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Vapour-deposited CdS films and their dependence on the source material

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An investigation has been made of the conditions required for the formation of vapour-deposited CdS thin films with reproducible characteristics suitable for use in photovoltaic solar cells. Cathodoluminescence spectroscopy has been used to provide information on differences in composition between the deposited films and the source material from which they were produced, and particular consideration has been given to the influence of the source material structure and stoichiometry on the electrical properties of the resultant films. Under identical deposition conditions, four different high-purity sources were shown to produce films with very different electrical characteristics, but by selecting appropriate deposition conditions (substrate temperature and deposition rate) it was found that each material was capable of generating films with the required characteristics.

1. Introduction

In the search for semiconducting materials which might be used in the production of low-cost, thin-film photovoltaic solar energy converters, particular attention has been given to CdS, partly because of the vast experience previously built up during the development of this material for use in a variety of thin-film photoconductive and luminescent devices and displays. This interest in CdS as a solar cell material has been encouraged by its successful application in heterojunction photovoltaic devices employing one of several binary or tertiary compound photon absorber layers (e.g. Cu_2S, CdTe, InP and $CuInSe_2$).

The system which has received most attention is the $CdS-Cu_2S$ combination but the $CdS-CuInSe_2$ system is currently considered to be a particularly promising contender for large-scale commercial exploitation [1]. However, for the large-scale production of any device, reproducibility is of prime importance and, accordingly, the fabrication process must be extremely well controlled. Many methods for depositing CdS thin films have been examined (including thermal evaporation, sputtering, spraying and electrophoresis) but the highest efficiency thin-film devices have been achieved with thermally evaporated CdS layers. There is clearly a need to control the evaporation process in order to produce films with designated characteristics. For example, it is generally agreed that the best $CdS-Cu_2S$ cells are obtained using CdS layers with resistivity in the region of $10\,\Omega\,cm$, corresponding to a carrier concentration of $\sim 10^{17}\,cm^{-3}$ [2]. However, there is some disagreement concerning the deposition parameters necessary to achieve these required characteristics. The CdS source material is obviously one of the factors which can influence the properties of the films but, although the purity of the material is usually given careful consideration, less interest has generally been paid to the physical structure of the source which can be in the form of crushed crystals or a powder either in the raw state or compressed into pellets. In order to investigate this aspect of the problem, two different commercial sources of high-purity CdS powder with different particle size distributions have been compared both before and after changing the structure of the powders by an annealing and sintering process. Films produced from these different sources were found to have significant differences in their electrical and luminescence properties, but the effects on these properties of changes in the deposition parameters (substrate temperature and deposition rate) were found to follow a similar trend. In this investigation we have limited consideration to films with a thickness of 20 to $30\,\mu m$ and a range of deposition parameters appropriate for the production of CdS films suitable for photovoltaic solar cell fabrication.

2. Experimental details

The two types of CdS powder employed in this study were Koch-Light, high purity (5N) grade (KL) and General Electric, high purity, large particle material (GE). These were used either in the "as-received" form or after sintering. The sintering process was carried out in two stages. Firstly, the CdS powder was heated for 10 h at 400° C in a quartz tube which was maintained at a pressure of 10^{-5} torr by a vacuum pump connected via a liquid nitrogen trap. Secondly, the evacuated quartz tube containing the powder was sealed off and then baked for 2 days at 900° C.

Using each of these powders as the evaporation source, CdS layers of 20 to $30\,\mu m$ thickness were deposited on to zinc-plated copper sheets maintained at a fixed temperature in the range 200 to 300° C. A conventional 12 in. (305 mm) vacuum evaporator system was employed with the pressure during evaporation always below 10^{-5} torr. The CdS source was placed in a cylindrical quartz crucible heated by a coiled element of molybdenum foil. The substrate holder consisted of an electrically heated stainless steel

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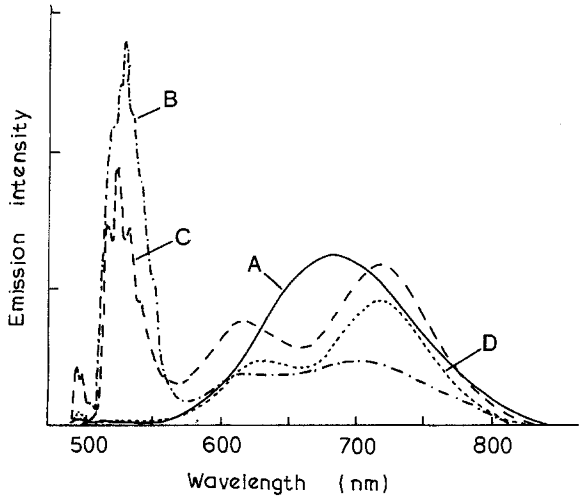

Figure 1 Cathodoluminescence emission spectra for four samples of CdS powder: (A) as-received KL; (B) sintered KL; (C) as-received GE; (D) sintered GE.

block located at a distance of 20 cm vertically above the source crucible. The space between the crucible and the substrate was enclosed by an independently heated glass cylinder ("hot wall") which was maintained at a temperature of 200° C during evaporation. To improve the quality and reproducibility of the CdS films, the substrate was initially heated to 300° C and then cooled to the required temperature before starting the evaporation.

In order to compare the properties of the resultant CdS films, an evaporated indium contact was applied to the upper surface of each film so that the electrical resistivity could be determined. Also an evaporated gold contact was formed in order to produce a Schottky junction. A Boonton capacitance meter was employed to measure the junction capacitance C and from the gradient of the C^{-2}–bias voltage relationship, the free carrier concentration was determined in the standard manner. Further information about the source powders and the resultant films has been provided by cathodoluminescence measurements. The luminescence was generated using a 10 keV electron gun with a beam density of $5\,\mu\mathrm{A\,cm^{-2}}$ and the luminescence spectra were obtained using a Hilger Monospec monochromator and a photomultiplier coupled to a phase-sensitive detector.

3. Results and discussion

3.1. The evaporation source material

Fig. 1 shows the cathodoluminescence emission spectra for the four different source powders, taken at 77 K. Curves A and C are for the as-received CdS powders while B and D are for the sintered powders. These curves include a number of features which are commonly observed with CdS phosphors. The structured short-wavelength band centred at ~490 nm is due to bound exciton recombination [3] while the dominant green edge emission in the vicinity of 520 nm has been attributed to the interaction of free electrons with bound holes at shallow acceptors [4] or to donor–acceptor recombination [5]. The broader bands centred at ~610 nm and 720 nm are generally associated with excess cadmium [6] and defect–impurity complexes [7], respectively.

Curve A clearly cannot be described in terms of the characteristic features just described. As Curve A was obtained using the as-received, very finely powdered KL sample, the lack of any edge emission and the presence of a single broad emission band is probably associated with the serious surface damage and lattice strain introduced during the milling process. This strain would be expected to be relieved during the annealing process and, as Curve B demonstrates, the normal features including very strong edge emission are exhibited by a sample of the KL material after the sintering process. Curve C, for the coarse-grained GE powder, likewise shows all the characteristic features but the relative intensities are different. The edge emission for Curve C is weaker than in B while the longer wavelength bands are a little stronger. Use of the defect assignments referred to above leads us to associate the large 610 nm band of Curve C with an excess of cadmium as compared with B. As it has previously been shown that evaporation of non-stoichiometric CdS proceeds in such a way as to remove preferentially the excess component [8], the reduction of the 610 nm emission band in Curve C after annealing and sintering (Curve D) could be explained by the preferential loss of cadmium during the annealing of the cadmium-rich sample, but it is surprising to find that this is accompanied by a substantial reduction in the edge emission.

While the intention of sintering was to change the physical structure of the source material from a powder into a denser, coarser-grained form, it was expected that the pre-sintering vacuum annealing cycle would result in a change in stoichiometry. In fact, such an effect could be clearly observed. During the vacuum heat treatment with KL powder, a thin yellow layer of sulphur (or sulphur-rich CdS) was seen to be deposited on the quartz tube of the cold trap, while for the GE powder a dark layer of cadmium-rich CdS was deposited. Thus it can be concluded that during the sintering process, the Cd/S atomic ratio was increased for the KL powder and decreased for the GE material.

3.2. Effect of source material on deposited films

Marked variations have been found in the electrical properties of the films produced using the four different CdS sources. This is illustrated by the results in Table I, which relate to films deposited at the same substrate temperature (235° C) and at the same deposition rate ($0.6\,\mu\mathrm{m\,min^{-1}}$). It can be seen that these

TABLE I Carrier concentration and resistivity values of CdS thin films obtained using different CdS source powders

Source material	Carrier concentration ($\mathrm{cm^{-3}}$)	Resistivity (Ω cm)
GE CdS powder	5.3×10^{16}	42.7
Sintered GE CdS powder	8.5×10^{15}	1050
KL CdS powder	2.4×10^{17}	25.0
Sintered KL CdS powder	8.5×10^{17}	7.3

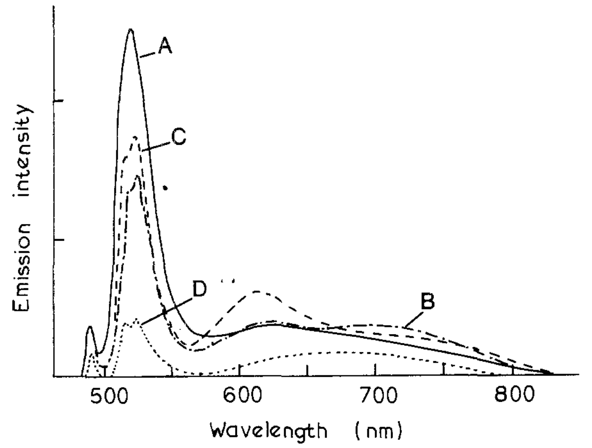

Figure 2 Cathodoluminescence emission spectra for CdS thin films prepared from different CdS powders using a substrate temperature of 235° C and a deposition rate of 0.6 μm min^{-1}. Source materials: (A) as-received KL; (B) sintered KL; (C) as-received GE; (D) sintered GE.

fixed deposition conditions lead to values for carrier concentration and film resistivity which are spread over more than two orders of magnitude. The cathodoluminescence results for these films in Fig. 2 also show significant variations and, as expected, these spectra are quite different from the spectra for the corresponding source materials in Fig. 1. As could be anticipated, the 610 nm peak associated with cadmium-rich material is particularly strong in Curve C (with the as-received GE powder as source) and is significantly diminished in Curve D (for a film obtained using sintered GE material as source). It might have been further anticipated that as-received GE powder (Curve C) would display the highest free carrier concentration but, as Table I shows, this is not the case. Indeed, it is unlikely that any one feature of the luminescence spectrum would correlate with the observed electrical properties, which are dependent on the corporate effects of all the impurities and defects within the material. Likewise, the observed luminescence spectrum is dependent on non-radiative as well as radiative recombination processes. However, in the context of CdS films for the fabrication of CdS–Cu_2S solar cells, it is interesting to note that those films which display weak cathodoluminescence (e.g. Curve D in Fig. 2) generally result in low-efficiency cells. Table I shows that the carrier concentration for the sintered GE film (Curve D) was well below the optimum value required for a high-efficiency cell.

3.3. Effect of deposition conditions on film properties

The results for films produced from sintered KL powder and as-received GE material are summarized in Table II. The results obtained with unsintered KL powder were not sufficiently reproducible to merit inclusion in the table. This was due to the very fine particle structure of the KL powder. Even when using a quartz wool plug in the source crucible, fine particles of CdS tended to be projected on to the substrate during the evaporation process. This same problem arose to some extent with all the sources at sufficiently high evaporation rates, and it is for this reason that the results in Table II are limited to deposition rates of not more than 1 μm min^{-1}. Similar technical factors determined the possible range of substrate temperatures. At temperatures greater than 300° C, the process of re-evaporation from the growing film became sufficiently efficient to prevent the formation of a CdS layer of the required thickness ($> 20\,\mu$m) and a temperature of less than 200° C could not be maintained throughout a complete deposition cycle due to radiative heating from the source furnace. For all the films quoted in the table, great care was taken to ensure that all the deposition conditions, other than those stated, were identical during the different evaporation cycles.

The results show that for films produced with either as-received GE powder or sintered KL material, the resistivity increases with increasing substrate temperature and decreases with increasing deposition rate. Scanning electron microscope studies have revealed no significant differences in the grain structure of the films. All the layers had the characteristic columnar structure and although the grain size was marginally larger for the higher substrate temperature depositions, it appears from Table II that the variations in

TABLE II Carrier concentration and electrical resistivity of CdS films prepared at different substrate temperatures and deposition rates

Source material	Deposition rate (μm min^{-1})	Substrate temperature (° C)	Carrier concentration (cm^{-3})	Resistivity (Ω cm)
As-received GE CdS powder	1.0	235 ± 5	2.1×10^{17}	9.5
	0.6	235 ± 5	5.3×10^{16}	42.7
	0.3	235 ± 5	1.5×10^{16}	187.5
	0.07	235 ± 5	7.3×10^{15}	944
	1.0	205 ± 5	8.0×10^{17}	5.1
	1.0	235 ± 5	2.1×10^{17}	9.5
	1.0	265 ± 5	5.0×10^{16}	450
	1.0	295 ± 5	2.1×10^{15}	3063
Sintered KL CdS powder	1.0	235 ± 5	1.4×10^{18}	1.0
	0.6	235 ± 5	8.5×10^{17}	7.3
	0.5	235 ± 5	6.2×10^{17}	9.5
	0.3	235 ± 5	3.4×10^{17}	14.7
	0.5	205 ± 5	1.6×10^{18}	1.2
	0.5	235 ± 5	6.2×10^{17}	9.5
	0.5	265 ± 5	8.9×10^{16}	340

electrical resistivity are associated with changes in carrier concentration rather than in carrier mobility.

The observed trends in carrier concentration and resistivity are in general agreement with the reports of some other workers [9, 10] but in the case of the dependence of film resistivity on deposition rate the opposite trend has also been observed [11]. In the latter case, however, the films examined were less than 5 μm thick so that a direct comparison with the results obtained here would not be valid. It is well known that in thin layers the orientations of the crystallites are randomly distributed and that the *c* axis takes on a preferential alignment perpendicular to the substrate as the thickness increases, giving the layer its characteristic columnar structure. This is one of the reasons why a film thickness in excess of 20 μm is usually required for solar cell construction.

Although the influence of substrate temperature and deposition rate on the carrier concentration follows the same pattern of behaviour for both sets of films in Table II, it is clear that when prepared under identical conditions there is approximately an order of magnitude difference. Such differences, like those observed between the cathodoluminescence spectra discussed above, are to be expected from sources of differing stoichiometry even if no account is taken of differences in the nature and concentrations of trace impurities. However, of more importance in terms of their application in photovoltaic cells, it is clear that either source material can be used to generate films with a particular carrier concentration (in the range 10^{15} to $10^{18}\,\mathrm{cm}^{-3}$) by means of a suitable choice of substrate temperature and deposition rate.

4. Summary and conclusions

Cathodoluminescence and electrical measurements have been used to investigate how the origin and structure of the source material influences the properties of vapour-deposited, polycrystalline CdS films. From a comparison of cathodoluminescence emission spectra generated by Koch-Light and General Electric high-purity powders, and from observations of the effects of sintering, a difference in stoichiometry between these two sources was indicated, such that the Cd/S atomic ratio was greater for the GE powder than for the KL material. Changes in stoichiometry occur as a result of sintering and the composition of each deposited film differs significantly from that of the source material from which it was produced. However, the defect structure and associated electrical properties of the films are also dependent on the deposition parameters. For both source powders, it was found that a change of approximately one order of magnitude in the carrier concentration for the films could be achieved either (i) by maintaining a fixed substrate temperature and varying the deposition rate between 0.3 and 1.0 $\mu\mathrm{m\,m}^{-1}$, or (ii) by maintaining a fixed deposition rate and varying the substrate temperature between 205 and 265° C.

It is clear that, even when using sources of similar high purity, the resultant films will not be identical unless the stoichiometry and particle structure of the powders are also well matched. Accordingly, it is not possible to prescribe a set of universally applicable deposition parameters for the production of films with specific characteristics; but using a high-purity source material, the conductivity of the resultant vapour-deposited films can be determined, within broad limits, by suitable choice of deposition rate and substrate temperature.

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