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Effects of $CdCl_2$ on the electrical properties of sintered CdS films

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CdS films on glass substrates with various amounts of $CdCl_2$ have been prepared by coating and sintering, and their microstructure, electrical resistivity, carrier concentration and mobility have been investigated. The sintering rate is strongly increased near the melting temperature of $CdCl_2$ and the enhancement in the sintering is via a liquid-phase sintering mechanism. Doping of chlorine also occurs during the sintering and the solubility of chlorine in CdS is of the order of $10^{18}\,cm^{-3}$ at 650° C. The electron concentration of the sintered CdS films which contained $CdCl_2$ before sintering increases with increasing grain size. The electron mobility increases sharply with increasing average grain size due to a sharp decrease in the total trap density, which is proportional to the total grain-boundary area.

1. Introduction

Cadmium sulphide, with an energy band gap of 2.43 eV at 300 K, is a suitable window material for CdS–CdTe and CdS–Cu_2S heterojunction solar cells. The production of CdS films by various methods for the purpose of application in heterojunction solar cells has been reported. The electrical properties of these films prepared by a vacuum evaporation method [1, 2] and by spray pyrolysis [3, 4] have been reported, and solar cells have been produced by the deposition of n-CdS films by these methods on p-CdTe single crystal substrates with a solar efficiency of over 6%.

The method of sintering is a convenient and economical method for the mass production of material in the form of thin films on a substrate. Recently Nakayama *et al.* [5] reported the production of sintered all-polycrystal n-CdS–p-CdTe solar cells, doping gallium into CdS and copper into CdTe, with an efficiency of over 8%. However, in the papers reported by the Matsushita group [6, 7], the properties of the sintered CdS films with 10 wt % $CdCl_2$ were described in terms of solar cell parameters.

There are therefore ample necessity and motivation to understand the effects of $CdCl_2$ on the electrical and optical properties of sintered CdS films on a substrate. CdS films produced in the present investigation result in all-polycrystal CdS–CdTe solar cells with an efficiency of over 7% when even undoped CdTe films are used, and the properties of the solar cells will be presented elsewhere. In this paper we report the results of a detailed investigation of the electrical properties of such films as a function of the amount of $CdCl_2$ added and the sintering conditions.

2. Experimental procedure

CdS and anhydrous $CdCl_2$ powders with 5 N purity were used in the present investigation. CdS powders with an average particle size of 0.45 μm were calcined at 700° C for 2 h in a nitrogen atmosphere, and crushed to obtain a powder with a larger particle size. Slurries consisting of the calcined powder with an average particle size of 2 μm, propylene glycol and various amounts of $CdCl_2$ were prepared by mixing with a mortar and pestle. The slurries were coated on borosilicate glass substrates using a screen printer fabricated with 165 mesh stainless steel screen and dried at 120° C for 2 h in air. Coated CdS films were placed in a quartz boat with a cover and then sintered in a nitrogen atmosphere using a tube furnace with a quartz tube at temperatures ranging from 530 to 650° C.

Ohmic contacts were deposited by the evaporation of indium in 10^{-6} torr vacuum and by metallization at 100° C for 10 min in a nitrogen atmosphere, and were checked by taking an I–V curve. Sheet resistance at 300 K and the temperature dependence of the sheet resistance were measured in an argon atmosphere using a four-probe method. Electrical resistivity was determined by measurement of the sheet resistance of the film and the film thickness. Carrier concentration and carrier mobility were measured by the van der Pauw method. The crystal structure and texture of the sintered polycrystal film were analysed using an X-ray diffractometer. Photographs were taken from a cross-sectional area as well as the film surface of each sample with a scanning electron microscope (SEM).

3. Results and discussion

The variation of electrical resistivity of CdS films sintered at 650° C for 30 min in a nitrogen atmosphere as a function of the amount of $CdCl_2$ added is shown in Fig. 1. It should be pointed out that since the vapour pressure of $CdCl_2$ is high [8], the $CdCl_2$ added in the slurry state evaporates through the gap between the sintering boat and the cover at the sintering temperatures used in the present investigation. Thus the amount of $CdCl_2$ means the amount before sintering unless otherwise specified. Fig. 1 shows that the resis-

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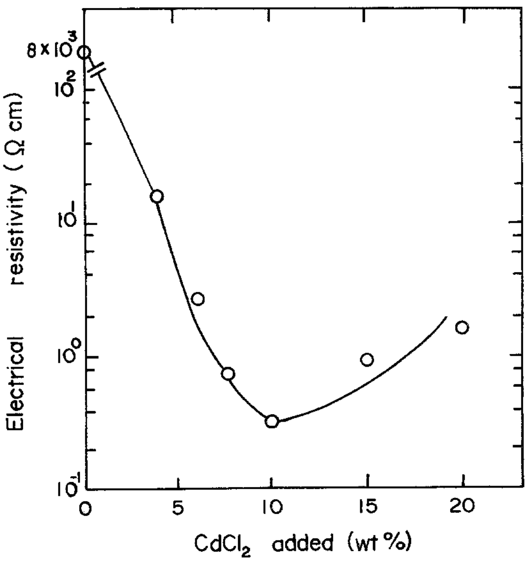

Figure 1 Electrical resistivity of CdS films as a function of CdCl$_2$ added. Films were sintered at 650° C for 30 min in nitrogen.

tivity of the sintered CdS film without any CdCl$_2$ is $8 \times 10^3\,\Omega$ cm and decreases with increasing amounts of CdCl$_2$ up to 10 wt %. The resistivity shows a minimum at 10 wt % CdCl$_2$ and is 0.34 Ω cm and then increases with increasing CdCl$_2$. Fig. 2 shows surface photographs of the sintered CdS films for samples which contained 0, 6, 10 and 20 wt % of CdCl$_2$ before sintering. As can be seen in Fig. 2, the sample which did not contain any CdCl$_2$ is hardly sintered, and the average grain size increases with increasing amounts of CdCl$_2$ up to 10 wt %. The sample which contained 10 wt % CdCl$_2$ before sintering shows a clean surface and fewest voids, while the sample which contained 20 wt % CdCl$_2$ shows some secondary phase on the grain boundaries and on the surfaces of the grains. The average grain size of the sintered CdS films determined by the linear intercept method were 2.5, 7.5, 13.6 and 14.5 μm for the samples which contained 0, 4, 6, 8 and 10 wt % of CdCl$_2$, respectively. When the sample which contained 20 wt % CdCl$_2$ and had been sintered at 650° C for 30 min was sintered for another 30 min at 650° C, the second phase almost disappeared as shown in Fig. 3. From the energy dispersive analysis of X-ray (EDAX) data in Fig. 4, it appears that the second phase is recrystallized CdCl$_2$ that did not evaporate during sintering and was left in the sample. SEM photographs of the cross-sectional area of the sintered CdS films corresponding to those samples in Fig. 2 are shown in Fig. 5. It can be seen that the thickness of the sintered films is about 25 to 30 μm, and the grain size of the sample which contained 20 wt % CdCl$_2$ is smaller than that of the sample which contained 10 wt %. This kind of phenomenon is often observed in the sintering of oxides with a sintering aid which exists in a liquid phase during sintering [9].

Fig. 6 shows the variation of the electrical resistivity of CdS films which contained 10 wt % CdCl$_2$ or no CdCl$_2$ as a function of the sintering temperature. As seen before, the sample which contained no CdCl$_2$ is hardly sintered and the resistivity is larger than $10^3\,\Omega$ cm. The resistivity of the samples which contained 10 wt % CdCl$_2$ and were sintered for 30 min below 560° C is still larger than $10^2\,\Omega$ cm, decreases sharply with increasing sintering temperature up to 620° C and then stays at about the same value at 650° C. Fig. 6 also shows that the longer period of sintering reduces the resistivity of the films which were sintered below 590° C and causes no significant change in the resistivity of samples which were sintered above 620° C.

Fig. 7 shows SEM photographs of the CdS films which contained 10 wt % CdCl$_2$ and were sintered for 30 min at various temperatures. It is seen that significant sintering took place in the samples which were

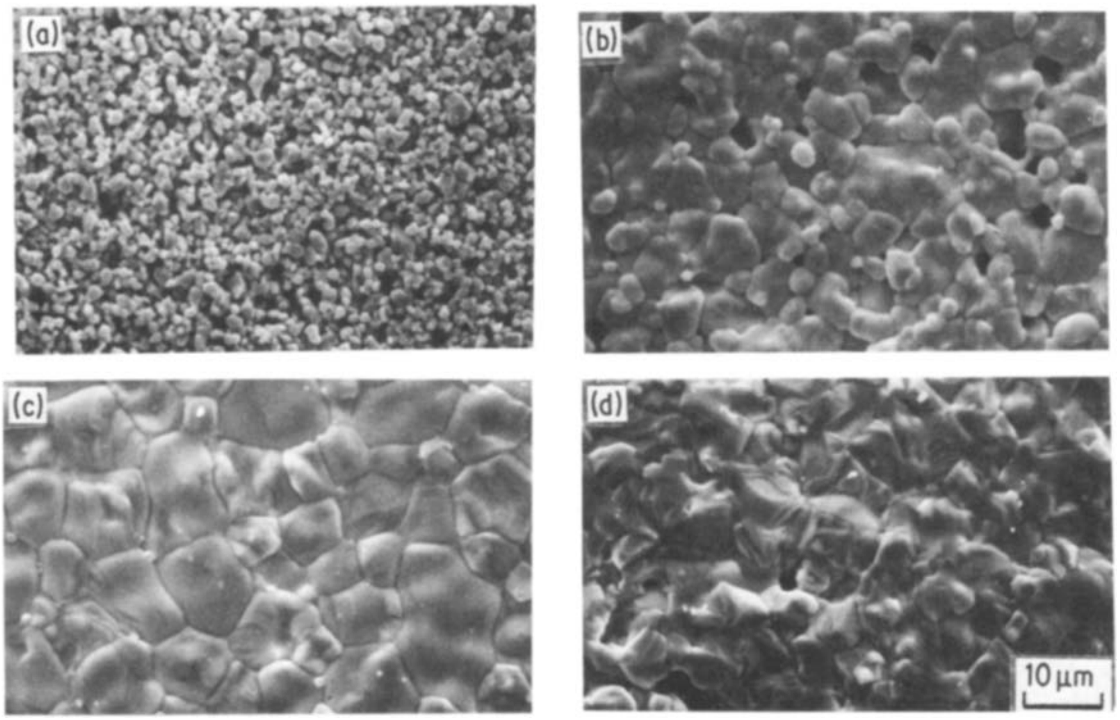

Figure 2 Microstructure of CdS films with various amount of CdCl$_2$ sintered at 650° C for 30 min: (a) 0 wt %, (b) 6 wt %, (c) 10 wt %, (d) 20 wt % CdCl$_2$.

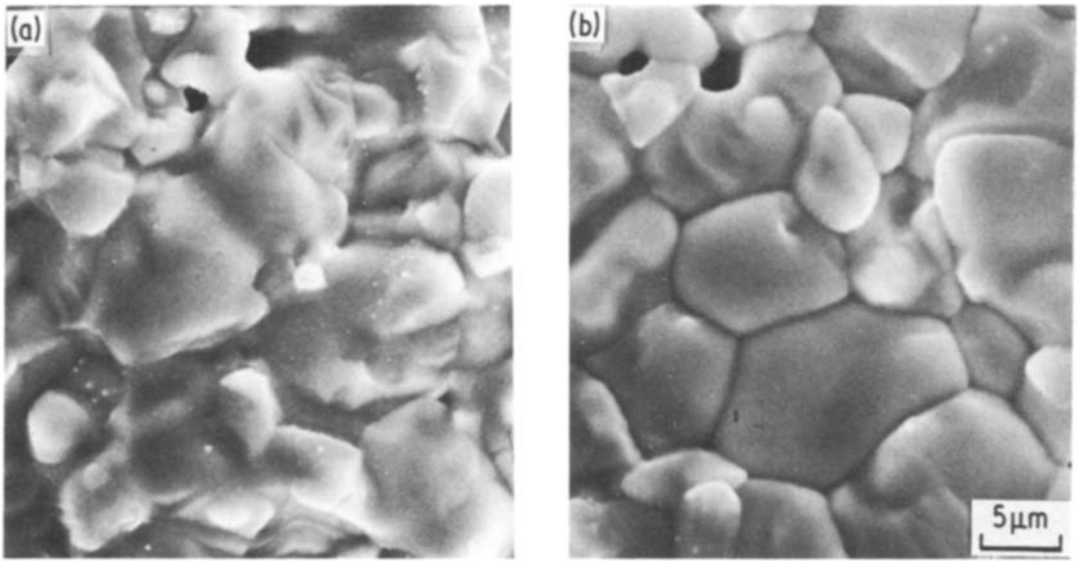

Figure 3 SEM photographs of CdS films which contained 20 wt % $CdCl_2$ in the slurry and (a) were sintered at 650° C for 30 min, and (b) were resintered.

sintered above 560° C. From observation of the microstructures of the samples which were sintered for 10 min, it may be concluded that the sintering enhancement of $CdCl_2$ is by a liquid-phase sintering mechanism. It is interesting, however, to note that significant sintering occurred in the sample which was sintered at 560° C, which is lower than the melting temperature of 568° C for $CdCl_2$. Similar behaviour has been observed in the growth of CdTe films by quasi liquid-phase epitaxy [10]. This could, as explained in the quasi liquid-phase epitaxial growth case, be due to the difference in melting temperature between the surface and the bulk of fine particles.

To clarify the variation of the electrical resistivity as a function of the amount of $CdCl_2$ added and the sintering conditions, the carrier concentration and mobility were measured by the van der Pauw method. Fig. 8 shows the variation of electron concentration and electron mobility of CdS films which were sintered at 650° C for 30 min in nitrogen, as a function of the amount of $CdCl_2$ added in the slurry state of the samples. The electron concentration is $2 \times 10^{14}\,cm^{-3}$ for the sample which did not contain any $CdCl_2$, and increases with increasing amounts of $CdCl_2$ up to 6 wt % and then is almost independent of the amount of $CdCl_2$. The electron mobility, on the other hand, increases with the increasing amount of $CdCl_2$ up to 10 wt % and then decreases with further increase in the amount of $CdCl_2$. The impurity concentration and the free carrier concentration are in general not identical in polycrystalline semiconductors. Ghosh *et al.* [11], modifying and simplifying the theory of Seto [12], reported that the dopant concentration at which the mobility minimum and the sharp increase in free majority-carrier concentration occurs follows roughly the relation

$$N_d \sim 10^{12}/d$$

where d is the grain size in cm and N_d is the doping density. This relation was derived for polycrystalline silicon using the value of $10^{12}\,cm^{-2}$ reported by other investigators [12, 13] for the trap density at a grain boundary. The trap density at a grain boundary for sintered CdS has not been reported, but Orton *et al.* [14] reported a trap density of $7 \times 10^{11}\,cm^{-2}$ for undoped CdS prepared by a spray pyrolysis method, where a dense film with sub-micrometre grains should be obtained. If we assume that the relation of Ghosh *et al.* [11] holds for polycrystalline CdS, and that the trap density of sintered CdS film is about the same as the value found by Orton *et al.* [14], we should observe a mobility minimum and a sharp increase in free carrier concentration near a dopant concentration of approximately $4 \times 10^{15}\,cm^{-3}$ for the sample with grain size of 2.5 μm (the sample which did not contain any $CdCl_2$). This implies that the concentration of sulphur vacancies which supply free electrons when ionized [15] is of the order of $10^{15}\,cm^{-3}$ for films which contained no $CdCl_2$ and that the grain-size effect can be ignored, as far as the electron concentration is concerned, in our samples with free carrier density higher than $10^{17}\,cm^{-3}$ and with grain size larger than 2.5 μm. It has been reported that chlorine acts as a donor when doped into CdS with a donor ionization

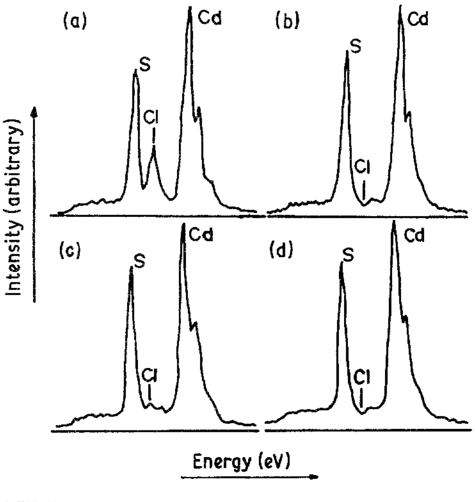

Figure 4 EDAX energy spectra of the cross-sectional area of sintered films: (a) as-coated, 10 wt % $CdCl_2$; (b) sintered at 650° C for 30 min, 10 wt % $CdCl_2$; (c) sintered at 650° C for 30 min, 20 wt % $CdCl_2$; (d) re-sintering of (c) at 650° C for 30 min.

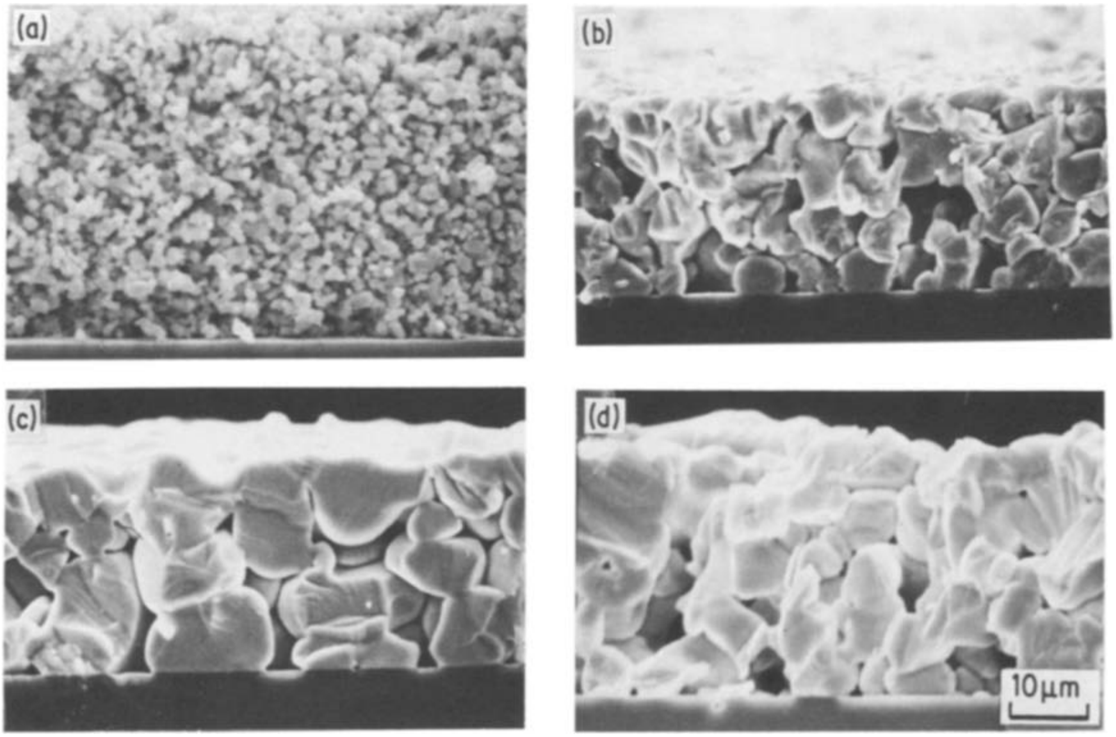

Figure 5 Microstructures of the cross-sectional area of CdS films which contained various amounts of $CdCl_2$ in the slurry and were sintered at 650° C for 30 min: (a) 0 wt %, (b) 6 wt %, (c) 10 wt %, (d) 20 wt % $CdCl_2$.

energy of 0.03 eV [16]. Thus it may be reasonable to say that the high electron concentrations observed in the samples which contained more than 6 wt % $CdCl_2$ before sintering in Fig. 6 correspond to the concentrations of the chlorine that doped during the sintering. The maximum in the curve of electron mobility against the amount of $CdCl_2$ added in the slurry state appears to be related to the grain size of the samples. It was pointed out above that the samples which contained 10 wt % $CdCl_2$ sintered the best and had the largest average grain size. It can be seen in Fig. 8 that the electron concentration in that sample is also the largest. Thus the combined effect of the largest carrier concentration and the smallest total trap density due to the smallest total grain-boundary area appears to cause a sharp maximum in the curve.

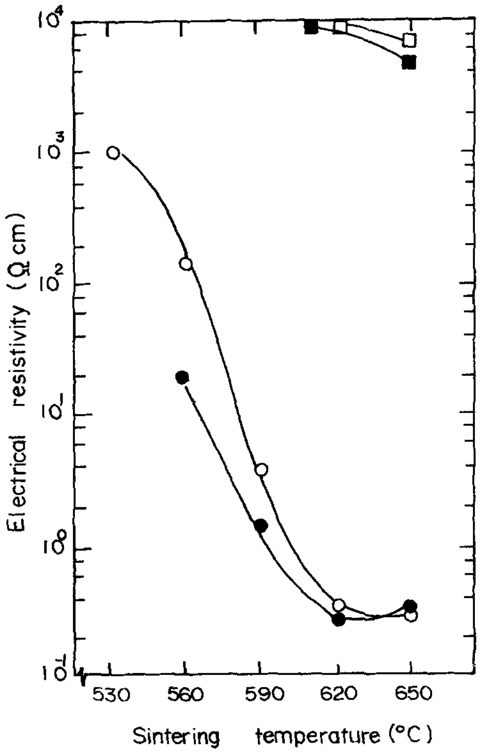

Figure 6 Electrical resistivities of CdS films as a function of sintering temperature: (□) 30 min, no $CdCl_2$; (○) 30 min, 10 wt % $CdCl_2$; (■) 60 min, no $CdCl_2$; (●) 60 min, 10 wt % $CdCl_2$.

The electron mobility and the electron concentration of the samples which contained 10 wt % $CdCl_2$ and were sintered for 30 and 60 min in nitrogen at various temperatures are shown in Figs. 9 and 10, respectively. Again, it was observed that the electron mobility is proportional to the average grain size. Comparing the electron concentration against sintering temperature curves for the samples that sintered for 30 and 60 min, it appears that the solubility of chlorine in CdS at 650° C is of the order of $10^{18}\,cm^{-3}$.

4. Conclusions

Based on the results of analyses of the microstructure and electrical properties of CdS films which contained various amounts of $CdCl_2$ before sintering and which were sintered under various conditions, the following conclusions can be drawn:

1. The presence of $CdCl_2$ in a CdS film during the sintering process strongly enhances the sintering.
2. From the fact that the enhancement of sintering occurs near the melting temperature of $CdCl_2$, and from observation of the microstructure, it appears that the enhancement is via a liquid-phase sintering mechanism.
3. The high electron concentration of the sintered CdS films which contained $CdCl_2$ before sintering is due to chlorine doping during the sintering.

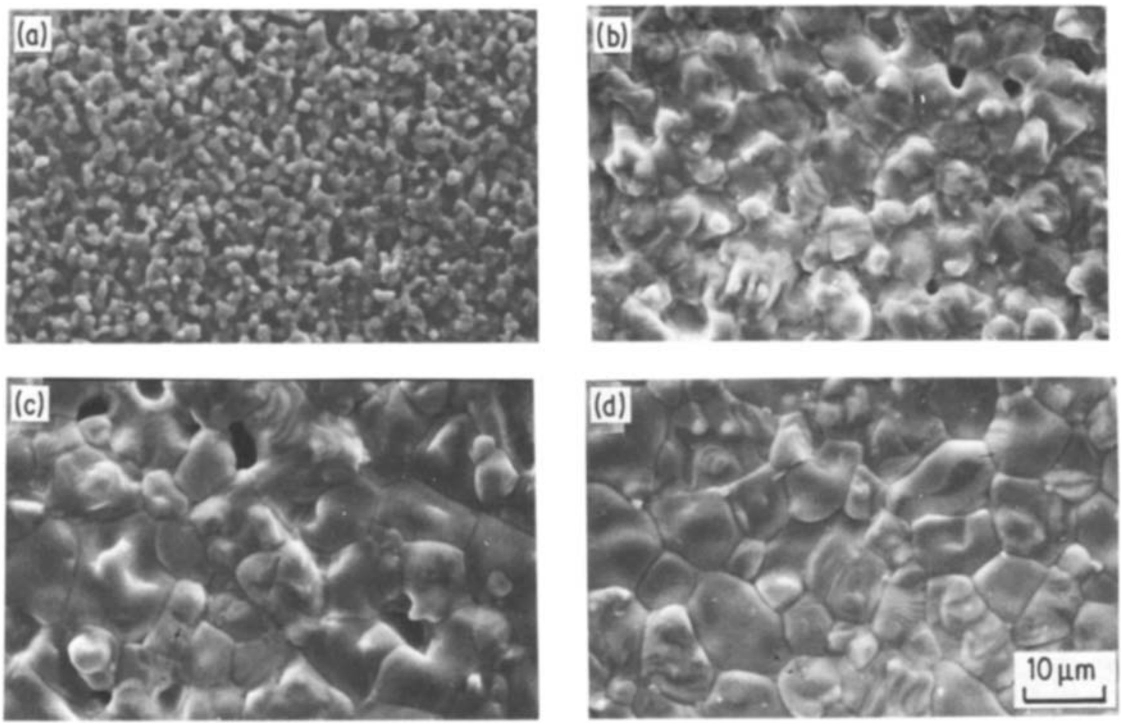

Figure 7 SEM photographs of CdS films which contained 10 wt % $CdCl_2$ and were sintered for 30 min at various temperature: (a) 350° C, (b) 560° C, (c) 600° C, (d) 650° C.

4. The solubility of chlorine in CdS is approximately $10^{18}\,cm^{-3}$ at 650° C.

5. The electron mobility of sintered CdS films depends on the carrier concentration and average grain size.

6. Both the electron mobility and the carrier concentration increase with increasing grain size.

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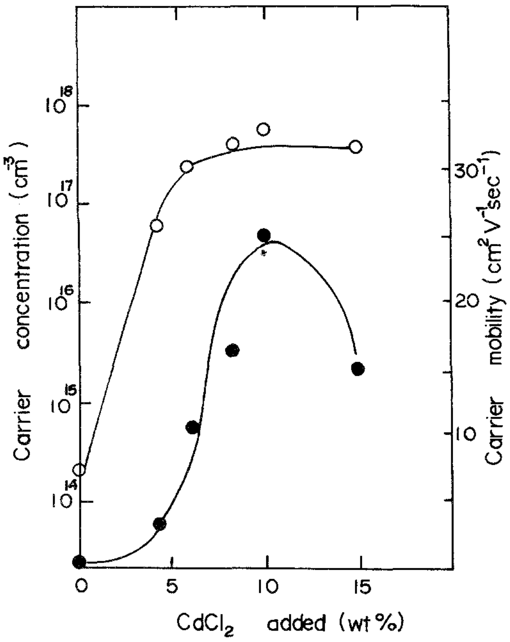

Figure 8 (O) Carrier concentration and (O) mobility of CdS films which contained various amounts of $CdCl_2$ before sintering. Films were sintered at 650° C for 30 min in nitrogen.

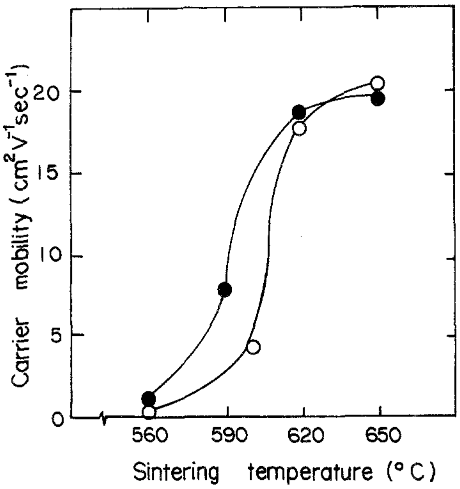

Figure 9 Electron mobilities of CdS films which contained 10 wt % $CdCl_2$ before sintering and were sintered at various temperatures for (O) 30 min and (●) 60 min.

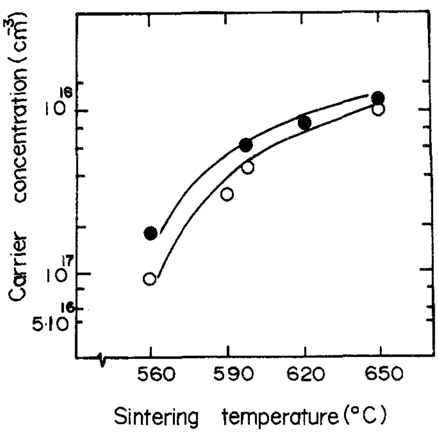

Figure 10 Carrier concentrations of CdS films which contained 10 wt % $CdCl_2$ and were sintered at various temperatures for (O) 30 min and (●) 60 min.

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