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Undoped and indium-doped CdS films prepared by chemical vapour deposition

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Undoped and In-doped films of CdS were deposited at different temperatures by the chemical vapour deposition technique on glass and In-coated (30 nm) glass, respectively. Both kinds of film present a columnar microstructure, low porosity and good adherence to the substrate. The doped films have higher electron mobility values compared with the undoped ones. Shifts in the transmission spectra (Moss–Burstein effect) were observed with increased doping. Small crystals grew over the doped films during the deposition stage, mainly at the higher substrate temperatures.

1. Introduction

CdS is one of the most extensively investigated semiconductors in thin-film form. Several deposition techniques have been utilized to obtain good-quality layers for solar cell devices as a window for InP, CdTe, $Cu_{2-x}Se$ and $CuInSe_2$ [1]. High light transmission and a resistivity lower than 100 Ω cm are required.

The chemical vapour deposition (CVD) technique has been used in different configurations for the epitaxial growth of CdS films on Ge [2], GaAs [3], InP [3–6] and CdTe [7] crystals. Yamaguchi *et al.* [8] add an In source to dope the films during the deposition and Romeo [9] deposited CdS on quasi-liquid layers in order to obtain films with large crystalline grains. We report in this paper CdS films deposited at different temperatures by the CVD method on substrates of glass (undoped films) and indium-coated glass (In-doped films). These films can be particularly useful in solar cells where lateral current collection is taking place in the window.

2. Experimental set-up and preparation of films

The growth apparatus is shown in Fig. 1 and consists of a horizontal quartz tube (3.4 cm inner diameter, 45 cm long) containing the source and the substrate which can be moved along the axis of a three-zone furnace. By an appropriate adjustment of the furnace temperatures the CdS in the source, located in the first zone, can be decomposed by the action of the carrier gas (H_2) and deposited as a film on the substrate located in the third zone. The CdS source was kept at 700 °C, while in the deposition zone the temperature varied along the axis between 310 and 520 °C. The reaction taking place in the reactor is

$$CdS(s) + H_2(g) \rightleftharpoons Cd(g) + H_2S(g)$$

and was extensively described before for Cd and Zn sulphides [2].

The CdS material used as a source was obtained by precipitation with H_2S in a $CdSO_4$ solution. This solution was prepared by the action of H_2SO_4 on 99.999% pure cadmium metal, using platinum wire as a catalyst. The precipitate was washed, dried, calcined at 700 °C for 2 h in a nitrogen atmosphere and vacuum-sublimated in order to lower the concentration of impurities. The crystals obtained were crushed in an agate mortar until a powder with an average particle size of 1 μm was achieved. Films were grown on soda-glass and In–soda-glass substrates. Substrates containing In (99.9999%) were prepared by evaporation of a 30 nm layer in a vacuum of 10^{-5} torr.

The H_2 flow rate was 0.3 l min^{-1} and the growing time was 5 h. The films were grown simultaneously at different temperatures by placing several substrates along the tube in the deposition zone. The thickness of the evaporated In layer was measured with a Veeco QM-311 monitor. The CdS film morphology, thickness and composition were studied by means of a scanning electron microscope (SEM) and a wavelength-dispersive X-ray (WDX) microprobe. X-ray diffraction spectra were obtained using CuK_α radiation. Optical transmittance and photoconductivity were measured with a Bausch & Lomb monochromator with a halogen lamp light source, an EG&G SGD-100A silicon photodetector and a Keithley 570 data acquisition system. The resistivity and mobility were measured by the Van der Pauw technique.

3. Results and Discussion

3.1. CdS films on glass substrates

On glass substrates the adhesion of films deposited at substrate temperatures from 320 to 517 °C is very good. Fig. 2 shows the dependence of the thickness of the films on the deposition temperature. It can be seen that the deposition rate increases with temperature. Increasing the substrate temperature from 320 to 517 °C increases the grain size from 0.5 to 4 μm. Fig. 3

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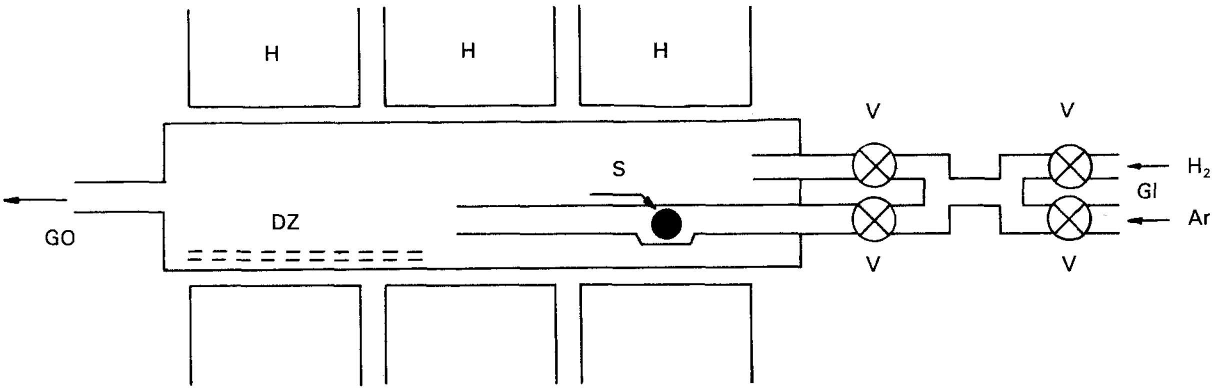

Figure 1 Schematic diagram of the apparatus used to grow CdS films: (S) CdS source, (DZ) deposition zone, (H) separately heated and controlled furnaces, (GI) gas inlet (GO) gas outlet, (V) valves.

shows SEM photographs of the surfaces of these films and Fig. 4 is a cross-sectional view of a film deposited at 499 °C, showing the columnar nature of the microstructure without grain boundaries in the direction normal to the substrate.

X-ray diffractograms of both the CdS powder used as source and the grown films are shown in Fig. 5.

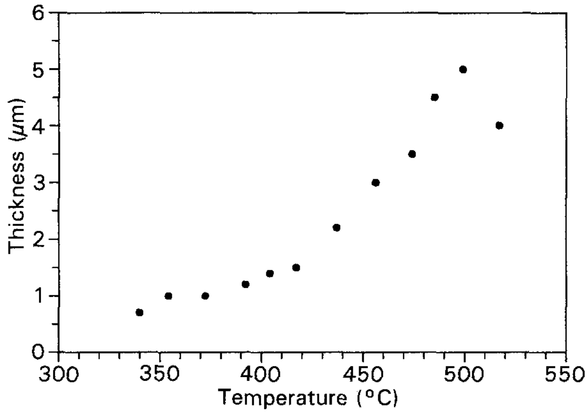

Figure 2 Thicknesses versus deposition temperature for CdS films grown on glass substrates.

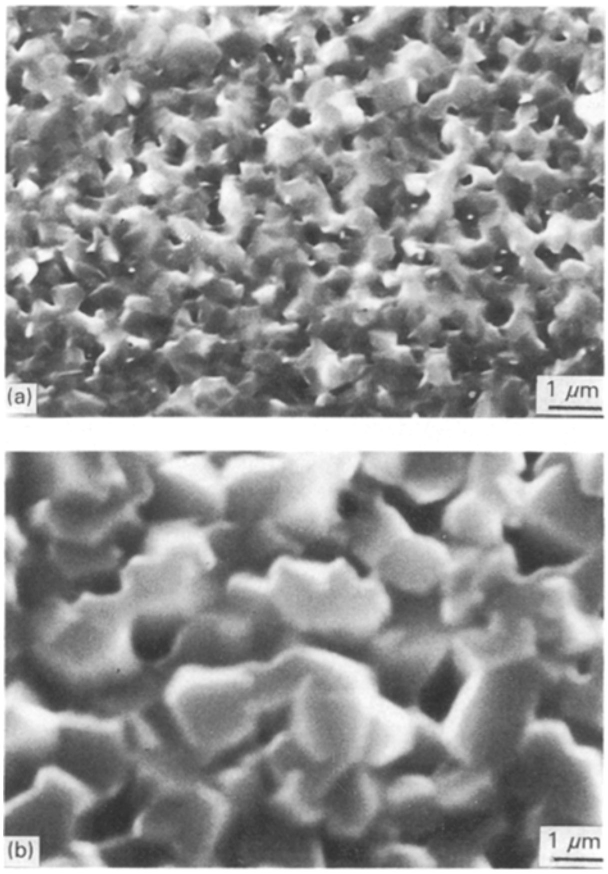

Figure 3 SEM photographs of the surface of CdS films grown at (a) 354 °C, (b) 467 °C.

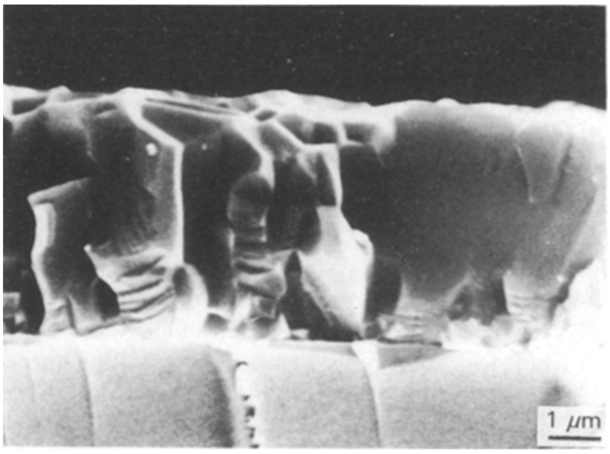

Figure 4 SEM photograph of a cross-sectional view of a CdS film grown at 499 °C.

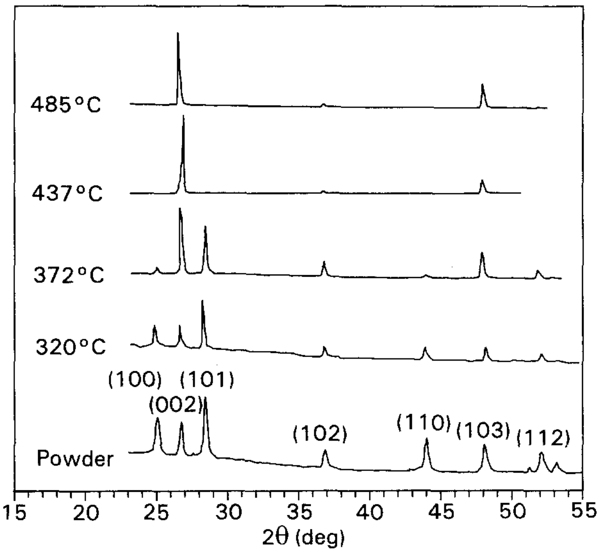

Figure 5 X-ray diffraction spectra of CdS films grown at different substrate temperatures and of the powder used as source.

Analysis of the diffraction spectra indicates that the CdS films had a hexagonal wurtzite structure. It can be seen that there is a stronger alignment of the *c* axis perpendicular to the substrate surface when the deposition temperature is raised.

The films have good optical transmittance, higher than 90% when measured at 0.8 μm wavelength. Fig. 6 is a typical spectrum. The photoconductivity spectrum of a film is shown in Fig. 7.

The mobilities were lower than $3\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$. Although the grain size increases at higher deposition temperatures and the mobility is dominated by the grain boundaries, measurements of electrical resistivity for all the samples give almost the same value of $20\ \Omega\,\mathrm{cm}$ as shown in Fig. 8.

Lateral collection of carriers is not advisable because the small thickness would give rise to a high series resistance in the device. The use of these films as windows in solar cells requires the previous application of a transparent conductive contact on the glass. However, oxide films like SnO_2 cannot be used due to the reduction produced by hydrogen in the CdS deposition process. One solution to this is to deposit the CdS film over the absorber and then make a transparent contact to it.

In this work we investigate another possibility, consisting in the doping of the film during the growth as will be described in the next section.

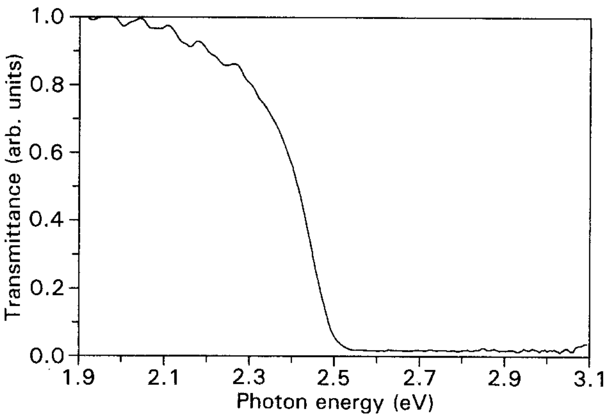

Figure 6 Transmission spectrum of a CdS film grown at 517 °C.

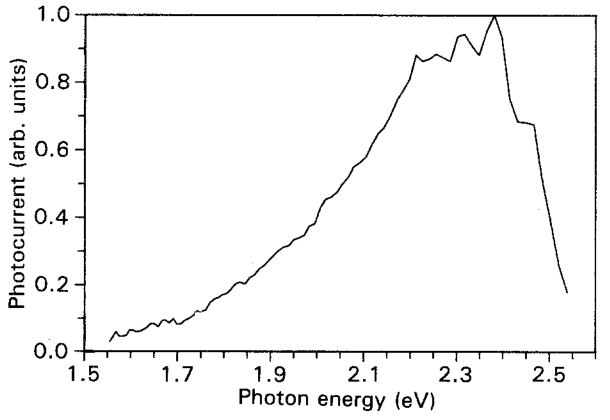

Figure 7 Photoconductivity spectrum of a CdS film deposited at 474 °C.

3.2. CdS on In-coated glass

CdS films were grown on indium (30 nm) coated soda–lime glass at substrate temperatures ranging from 312 to 433 °C. At these temperatures the indium is liquid and one expects an enhanced growth process due to the higher surface mobility of the deposited atoms [9].

Fig. 9 shows SEM photographs of the surface and a cross-sectional view of a sample grown at 398 °C. The deposit consists of a thin, continuous film over which many crystals of different lengths and hexagonal cross-section have grown, mainly at the higher temperatures. The continuous films thickness ranges from

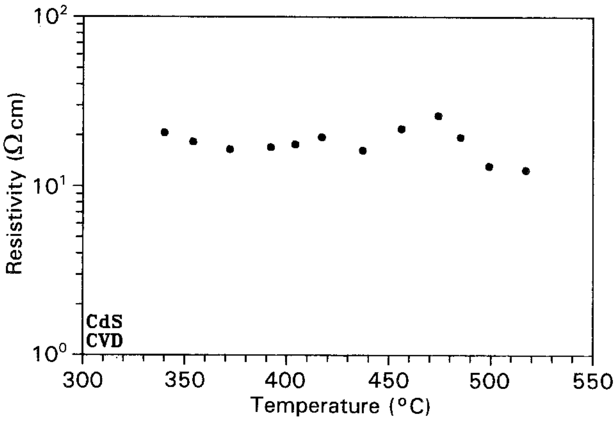

Figure 8 Resistivity versus deposition temperature for CdS films grown on glass substrates.

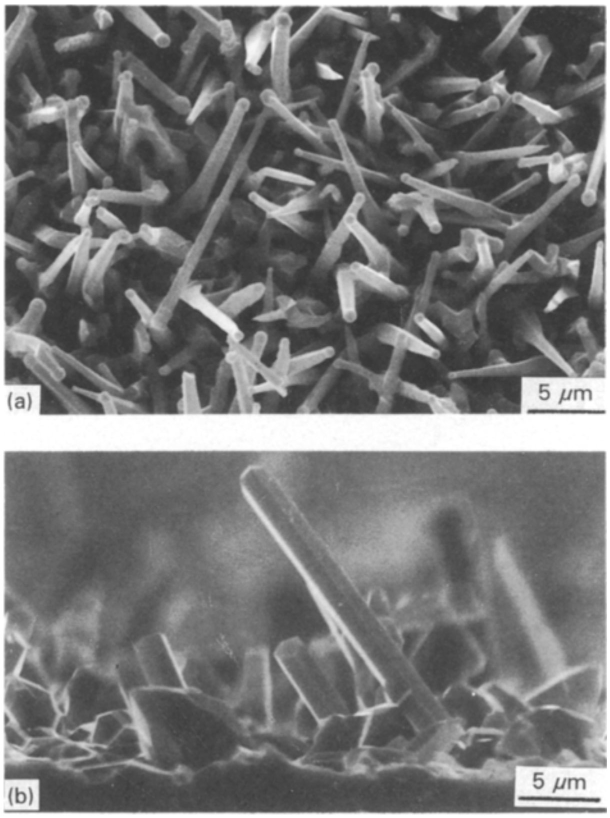

Figure 9 SEM photographs of In-doped CdS film grown at 398 °C: (a) surface, (b) cross-sectional view. The glass was intentionally darkened during the photographic processing in order to enhance the location of the interface.

0.5 μm (312 °C) to 4 μm (433 °C), while the length of the thin crystals ranges from 1 μm at the lowest substrate temperature up to 25 μm at the highest.

SEM–WDX analysis indicated that the concentration of In was the same in the film and in the crystals. At substrate temperatures lower than 360 °C there were small In droplets at the end of some crystals; their formation may be due to an excess of In concentration above its solubility limit in CdS [10].

The X-ray diffraction spectra shown in Fig. 10 show a behaviour similar to those observed for undoped CdS: a major alignment of the *c* axis of the wurtzite structure normal to the substrate at higher deposition temperatures. The lattice parameters are the same as those obtained for the undoped films, a result in agreement with the measurements of Hayashi *et al.* [11].

The films have a fairly good optical transmittance, higher than 80% at 0.8 μm wavelength; Fig. 11 shows the spectra for films grown at different temperatures. The absorption edge shifts toward lower energies when the deposition temperature increases, reaching the same value as that of the undoped film. As we noted above, a higher deposition temperature produces a thicker film and, since all samples were grown over the same indium thickness, a less degenerate doping condition is obtained. This could be the reason for the observed shifts according to the Moss–Burstein effect [12].

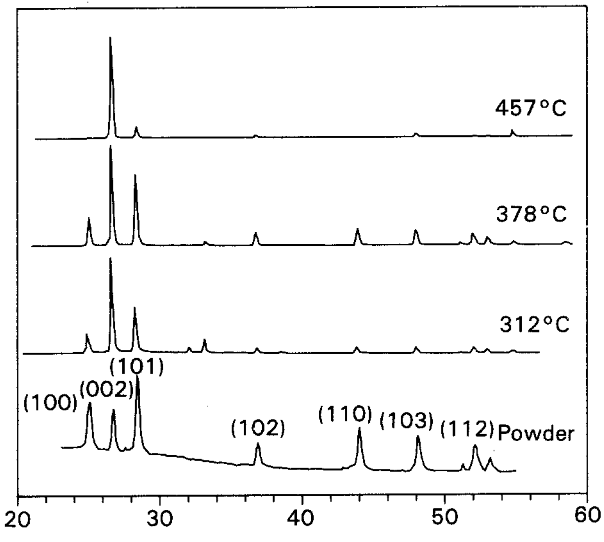

Figure 10 X-ray diffraction spectra of In-doped films grown at different substrate temperatures and of the powder used as source.

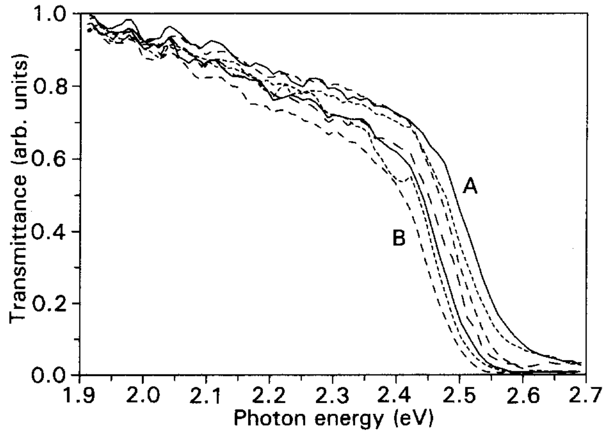

Figure 11 Spectral responses of the transmittance of In-doped CdS film grown at different substrate temperatures. Curves from A to B (—) 312 °C, (‑‑‑) 328 °C, (‑‑) 339 °C, (——) 354 ′C, (—) 378 °C, (‑‑‑) 394 °C, (‑‑) 405 °C.

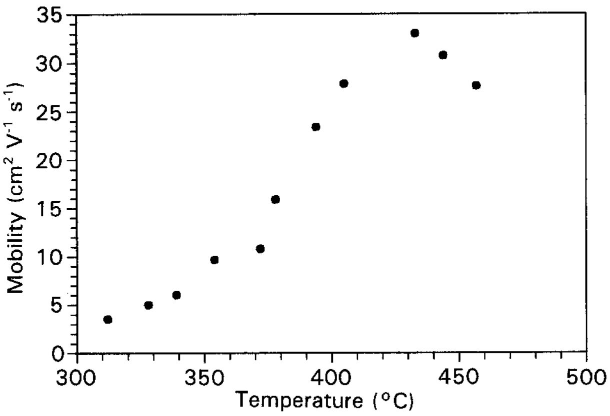

Figure 12 Measured mobilities of In-doped CdS films deposited at different substrate temperatures.

Fig. 12 shows the mobility as a function of growth temperature. It can be seen that the doped samples have mobilities about an order of magnitude greater than the undoped ones, as reported previously for CdS obtained by other techniques [13].

Although we only present results obtained for films grown over a 30 nm In layer, we also prepared films over In layers of thicknesses ranging from 6 to 50 nm. The results are similar to the ones presented here, except that for thicknesses greater than 45 nm the formation of indium droplets (about 3 μm in diameter) was observed, probably formed by the surface tension of the layer.

4. Conclusions

Undoped and In-doped CdS films were deposited by a CVD technique. The adherence, transparency and morphology of the films are good. We found that In-doped films have a higher mobility than the undoped ones.

For solar cell applications, the quality of the doped films is impaired by the presence of CdS crystals which at the highest deposition temperature (433 °C) reach lengths of up to 25 μm. However, we are now studying the possibility of using these films as windows for CdTe grown by isothermal close-spaced vapour transport [14, 15]. Preliminary observations made on cells prepared in this way indicate that the thin crystals on the surface of the doped films are etched away during the CdTe deposition.

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