aluminium sheet; (b) on conducting tin oxide; (c) on mica.

4. CONCLUDING REMARKS

The dip technique as used for the preparation of sulphide films is a modification of the well-known spray pyrolysis method. In the latter technique the reactants,

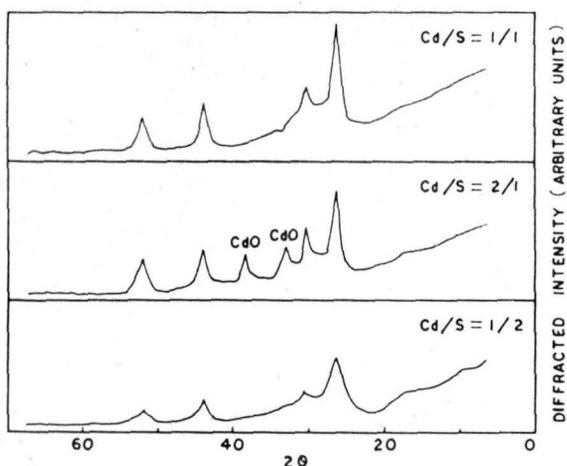


Fig. 5. X-ray diffractograms of CdS thin films on glass for different Cd:S ratios (double dipping; $T_B = 400^\circ\text{C}$; Cu K α radiation).

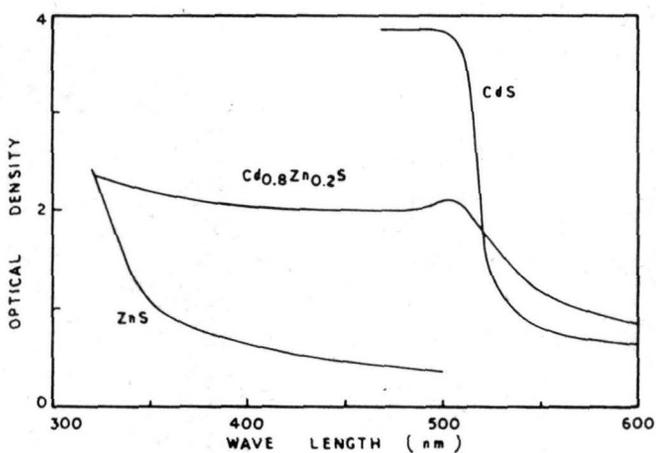


Fig. 6. Optical absorption curve of CdS (ten dippings), ZnS (double dipping) and Cd_{0.8}Zn_{0.2}S (double dipping) films on soda-glass substrates (M:S = 1:1; $T_B = 400^\circ\text{C}$).

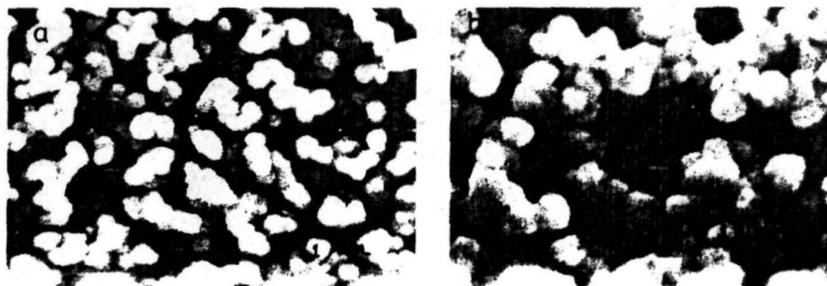


Fig. 7. Electron micrographs of (a) ZnS and (b) Cd_{0.8}Zn_{0.2}S thin films deposited on glass substrates (double dipping; M:S = 1:1; $T_B = 400^\circ\text{C}$).

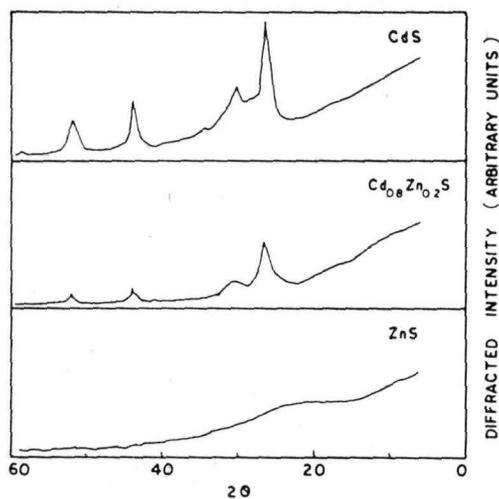


Fig. 8. X-ray diffractograms of CdS, ZnS and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ on glass substrates (double dipping; M:S = 1:1; $T_B = 400^\circ\text{C}$; Cu $K\alpha$ radiation).

originally at a temperature of about 30°C , impinge on the preheated substrate when the film-forming chemical reaction takes place. In contrast, the present method allows the reactants and the substrate to rise in temperature at the same rate. CdS films formed by the two techniques are very similar. However, for ZnS and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ films, there are significant differences. The dip technique is an extremely simple and low-cost method for the preparation of thin films, which should be useful for various device applications.

ACKNOWLEDGMENT

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REFERENCES

1. K. L. Chopra and I. Kaur, *Thin Film Device Applications*, Plenum, New York, 1983.
2. H. Schroeder, *Oxide layers deposited from organic solutions*. In G. Hass and R. E. Thun (eds.), *Physics of Thin Films*, Vol. 5, Academic Press, New York, 1969, pp. 87-141.
3. M. K. Karanjai and D. Dasgupta, *Mater. Lett.*, **4** (1986) 368-369.
4. R. Banerjee, S. Roy and A. K. Barua, *Indian J. Phys. A*, **58** (1984) 166-175.

A simple and novel technique for the deposition of conducting tin dioxide films

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Abstract. Transparent conducting films of both undoped and antimony-doped tin dioxide have been prepared by a novel technique. In this method, the substrate with a band of SnCl_2 paste painted near its lower edge is heated in a vertical configuration. The SnCl_2 undergoes oxidation to yield SnCl_4 (vapour) as one of the reaction products, which rises upward and is hydrolysed on the heated substrate surface to produce the oxide. The films are smooth and strongly adherent over a region ≈ 5 cm in length. The best films obtained have a sheet resistance in the region of $100 \Omega \square^{-1}$ and 70% average optical transmission.

Tin dioxide has been widely used as a transparent conducting thin film material [1, 2]. Usually Sb or F is used as a dopant to increase the conductivity of SnO_2 thin films. In this paper we describe an extremely simple and low-cost method for the preparation of undoped and Sb-doped conducting tin dioxide films, which can be carried out in any laboratory. The method utilises the hydrolysis of SnCl_4 on the surface of a hot substrate which is also the basis of the familiar spray pyrolysis and chemical vapour deposition processes.

A paste of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (along with the requisite quantity of SbCl_3 as dopant, if added) is made with the minimum quantity of water and allowed to stand for 1–3 days. When nearly dry, the mass is thoroughly stirred mechanically and a band approximately 3 mm wide applied near one end of the substrate with a paint brush. The substrate is then heated using the arrangement shown in figure 1(a).

The substrate is kept initially in a position so that only that portion of the substrate over which the film is to be deposited receives direct radiation from the heater. After the substrate has attained the desired temperature ($\approx 400^\circ\text{C}$) it is raised so that the SnCl_2 'band' now also receives heat. The SnCl_2 mass first becomes dry, then melts into a glassy form and finally swells and starts to 'spit'. Simultaneously, white fumes are given off and seen to deposit SnO_2 film where they come into contact with the substrate. The thickness of the film being deposited can be visually monitored by looking at the reflection from the substrate and observing the interference colours. It was found that the best films in terms of conductivity, optical transmission and resistance to peeling-off and acids were obtained for a substrate temperature of the order of 400°C .

Essentially similar results are obtained if the substrate is positioned to receive direct radiation from the heater, while the region with the SnCl_2 band is shielded from the heater by a metallic strip (figure 1(b)). In this case no repositioning of the substrate is necessary, as the shielding ensures that the substrate is already at the required temperature before the SnCl_2 paste starts to decompose. Results reported in this paper were obtained for films deposited using the arrangement described earlier (figure 1(a)).

In an attempt to understand the chemistry of the film-forming process, an amount of SnCl_2 paste was strongly heated in a flask and the vapours given off condensed and collected. The condensate was chemically analysed and found to consist of SnCl_4 , HCl and H_2O . A separate chemical analysis showed that the SnCl_2 paste itself contains Sn mostly in the Sn^{II} state.

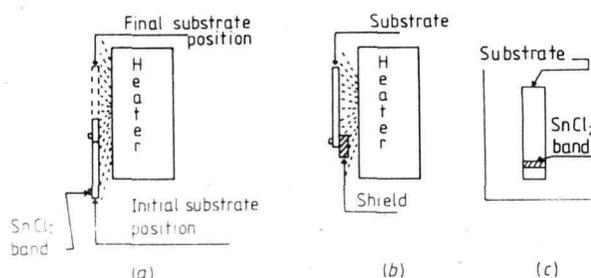
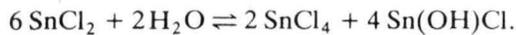


Figure 1. Arrangements for the deposition of SnO_2 films. Figure 1(c) shows the location of the SnCl_2 band with respect to the substrate.

It is well known [3] that in the presence of oxygen, an aqueous solution of SnCl₂ becomes turbid on account of the following reaction



It is suggested that at room temperature this reaction is relatively slow, but proceeds rapidly on heating, as during the film deposition process. The SnCl₄ vapour, which is one of the reaction products, is hydrolysed to produce the film on contact with the hot substrate, the necessary moisture coming from the starting material itself and also from the atmosphere.

The films are smooth over a length ≈ 5 cm from the position of the SnCl₂ band. The layer formed immediately adjacent to the band (up to a distance of ≈ 2 mm) has a high resistivity in comparison with the remaining portion. Even over the low-resistivity region, the thickness is not uniform, the layer being thicker nearer the band, as may be expected. The uniformity of the film can be improved by painting another band parallel to and at a distance ≈ 8 cm from the first one, and repeating the process with the substrate turned around. A region 3–5 cm long having a uniform thickness in the range 100–5000 Å, as ascertained from the interference colours [1], can thus be obtained.

The surface topography and x-ray diffractogram of a typical film are shown in figures 2 and 3, respectively. The grain size is seen to be $\approx 0.2 \mu\text{m}$. The crystal structure is in accordance with the usual tetragonal form of SnO₂.

By varying the amount of starting material, proportion of dopant, deposition time and the substrate temperature, films of various thicknesses having a sheet resistance from 100–5000 $\Omega \square^{-1}$ and average optical transmission of 70–90% could be routinely obtained. Typical optical transmission versus wavelength data for the films are shown in figure 4. In figure 5 are shown the sheet resistance–thickness relationships for undoped and 2 at.% Sb-doped films deposited at various substrate temperatures. The sheet resistance of the films was measured by a standard four-probe method, whereas optical transmission data were obtained by a

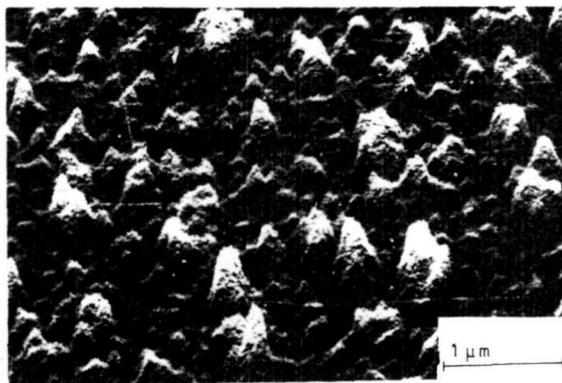


Figure 2. A scanning electron micrograph of a typical SnO₂ film.

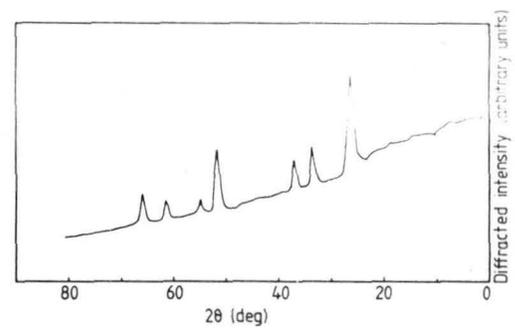


Figure 3. An x-ray diffractogram of a typical SnO₂ film.

SHIMADZU UV-240 double-beam spectrophotometer (air reference). The resistivity of the Sb-doped (2 at.%) films prepared at 400 °C is estimated to be $\leq 5 \times 10^{-3} \Omega \text{ cm}$. It may be noted here for comparison that the sheet resistance obtainable for SnO₂:Sb transparent conducting coatings prepared by spray pyrolysis is about $2 \times 10^{-3} \Omega \text{ cm}$ [2]. Films with useful conduction and optical transmission properties can be obtained even without the deliberate addition of dopant. However the sheet resistance and optical transmission values show a very wide scatter in this case.

Conducting tin dioxide films are usually prepared by various methods such as spray pyrolysis, chemical

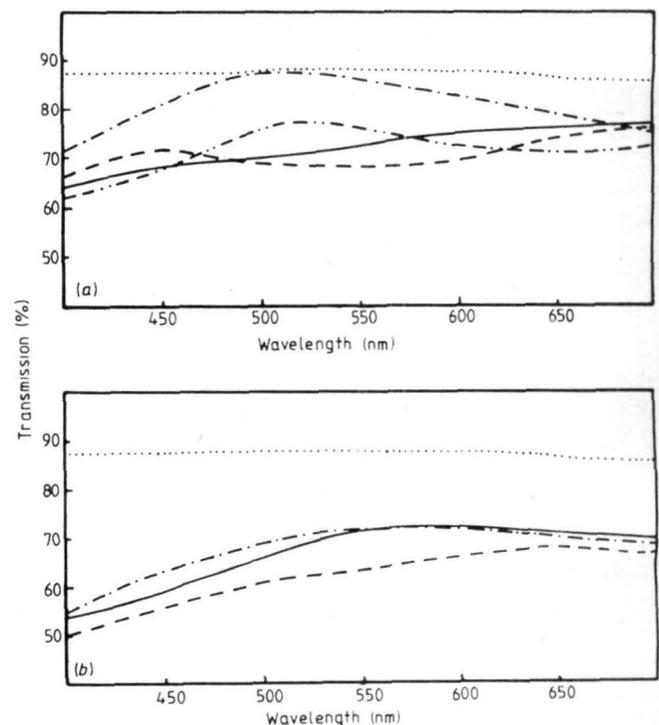


Figure 4. Optical transmission versus wavelength for typical SnO₂ films of various sheet resistance. (a) Undoped: (—), 475 $\Omega \square^{-1}$; (---), 670 $\Omega \square^{-1}$; (— · —), 860 $\Omega \square^{-1}$; (· · · · ·), 1400 $\Omega \square^{-1}$; (· · · · ·), bare substrate. (b) Sb-doped (2 at.%): (—), 110 $\Omega \square^{-1}$; (---), 550 $\Omega \square^{-1}$; (— · —), 870 $\Omega \square^{-1}$; (· · · · ·), bare substrate.

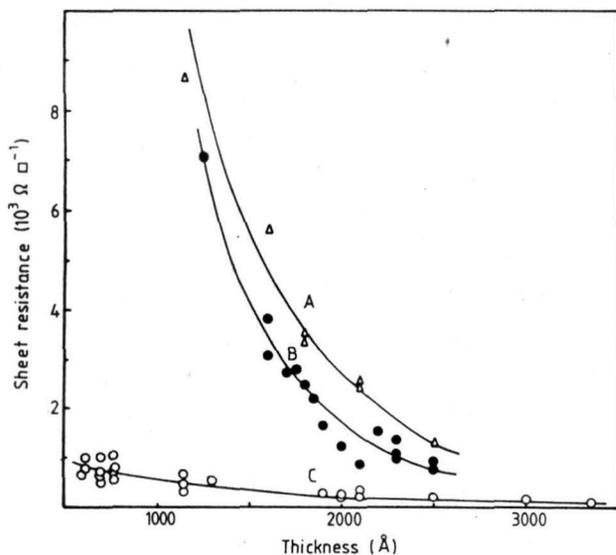


Figure 5. Sheet resistance–thickness relationship for undoped (curves A and B) and 2 at.% Sb-doped (curve C) SnO_2 films prepared at various substrate temperatures: A, 370 °C; B, 430 °C; C, 400 °C.

vapour deposition, sputtering and activated reactive evaporation, each method requiring its own specialised experimental arrangement. The main virtue of the present method is its extreme simplicity, which should make it useful for various device applications. Elec-

tro luminescent cells (ZnS:Mn thin film EL with double insulating layer structure) [4], using ZnS:Mn as phosphor, and tin dioxide transparent electrode prepared by this method have already been successfully fabricated in our laboratory.

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References

- [1] Vossen J L 1977 *Physics of Thin Films* vol 9, ed. G Hass, M H Francombe and R W Hoffman (New York: Academic) pp 1–71
- [2] Chopra K L and Major S 1985 *Thin Film Technology and Applications* ed. K L Chopra and L K Malhotra (New Delhi: Tata McGraw-Hill) pp 224–36
- [3] Partington J R 1950 *A Text-book of Inorganic Chemistry* 6th edn (London: MacMillan) p 829
- [4] Inoguchi T and Mito S 1977 *Electroluminescence* ed. J I Pankove (Berlin: Springer) pp 197–210

Photoconductive properties of dip-deposited CdS:Cu, Cl thin films sensitised *in situ*

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Abstract. Photoconductive CdS:Cu, Cl thin films have been prepared by immersion of dip-deposited CdS films in an aqueous solution containing CdCl₂ and CuCl₂ followed by a high-temperature bake in air. The films have a high photosensitivity in the visible range and show photo-electronic behaviour typical of such films prepared by traditional techniques. Evidence of coalescence of the grains as a result of the CdCl₂ treatment was found.

1. Introduction

Cadmium sulphide (CdS) thin films are widely used in a large number of solid-state device applications such as photoconductive (PC) detection, xerography, photovoltaic solar energy conversion and thin-film transistor electronics. Various deposition methods, ranging from the simple such as spray pyrolysis to highly sophisticated techniques such as molecular beam epitaxy have been used for these films [1].

The dip technique is a relatively simple method for the deposition of sulphide thin films [2, 3]. As a first step towards studying the usefulness of dip-deposited films for various applications, we report in this paper a study of the preparation and performance of PC cells using CdS thin films deposited by this technique. These cells are found to be capable of achieving a high sensitivity and are similar in their photo-electronic properties to those prepared by traditional methods [4].

2. Experimental details

CdS thin films were prepared on soda-glass substrates by the dip technique as follows. The substrate was withdrawn vertically at a speed of 1.3 mm s⁻¹ from a methanol solution at room temperature containing 58 g of thiourea per litre and 235 g of Cd(NO₃)₂·4H₂O per litre (approximately 0.762 mol l⁻¹ each). It was then baked, together with the liquid film adhering to it, in air for 10 min at a temperature of 400 °C, when the two

components chemically reacted to produce the CdS film. Two such dip-bake cycles yielded a film about 10000 Å in thickness. More details have been given in [3].

To carry out the sensitisation with copper and chlorine, the films were immersed at room temperature for about 2 min in an aqueous solution containing 2.5×10^{-4} mol of CuCl₂ per litre and $(7.5-17.5) \times 10^{-2}$ mol of CdCl₂ per litre. These were then baked in air at a temperature of 550 °C for 1–7 min. The fabrication of the PC cells was completed by evaporation of aluminium electrodes in the usual comb-like configuration [1]. The electrodes, which were deposited over an area of 3.5 cm × 2.5 cm, had a total length of about 10 cm and were 1 mm apart.

The dark current and photocurrent of the PC cells were measured as a function of various processing parameters. The results are shown in table 1. The cells with the best photosensitive properties were chosen for further study as discussed below.

Voltage-current characteristics for different light intensities and equivalent resistance as a function of light intensity were measured using an incandescent tungsten filament source calibrated with a lux meter. The spectral response of photosensitivity was determined with the help of a spectromom 202 spectrophotometer, by measuring the photocurrent as a function of wavelength of the PC cell placed at the detector position.

3. Results and discussions

As table 1 shows, a higher concentration of CdCl₂ in the sensitising solution leads to an increase in the dark

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Table 1. Dark current and photocurrent of CdS:Cu, Cl PC cells for various processing parameters.

| Concentration of CdCl ₂ in sensitising solution (mol l ⁻¹) | Baking time (min) | Dark current (μA) | Photocurrent (μA) |
|---|-------------------|-------------------|-------------------|
| 7.5 × 10 ⁻² | 1 | <1 | 20 |
| 7.5 × 10 ⁻² | 3 | <1 | 84 |
| 7.5 × 10 ⁻² | 5 | <1 | 81 |
| 7.5 × 10 ⁻² | 7 | <1 | 72 |
| 7.5 × 10 ⁻² | 9 | <1 | 61 |
| 12.5 × 10 ⁻² | 1 | 50 | 4 |
| 12.5 × 10 ⁻² | 3 | 2 | 94 |
| 12.5 × 10 ⁻² | 5 | 3 | 90 |
| 12.5 × 10 ⁻² | 7 | 3 | 88 |
| 12.5 × 10 ⁻² | 9 | 3 | 84 |
| 17.5 × 10 ⁻² | 1 | 84 | 0 |
| 17.5 × 10 ⁻² | 3 | 4 | 92 |
| 17.5 × 10 ⁻² | 5 | 10 | 91 |
| 17.5 × 10 ⁻² | 7 | 15 | 88 |
| 17.5 × 10 ⁻² | 9 | 14 | 86 |

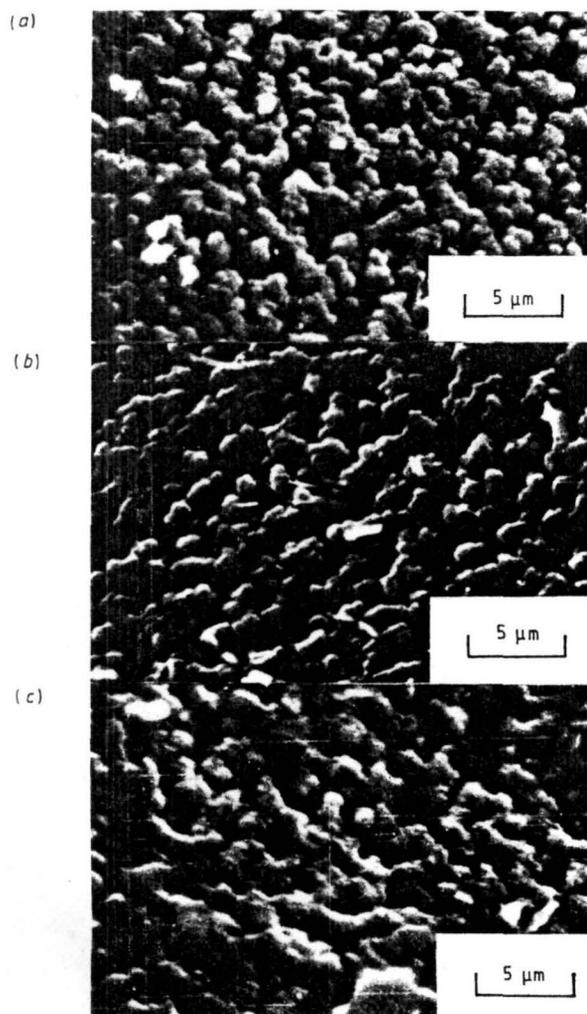


Figure 1. Scanning electron micrographs showing the effect of CdCl₂ concentration in the sensitising solution on the morphology of CdS thin films (baking time, 3 min): (a) 7.5 × 10⁻² mol l⁻¹; (b) 12.5 × 10⁻² mol l⁻¹; (c) 17.5 × 10⁻² mol l⁻¹.

current, while the photocurrent remains essentially the same. From the scanning electron micrographs (figure 1), it can be seen that the CdS grains have a greater tendency to coalesce as the concentration of CdCl₂ is increased. It is well known [5] that CdCl₂ acts as a flux, promoting recrystallisation of CdS grains. The result is thus consistent with the elimination of a number of grain boundaries and a consequent decrease in the number of high-resistance paths as a result of CdCl₂ treatment.

From table 1, it can also be seen that for a given concentration of CdCl₂ in the sensitising solution the photoresponse reaches a maximum for a baking time of about 3 min and then decreases slowly. The latter is probably caused by partial decomposition of the CdS thin-film material, as indicated by a separate experiment in which prolonged (about 30 min) immersion of the film in the sensitising solution destroyed the CdS film. It was found, however, that within the range 1–8 min the time for which the film was kept immersed in the sensitising solution did not have any noticeable influence on the photosensitivity of the final device.

The voltage-current (*V-I*) characteristics shown in figure 2 are essentially linear and characteristic of ohmic contact at the electrodes. Aluminium electrodes produce an ohmic contact with CdS [5] provided that the CdS surface is sputter cleaned before evaporation, as was done in this case. The equivalent luminance-resistance (Φ -*R*) curves (figure 3) are found to have a slope of less than unity on a log-log scale and to increase slowly with increasing luminance. Such a variation was deduced for polycrystalline layers in [6] from a theoretical consideration of the lowering of inter-crystalline potential barriers under illumination. It has been found [7] from thermo-electric power measurements that the effective mobility of carriers in copper-sensitised CdS films increases with increasing illumination, presumably owing to a barrier-lowering mechanism.

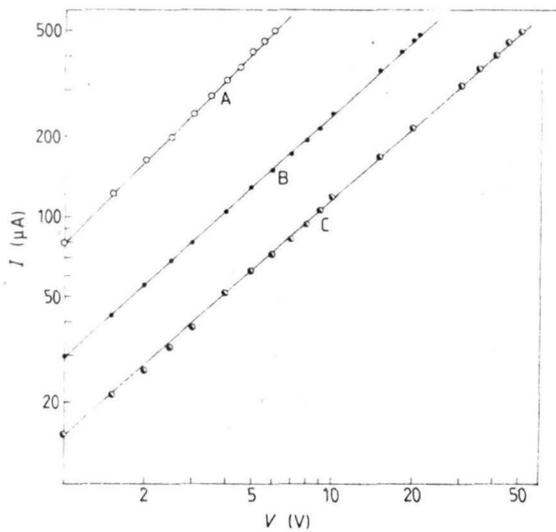


Figure 2. Voltage-current ($V-I$) characteristics of a typical photoconductive cell for different illumination levels: line A, 1000 lx; line B, 200 lx, line C, 50 lx.

The spectral response of photoconductivity for pure (unsensitised) CdS (figure 4) shows a maximum at 520 nm, corresponding to a band gap of 2.4 eV. For the sensitised samples (figure 5) a sharp peak at 505 nm and a broad peak at 590 nm are observed, the first being caused by intrinsic excitation, while the second arises as a result of the impurity levels produced by the copper acceptor.

The maximum photosensitivity obtained by the fabrication process described in this paper is 10 mA l m^{-2} .

4. Concluding remarks

CdS films deposited by the dip technique have been shown to be capable of being sensitised by a simple treatment. Except for the vacuum evaporation of the

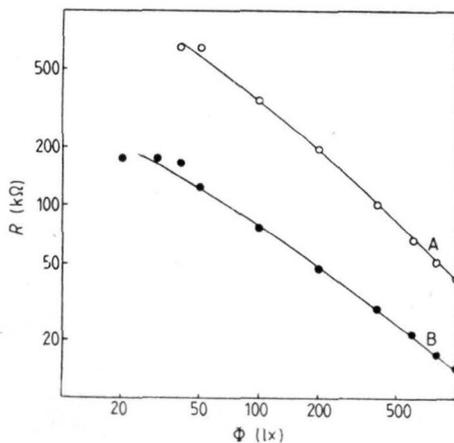


Figure 3. Equivalent luminance-resistance ($\Phi-R$) relation for a typical photoconductive cell, for two different baking times: curve A, 7 min; curve B, 3 min.

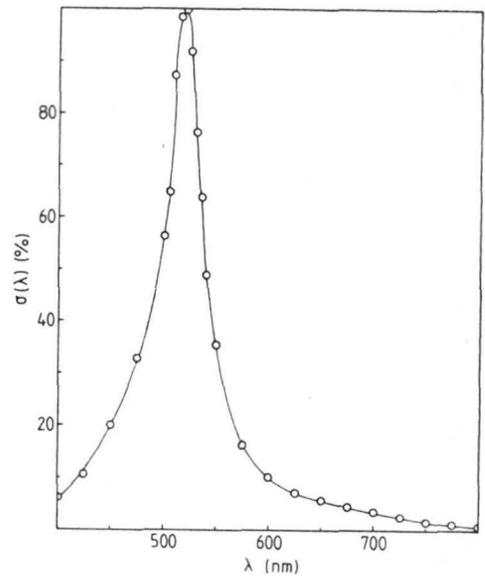


Figure 4. Normalised spectral response of photoconductivity for pure CdS (unsensitised) film.

electrodes, all the steps involved in the fabrication of photoconductive cells using this technique are simple and inexpensive. The cells have a high sensitivity to visible light in the wavelength range 500–700 nm.

Evidence of the coalescence of the CdS grains as a result of treatment in aqueous CdCl_2 solution followed by baking has been found. This may prove to be useful in the fabrication of devices such as solar cells, where an increase in grain size leads to an improvement in performance.

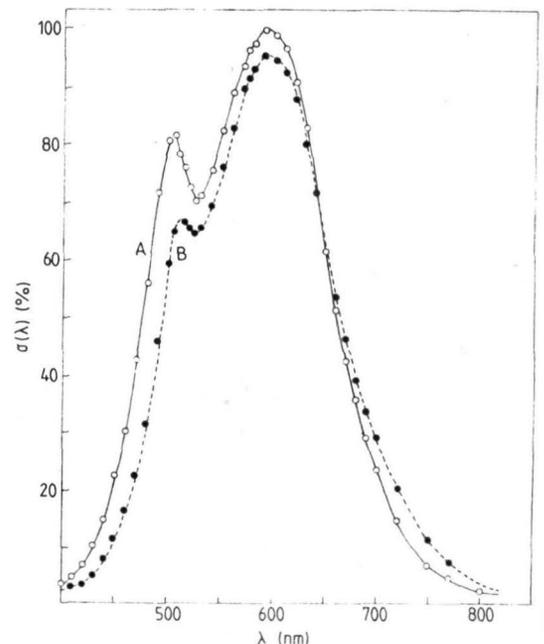


Figure 5. Spectral response of photoconductivity for sensitised CdS films (normalised with respect to the maximum of the more sensitive sample) for two baking times: curve A, 3 min; curve B, 7 min.

Acknowledgment

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References

- [1] Chopra K L and Kaur I 1983 *Thin Film Device Applications* (New York: Plenum)
- [2] Karanjai M K and Dasgupta D 1986 *Mater. Lett.* **4** 368
- [3] Karanjai M K and Dasgupta D 1987 *Thin Solid Films* **155** 309
- [4] Porada Z and Schabowska E 1983 *Vacuum* **33** 179
- [5] Bube R H 1960 *Photoconductivity of Solids* (New York: Wiley)
- [6] Slater J C 1956 *Phys. Rev.* **103** 1631
- [7] Wu C, Feigelson R S and Bube R H 1972 *J. Appl. Phys.* **43** 756

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