

# Effects of $\text{CdCl}_2$ in CdTe on the properties of sintered CdS/CdTe solar cells

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Sintered CdS films on glass substrates with low electrical resistivity and high optical transmittance have been prepared by a coating and sintering method. All-polycrystalline CdS/CdTe solar cells with different microstructures and properties of the CdTe layer were fabricated by coating a number of CdTe slurries, which consisted of cadmium and tellurium powders, an appropriate amount of propylene glycol and various amounts of  $\text{CdCl}_2$ , on the sintered CdS films and by sintering the glass-CdS-(Cd + Te) composites at various temperatures. The presence of more than 5 wt% of  $\text{CdCl}_2$  in the (Cd + Te) layer enhances the sintering of the CdTe film and the junction formation by a liquid-phase sintering mechanism. A low sintering temperature results in poor densification of the CdTe layer and the CdS-CdTe interface, whereas a high sintering temperature results in a deeply buried homojunction. The optimum temperature for the sintering of the CdTe layer and for junction formation decreases with increasing amount of  $\text{CdCl}_2$ . All-polycrystalline CdS/CdTe solar cells with an efficiency of 10.2% under solar irradiation have been fabricated by a coating and sintering method using cadmium and tellurium powders for the CdTe layer.

## 1. Introduction

Cadmium telluride has a band gap of 1.43 eV which is a good match to the solar spectrum for solar cell applications. It is reported that a heterojunction structure is better suited for CdTe solar cells [1]. CdS, with band gap of 2.43 eV, is a suitable window material for a CdS/CdTe or CdS/ $\text{Cu}_2\text{S}$  solar cell. Thus much attention has been focused on thin-film CdS/CdTe heterojunction due to their promise as a low-cost solar cell. Fabrication of all-polycrystalline CdS/CdTe solar cells with efficiency of over 8% by electro-deposition [2, 3], close-spaced sublimation [4] and by screen printing and sintering [5, 6] methods has been reported.

In the screen printing and sintering method, sintered CdS film serves as a substrate for coating and sintering of a CdTe layer to obtain a dense CdTe layer and to form a heterojunction. It is reported that a certain amount of  $\text{CdCl}_2$  (9 to 13 wt%) in coated CdS films acts quite effectively as a sintering aid for the sintering of CdS films [7, 8]. The effects of microstructure and electronic properties of the sintered CdS films on the photovoltaic properties of the sintered CdS/CdTe have also been reported [6]. However, no reports on the effects of the preparation conditions of CdTe layer on the properties of CdS/CdTe solar cells are available.

There is, therefore, ample interest and motivation for the study of the effect of the various preparation conditions of the CdTe layers on the cell parameters of the sintered CdS/CdTe heterojunction solar cells. In the present paper we report mainly the results of an investigation of the effect of  $\text{CdCl}_2$  added to the (Cd + Te) slurry on the sintering behaviour of the

CdTe layer and on the photovoltaic properties of the sintered CdS/CdTe solar cells.

## 2. Experimental details

Commercial CdS, cadmium, tellurium and anhydrous  $\text{CdCl}_2$  powders (99.999% purity) were used in the present investigation. The as-received CdS powders, with an average particle size of 0.5  $\mu\text{m}$ , were calcined at 700°C for 2 h in nitrogen, and crushed. A slurry consisting of the calcined CdS powder, now with an average particle size of 1.5  $\mu\text{m}$ , 13 wt%  $\text{CdCl}_2$ , and 65 vol% propylene glycol (PG), was prepared by mixing with a mortar and pestle. The slurry was coated on boro-silicate glass (Corning 7059) substrates using a screen printer with a 165 mesh stainless steel screen. The glass substrates were cleaned in an ultrasonic bath with trichloroethylene, acetone and methanol before coating. The coated CdS films were dried at 120°C for 2 h in air to remove the binder (PG) and then placed in a quartz ampoule that had four 1 mm diameter holes. They were sintered at 600°C for 1 h. The furnace was flushed with nitrogen before sintering and a nitrogen flow rate of 250  $\text{cm}^3\text{min}^{-1}$  was used to maintain the nitrogen atmosphere during sintering. To obtain sintered CdS films with uniform properties, the sintered films placed in an open tray were heat treated at 625°C for 15 min in nitrogen.

A number of slurries, consisting of cadmium and tellurium powders, 60 vol% propylene glycol and various amounts of  $\text{CdCl}_2$  were also prepared by mixing with a mortar and pestle. The average particle sizes of the cadmium and tellurium powders were approximately 3 and 0.5  $\mu\text{m}$ , respectively. Each slurry

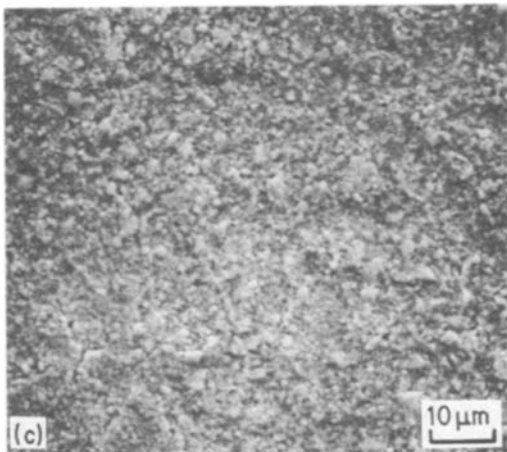
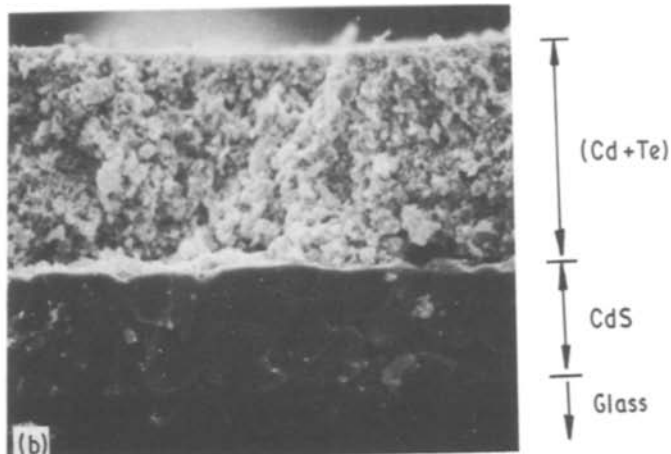
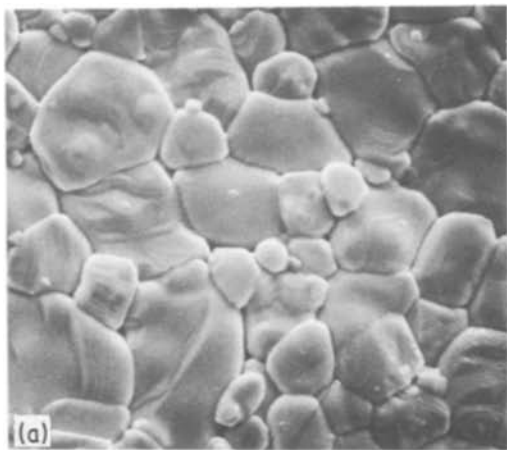


Figure 1 Scanning electron micrographs of (a) the surface of the CdS film which was sintered at 600°C for 1 h and was reheat-treated at 625°C for 15 min, (b) the cross-section of (Cd + Te) dried film coated on the sintered CdS film, (c) the surface of the dried (Cd + Te) film.

was coated on the sintered and heat-treated CdS films using a mask and a screen printer with 150 mesh silk screen to obtain CdTe films with an area of  $3 \times 25 \text{ mm}^2$  and with a thickness of approximately  $35 \mu\text{m}$ . The composite layers of glass-CdS-(Cd + Te) were then sintered, using another ampoule which had one 1 mm diameter hole, for 1 h in nitrogen. The sintering temperature was varied from 600 to 725°C.

Ohmic contacts were provided by coating an indium-silver paint (20% by weight In powder) on the CdS films and a carbon paint on the CdTe films. To improve the mechanical strength of the carbon contacts, silver paste was coated on the top of the contacts. Both contacts were annealed at 350°C for 10 min in nitrogen.

Solar cell parameters were measured both under sunlight and with an illumination of a  $50 \text{ mW cm}^{-2}$  tungsten lamp. Scanning electron microscope techniques (SEM) were used to investigate the microstructure of film surfaces and cross-sectional areas.

### 3. Results and discussion

The structure of CdS/CdTe solar cells fabricated in the present investigation is a back wall type, and the role of the sintered CdS layer is the front contact as well as the window of the solar cell. Thus low electrical resistivity and high optical transmittance of the sintered CdS layer are desirable and necessary. It is reported [8] that CdS films with such properties can be obtained by sintering them with CdCl<sub>2</sub> as a sintering aid. However, the CdS films sintered in this way often showed non-

uniform properties when the size of the CdS films was large. To obtain sintered CdS films with a large area and with uniform properties, a post-heat-treatment process was used. The electrical resistivity and the optical transmittance in the long wavelength region ( $h\nu < E_g$ ) of the CdS films, which contained 13 wt % CdCl<sub>2</sub> before sintering and were sintered at 600°C for 1 h in nitrogen, ranged from 10 to 30 Ω cm and 82 to 84%, respectively. The electrical resistivity decreased to 0.3 to 0.6 Ω cm and the optical transmittance was 81 to 83% after heat treatment of 625°C for 15 min, in an open tray, to remove by evaporation any CdCl<sub>2</sub> that remained in the sintered CdS films.

Fig. 1a shows a typical microstructure of the sintered CdS films after the post-heat-treatment, and the microstructures of the cross-section and surface of a

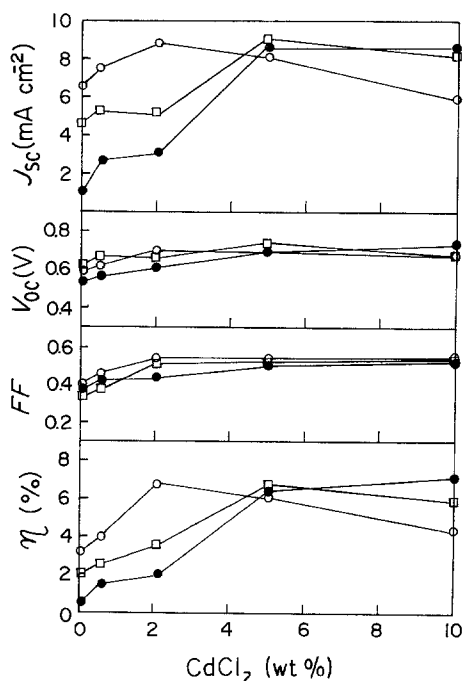


Figure 2 Cell parameters of the sintered CdS/CdTe solar cells as a function of amounts of CdCl<sub>2</sub> added to (Cd + Te), for various sintering temperatures. (○) 700°C, (□) 650°C, (●) 625°C.

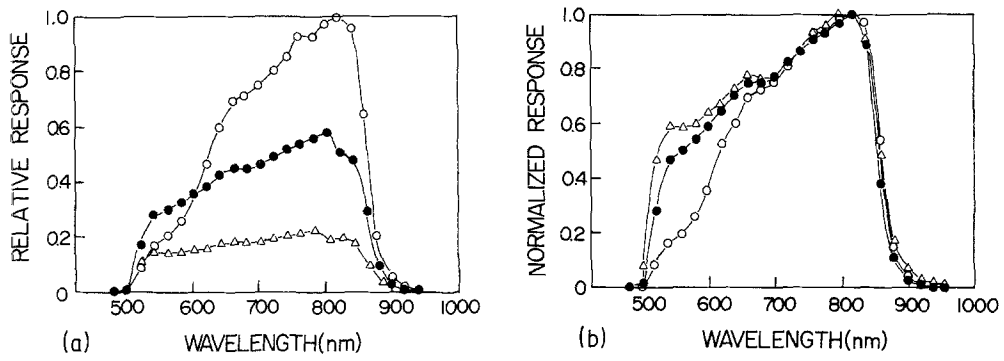


Figure 3 (a) Spectral response and (b) normalized spectral response of the CdS/CdTe solar cells which contained ( $\Delta$ ) 0 wt %, ( $\bullet$ ) 0.5 wt % and ( $\circ$ ) 10 wt % CdCl<sub>2</sub> in CdTe before sintering. CdTe films were sintered at 625°C.

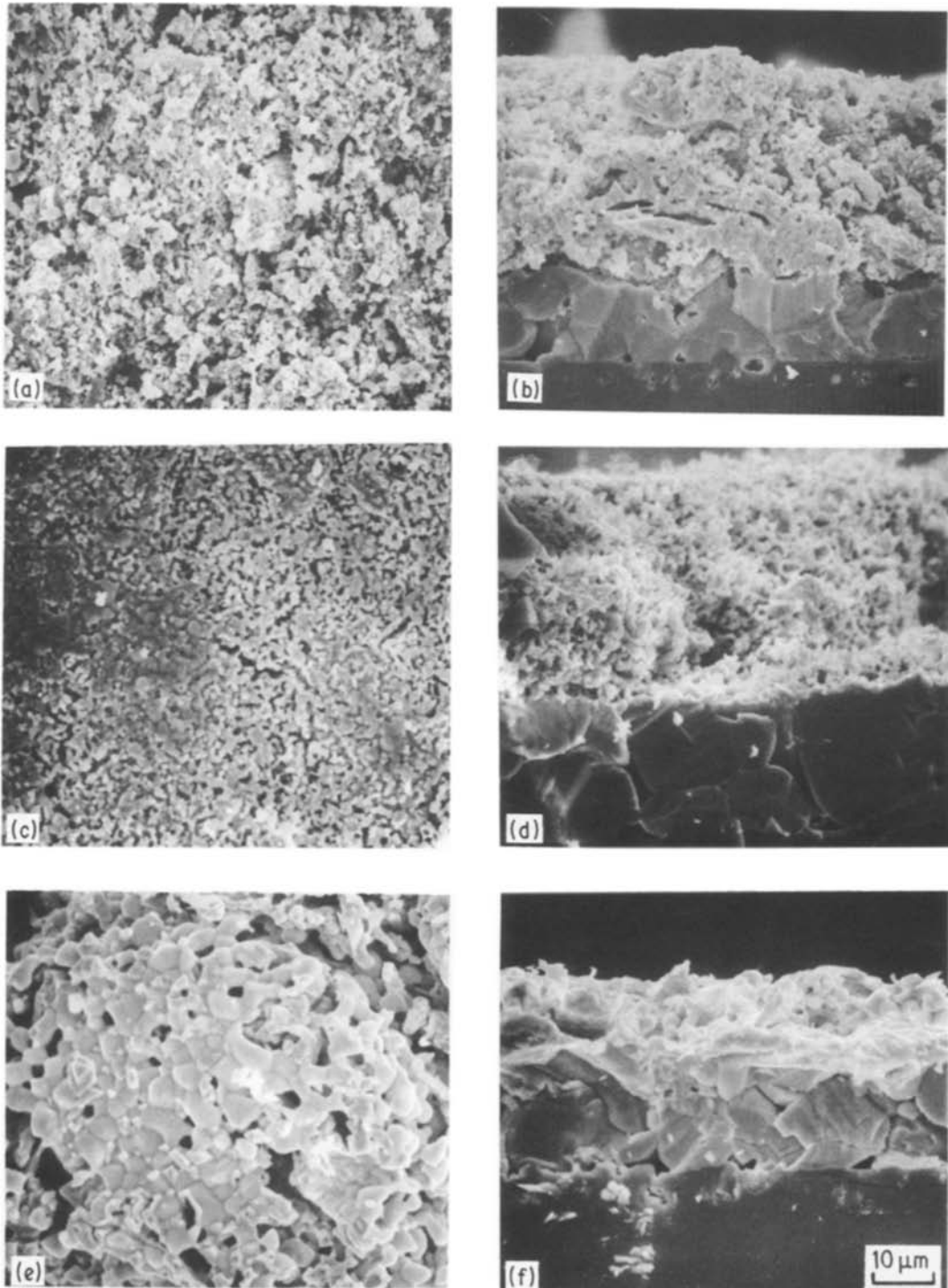


Figure 4 Scanning electron micrographs of the surfaces and the cross-sections of CdTe films which were coated on the sintered CdS films and which contained (a, b) 0 wt %, (c, d) 0.5 wt % and (e, f) 10 wt % CdCl<sub>2</sub> before sintering. CdTe films were sintered at 625°C.

(Cd + Te) layer coated on the sintered CdS film are shown in Fig. 1b and c. The sintered CdS film with a thickness of  $\sim 20 \mu\text{m}$  is dense and has an average grain size of  $\sim 12 \mu\text{m}$ , and the coated (Cd + Te) layer of thickness  $\sim 35 \mu\text{m}$  consists of sub-micrometre-sized particles (tellurium) and a few micrometre-sized particles (cadmium).

Fig. 2 shows the cell parameters of all-polycrystalline CdS/CdTe solar cells, made by sintering the glass-CdS-(Cd + Te) composites at 625, 650 or 700°C for 1 h in nitrogen, as a function of the amount of the CdCl<sub>2</sub> added in the (Cd + Te) layer. For the cells whose junctions were formed by sintering the composites at 625 or 650°C, the short-circuit current density ( $J_{sc}$ ) is a few mA cm<sup>-2</sup> up to the 2 wt % CdCl<sub>2</sub>, increases sharply to 8.5 mA cm<sup>-2</sup> for 5 wt % CdCl<sub>2</sub> and then stays at about the same value, the open-circuit voltage ( $V_{oc}$ ) and fill factor ( $FF$ ) increase slightly with increasing amount of CdCl<sub>2</sub>. Thus the variation of solar efficiency ( $\eta$ ) as a function of CdCl<sub>2</sub> added to the (Cd + Te) layer is similar to that of  $J_{sc}$ , because the efficiency is related to  $J_{sc}$ ,  $V_{oc}$  and  $FF$ .

For the cells whose junctions were formed by sintering at 700°C, on the other hand, the  $J_{sc}$  and  $\eta$  increase with increasing CdCl<sub>2</sub> content up to 2 wt % and then decrease with further increase in the amount of CdCl<sub>2</sub>. The optimum amount of CdCl<sub>2</sub> needed to obtain maximum  $\eta$  depends on the junction formation conditions (sintering temperature of the composites), i.e. the optimum amounts of CdCl<sub>2</sub> are 2, 5 and 10 wt % when the junctions were formed at 700, 650 and 625°C, respectively.

To explore the properties of the junction between the CdS and CdTe, the spectral response of the solar cell was measured. Spectral responses of the sintered CdS/CdTe solar cells which contained various amounts of CdCl<sub>2</sub> in the (Cd + Te) layer and were fabricated by sintering the glass-CdS-(Cd + Te) composites at 625°C for 1 h in nitrogen, are shown in Fig. 3a. The area under each curve represents the relative efficiency of the solar cell. In the long wavelength region ( $600 \text{ nm} < \lambda < 860 \text{ nm}$ ), the response is higher the larger the amount of CdCl<sub>2</sub>, whereas the response of the cell that contained 0.5 wt % CdCl<sub>2</sub>, is the highest in the short wavelength region ( $510 \text{ nm} < \lambda < 600 \text{ nm}$ ). The characteristics of the junctions are more clearly shown in the normalized spectral responses of Fig. 3b. The spectral response of the cell that contained 0 or 0.5 wt % CdCl<sub>2</sub> is more like that of a heterojunction, i.e. the response is large between 510 nm which corresponds to the energy band gap of CdS and 860 nm which corresponds to band gap of CdTe. On the other hand, the spectral response of the cell that contained 10 wt % CdCl<sub>2</sub> is similar to that of a buried homojunction, i.e. the response is poor in the short wavelength region. The microstructures of surface and cross-section of the solar cells of Fig. 3 are shown in Fig. 4. The CdTe layer which contained no CdCl<sub>2</sub> (a, b) is hardly sintered, and that which contained 0.5 wt % before sintering (c, d) shows early stages of sintering. However, the CdTe layer that contained 10 wt % CdCl<sub>2</sub> has a particle size of  $\sim 5 \mu\text{m}$  (e) and shows a rather dense structure at the interface

(f). The microstructure of the CdTe layer that contained 5 wt % CdCl<sub>2</sub> was similar to this one. Thus it appears that the presence of more than 5 wt % CdCl<sub>2</sub>, with melting temperature of 568°C, in (Cd + Te) layers before sintering enhances the sintering of the CdTe layer with a liquid-phase sintering mechanism and also forms a buried homojunction (n-p junction in CdTe) by enhancing the diffusion of the donor impurity from the CdS into the CdTe layer. As can be seen in Fig. 2,  $V_{oc}$  increases with increasing amount of CdCl<sub>2</sub>. The increase in  $V_{oc}$  must result from an increase in diode factor  $A$  or  $J_{sc}$ , or from decrease in  $J_0$ , the reverse saturation current of the junction, which are related by

$$V_{oc} = (AkT/q) \ln [(J_{sc}/J_0) + 1] \quad (1)$$

for an ideal junction neglecting parallel resistance leakage. It is reported [9] that the value of  $J_0$  is the most significant in determining the magnitude of  $V_{oc}$ . Fig. 5 shows the dark  $J$ - $V$  curves of the solar cells which contained 0.5 and 10 wt % CdCl<sub>2</sub> in the (Cd + Te) layer before sintering. The  $J_0$  of the solar cell that contained 10 wt % is an order of magnitude smaller than that of the solar cell that contained 0.5 wt % CdCl<sub>2</sub>. Thus it can be seen that the increase in  $V_{oc}$  as the amount of CdCl<sub>2</sub> increases was mainly caused by the decrease in  $J_0$  and increase in  $J_{sc}$  (Fig. 2). It appears that the improved microstructure of the CdTe layer that contained 10 wt % CdCl<sub>2</sub> is responsible for the improvement of  $FF$  through reduction of sheet resistance of the CdTe layer and series resistance of the solar cell. The series resistances of the cells which contained 0.5 and 10 wt % CdCl<sub>2</sub> were 27 and 13  $\Omega$ , respectively, and  $FF$  increased from 0.43 to 0.57.

As mentioned before, when the composites were sintered at 625°C to densify the CdTe layer and form

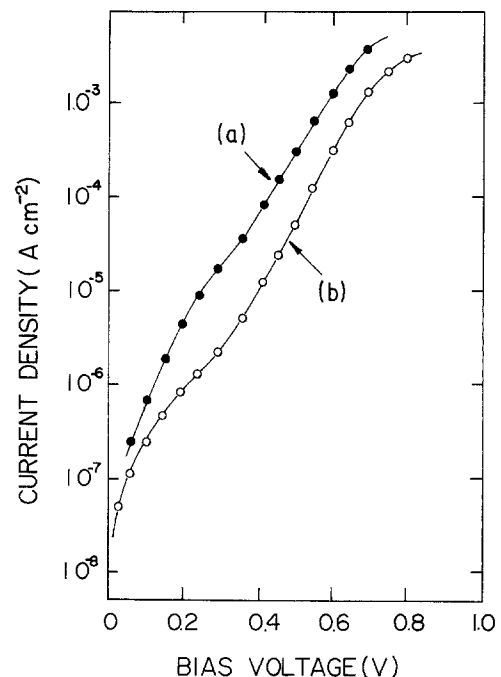


Figure 5 Dark  $J$ - $V$  characteristics of the sintered CdS/CdTe solar cells which contained (a) (●) 0.5 wt % and (b) (○) 10 wt % CdCl<sub>2</sub> in CdTe before sintering. CdTe films were sintered at 625°C. (a)  $A = 5.8$ ,  $J_0 = 1.3 \times 10^{-7} \text{ A cm}^{-2}$ , (b)  $A = 4.8$ ,  $J_0 = 3.5 \times 10^{-8} \text{ A cm}^{-2}$ .

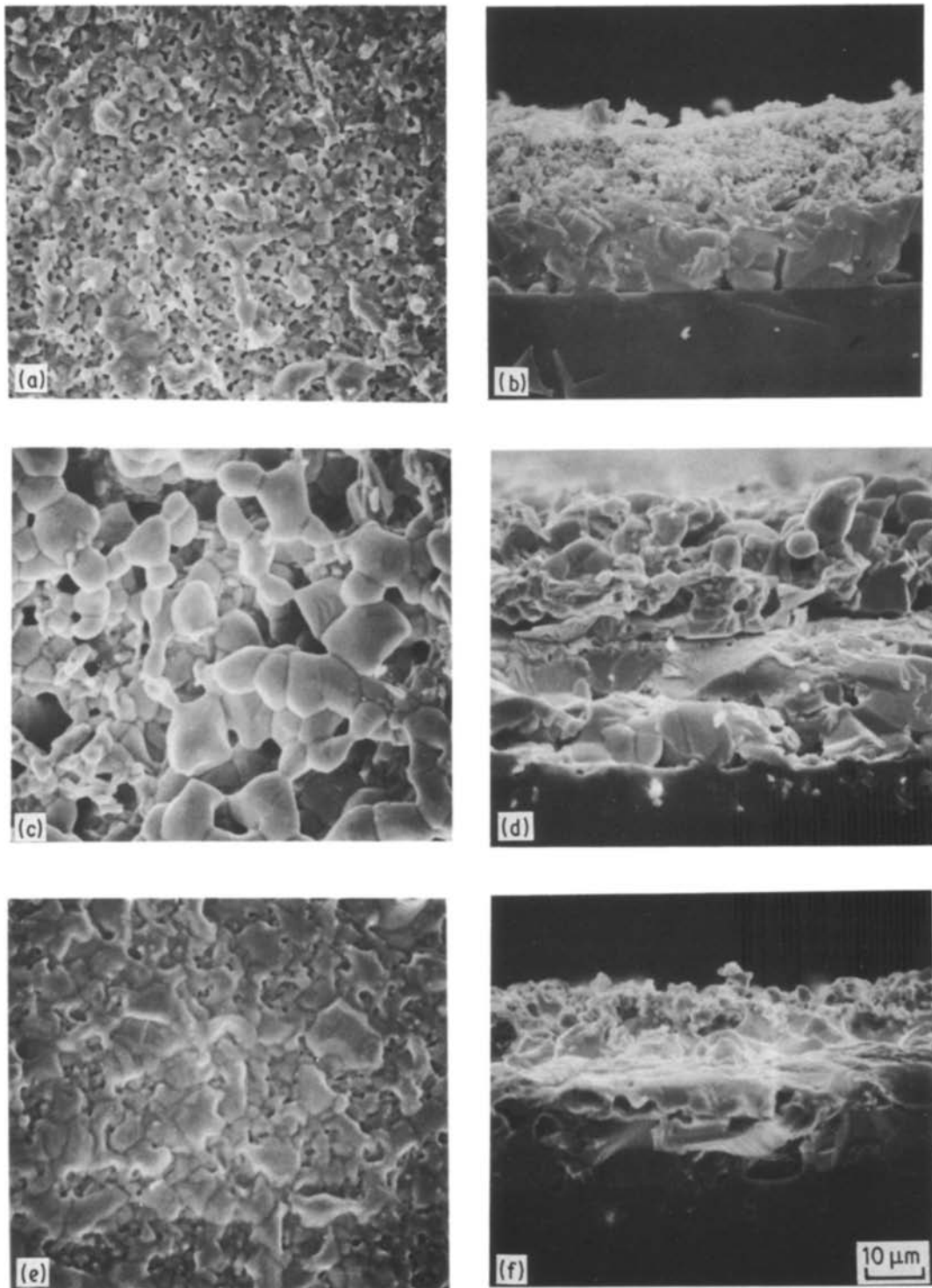


Figure 6 Scanning electron micrographs of the surfaces and cross-sections of CdTe films which were coated on the sintered CdS films and which contained (a, b) 0 wt %, (c, d) 2 wt % and (e, f) 10 wt % CdCl<sub>2</sub> before sintering. CdTe films were sintered at 700°C.

the junction, the CdTe layers that contained less than 2 wt % CdCl<sub>2</sub> show poor microstructures. The optimum sintering temperature for the cell that contained 2 wt % CdCl<sub>2</sub> was 700°C. Fig. 6 shows the microstructures of surfaces and cross-sections of the CdS/CdTe solar cells, which contained various amounts of CdCl<sub>2</sub> in the (Cd + Te) layer, fabricated by sintering the composites at 700°C. It again shows that the CdTe layers that contained no CdCl<sub>2</sub> and 2 wt % CdCl<sub>2</sub> were sintered by solid state sintering, whereas the CdTe layer that contained 10 wt % CdCl<sub>2</sub> was sintered via a liquid-phase sintering mechanism. It appears that abnormal grain growth occurred in the CdTe layer

that contained 2 wt % CdCl<sub>2</sub>, i.e. the grains are large but the porosity is also large. The solar cell that contained 10 wt % CdCl<sub>2</sub> has the most dense CdTe layer and heterojunction. However,  $J_{sc}$  and  $\eta$  are less than those of the cell that contained 2 wt % CdCl<sub>2</sub> (Fig. 2) may be because of the formation of a deep n-p junction which decreases the response in the short wavelength region as can be seen in Fig. 7.

To explore further the dependence of the solar efficiency on the preparation conditions of the CdTe layer, cadmium powder with an average particle size of  $\sim 0.5 \mu\text{m}$  was prepared using an automatic grinder. Sintered CdS/CdTe solar cells fabricated by coating a

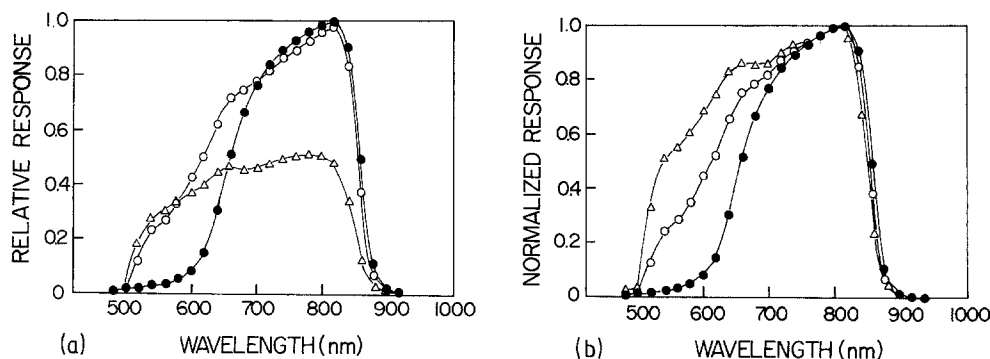


Figure 7 (a) Spectral response and (b) normalized spectral response of the CdS/CdTe solar cells which contained ( $\Delta$ ) 0 wt %, ( $\circ$ ) 2 wt % and ( $\bullet$ ) 10 wt % CdCl<sub>2</sub> in CdTe before sintering. CdTe films were sintered at 700°C.

CdTe slurry, which consisted of the finer (Cd + Te) powder, 2 wt % CdCl<sub>2</sub> and an appropriate amount of propylene glycol, on the sintered CdS films followed by sintering at 700°C for 1 h in nitrogen had  $J_{sc}$  of 13 mA cm<sup>-2</sup> and  $\eta$  of 9.5%. The efficiency of this cell with an active area of 3 × 11 mm<sup>2</sup> was 10.2% under solar irradiation with an intensity of 75 mW cm<sup>-2</sup>. The effects of various preparation conditions of the CdTe layer on the photovoltaic properties of CdS/CdTe solar cells are under investigation and the results will be presented elsewhere.

#### 4. Conclusion

Based on the results of analysis of the microstructure of CdTe films, which were coated on sintered CdS films and contained various amounts of CdCl<sub>2</sub> before sintering, and of the cell parameters of the sintered all-polycrystalline CdS/CdTe solar cells whose junctions were formed at various temperatures, the following conclusions can be drawn.

1. The presence of a small amount (< 2 wt %) of CdCl<sub>2</sub> in the (Cd + Te) film results in the formation of a nucleus for abnormal grain growth.
2. The presence of a large amount (> 5 wt %) of CdCl<sub>2</sub> in the (Cd + Te) film enhances the sintering significantly via a liquid-phase sintering mechanism.
3. The short-circuit current density ( $J_{sc}$ ) and the efficiency ( $\eta$ ) of sintered CdS/CdTe solar cells increase with increasing grain size of the CdTe layer.
4. The average grain size of the CdTe layer increases with increasing amount of CdCl<sub>2</sub> and with increasing sintering temperature of the glass-CdS-CdTe composites.

5. It appears that the depth of the buried homo-junction also increases with increasing amount of CdCl<sub>2</sub> in the CdTe layer and with increasing sintering temperature.

6. Thus there exists an optimum temperature in sintering the CdTe layer and the formation of a junction between CdS and CdTe, and the optimum temperature decreases with increasing amount of CdCl<sub>2</sub> in the (Cd + Te) layer.

7. When the amount of CdCl<sub>2</sub> is small, the use of cadmium and tellurium powders with finer particles improves the efficiency of the sintered CdS/CdTe solar cell.

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