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Effects of junction formation conditions on the photovoltaic properties of sintered CdS/CdTe solar cells

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Microstructures and properties of sintered CdS films on glass substrates and sintered CdTe films on polycrystal CdS substrates have been investigated. The CdS films, which contained 9 wt% $CdCl_2$ as a sintering aid and were sintered at 650° C for 1 h in nitrogen, are transparent and have an average grain size of $15\,\mu m$ and an electrical resistivity of $0.5\,\Omega cm$. The CdTe films, which were coated on the sintered CdS substrate and were sintered above 610° C for 1 h in nitrogen, have a dense structure with an average grain size larger than $5\,\mu m$. All polycrystal CdS/CdTe solar cells were fabricated by this successive coating and sintering method. The sintering temperature of CdTe films on the sintered CdS films was varied from 585 to 700° C. Compositional interfaces and p–n juctions are formed during sintering. The highest solar efficiency (7.18%) was found in a solar cell made by sintering the composite layer of glass–CdS–CdTe at 625° C for 1 h. A fabrication temperature below 610° C resulted in poor solar cell efficiencies due to the porous structure of the CdTe films and above 650° C also resulted in poor efficiencies due to the formation of a $CdS_{1-x}Te_x$ layer at the interface and a large p–n junction depth.

1. Introduction

CdTe with a band gap of 1.43 eV is suitable for making solar cells. It is known that the surface recombination velocity for CdTe is large so that a heterostructure is better suited for CdTe solar cells [1]. CdS with a band gap of 2.43 eV is suitable for the window material for a CdS/CdTe heterojunction solar cell. To reduce production costs, it is necessary to fabricate the solar cells with polycrystal CdS and CdTe films. Various methods, such as vacuum evaporation [2], close spaced sublimation [3], and spray pyrolysis [4], have been developed for the production of polycrystal CdS and CdTe films, and polycrystal CdS/CdTe solar cells with an efficiency of over 6% have been produced.

The method, which consists of coating slurry on a substrate and sintering, is economical for mass production of thin films and polycrystal solar cells. Recently, Nakayama *et al.* [5] reported the production of all polycrystal n-CdS/p-CdTe heterojunction solar cells, doping gallium into the CdS and copper into the CdTe, by a sintering method with an efficiency of over 8%. However, production of such solar cells has only been reported only by the Matsushita group, and the electrical properties of the CdS/CdTe solar cells produced were reported in papers presented by the Matsushita group [6, 7].

There is, therefore, ample interest for the study of the effect of the various preparation conditions on the microstructure and electrical properties of the sintered CdS and CdTe films, and on the parameters of the sintered CdS/CdTe heterojunction solar cells. In the present paper we report the results of an investigation of the microstructure and electrical properties of such films, and the effects of interface formation conditions on the parameters of all-polycrystal CdS/CdTe heterojunction solar cells. To simplify the p–n junction formation phenomena, we did not use dopants such as gallium or copper in the present investigation.

2. Experimental procedure

Commercial CdS, CdTe and anhydrous $CdCl_2$ powders with 5N purity were used in this investigation. The as-received CdS powders, with an average particle size of $0.45\,\mu m$, were calcined at 700° C for 2 h in nitrogen and crushed to obtain a powder with larger particle size. A slurry consisting of the calcined CdS powder with an average particle size of $2\,\mu m$, 9 wt% $CdCl_2$, and an appropriate amount of propylene glycol, was prepared by mixing with a mortar and pestle. The slurry was coated on $2.5 \times 4\,cm^2$ borosilicate glass substrates, which had been cleaned in an ultrasonic bath with trichloroethylene and acetone, using a screen printer with a 165 mesh stainless steel screen. The CdS films coated on the glass substrate were dried at 120° C for 2 h in air and then placed in a quartz ampoule which had four 1 mm diameter holes. They were sintered at 650° C for 1 h in a quartz tube furnace. The furnace was flushed with nitrogen, with 5N purity and a dew point of $-70°$ C, before sintering and a nitrogen flow rate of $100\,cm^3\,min^{-1}$ was used to maintain the nitrogen atmosphere during sintering.

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A slurry, consisting of CdTe powder, 1 wt % $CdCl_2$ and an appropriate amount of propylene glycol, was also prepared by mixing with a mortar and pestle. The CdTe slurry was coated on the sintered CdS films using a mask and the screen printer with silk screen to obtain CdTe films with area of $3 \times 11\,mm^2$ and with a thickness of approximately $25\,\mu m$. The composite layers of glass–CdS–CdTe were then sintered to obtain dense CdTe films and to form junctions between the CdS and the CdTe films. The sintering was performed in nitrogen for 1 h using another quartz ampoule and tube furnace. The sintering temperature was varied from 585 to 700° C.

Ohmic contacts were formed by the evaporation of indium on to the CdS films in 10^{-6} torr vacuum and by a coating of carbon paste on the CdTe films. To obtain mechanical strength of the contacts, silver paste (Dupont conductor composition 4929) was coated on the top of the indium and the carbon contacts. The contact pastes were cured at 350° C for 5 min in a nitrogen atmosphere. Sheet resistances of the CdS films were measured using the four-probe method. Electrical resistivity was determined by measurements of sheet resistance of the film and film thickness. The solar cell parameters were measured both under sunlight and illumination with a $50\,mW\,cm^{-2}$ tungsten lamp. Spectral response of the solar cells was measured with a monochromator and the tungsten light source. Photographs were taken of cross-sectional area as well as film surface of each sample with a scanning electron microscope (SEM).

3. Results and discussion

A CdS film which is to be used for a window layer of a CdS/CdTe heterojunction solar cell must have high optical transparency and low sheet resistance. It was reported that $CdCl_2$ in CdS films enhances the sintering of CdS films [7, 8] and that sintering temperatures between 620 and 650° C are optimum for the sintering of CdS films with 9 wt % $CdCl_2$ [8]. A typical microstructure of the CdS films on a glass substrate, which contained 9 wt % $CdCl_2$ in the slurry state is shown in Fig. 1. Fig. 1a shows the scanning electron micrograph of the specimen before sintering and Fig. 1b shows the microstructure of the specimen which was sintered at 650° C for 1 h in nitrogen. It can be seen that the sintered film has large grains and small voids. The thickness of the sintered CdS film was $20\,\mu m$. The average grain size determined by the linear intercept method was $15\,\mu m$ and the electrical resistivity of the films was $0.5\,\Omega cm$. Measurement of optical transmission of the sintered CdS films was difficult, due to the roughness of the sintered surface which caused diffuse scattering. The degree of optical transparency of the films corresponding to those in Fig. 1 is shown in Fig. 2. It is seen that the sintered film with small voids is quite transparent. It was reported that doping with chlorine occurs during the sintering of CdS films which contain $CdCl_2$ [8, 9]. The electron concentration and electron mobility of this type of sintered CdS film was of the order of $10^{18}\,cm^{-3}$ and $25\,cm^2\,V^{-1}\,sec^{-1}$, respectively, as reported previously [8].

Fig. 3 shows the microstructures of CdTe films which were coated on the sintered CdS films and were sintered for 1 h in nitrogen at 585, 625, 650 and 700° C. The specimen that was sintered at 585° C shows a porous structure with grain size of $\sim 10\,\mu m$, while the specimens which were sintered above 625° C show dense structures with an average grain size of $\sim 5\,\mu m$.

Photovoltaic properties of the sintered CdS/CdTe heterojunction solar cells measured under the tungsten light source, as a function of the sintering temperature of the CdTe films, are shown in Fig. 4. The short-circuit current density (J_{sc}) increases with increase in sintering temperature up to 625° C and then decreases with further increase in the sintering temperature. The open circuit voltage (V_{oc}), is about 0.65 V and is almost independent of the sintering temperature while the fill factor (FF) increases with increasing sintering temperature up to 610° C and then decreases slowly with further increase in sintering temperature. Since the solar efficiency (η) is related to J_{sc}, V_{oc}, FF, the efficiency against sintering temperature curve is similar to the curve for J_{sc} against the sintering temperature. A solar cell with an active area of $3 \times 11\,mm^2$ which was fabricated by sintering the composite glass–CdS–CdTe films at 625° C for 1 h in a nitrogen atmosphere showed the best photovoltaic

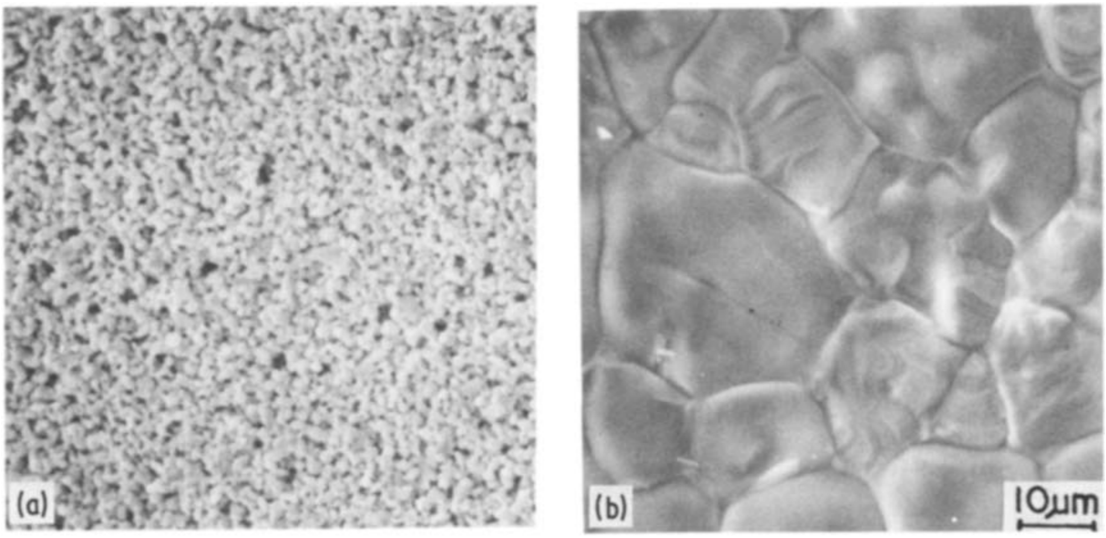

Figure 1 Scanning electron micrographs of the surface of a CdS film (a) before, and (b) after sintering, at 650° C for 1 h in nitrogen.

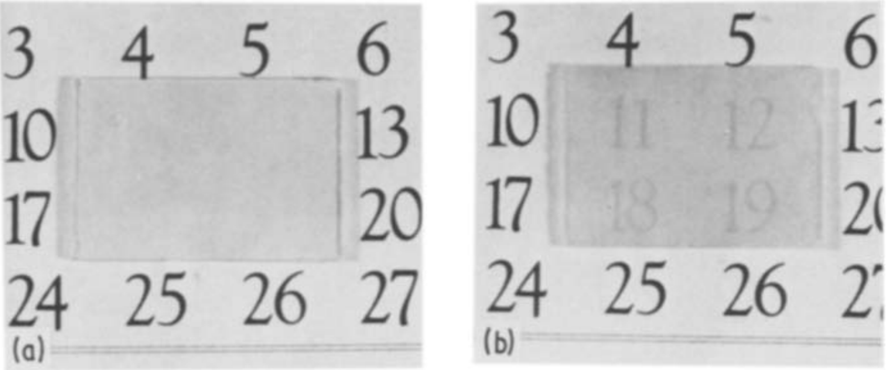

Figure 2 Photographs showing the degree of optical transparency of CdS films of area 2.5 × 4 cm^2 placed over printing: (a) dried, and (b) sintered film.

properties with J_{sc} of 8.48 mA cm^{-2} and an efficiency of 6.51% under illumination by a 50 mW cm^{-2} tungsten light source. A J–V curve under solar irradiation with an intensity of 45 mW cm^{-2} for this solar cell is shown in Fig. 5.

The appearance of a maximum in the J_{sc} and FF against sintering temperature curves for the composite layer indicates that some complex changes occur during sintering. Firstly, it was seen in Fig. 3 that the density of the sintered CdTe layer increased with increasing sintering temperature up to 625° C. This density increase causes decrease in the resistivity of CdTe layers resulting in a decrease in the series resistance, which is the sum of the resistance of the CdS layer, that of the CdTe layer and the contact resistance. This decrease in the series resistance appears to increase the fill factor as can be seen in Fig. 4. The increase in the density can also increase the CdS–CdTe junction area. We eliminate the possibility of an increase in average grain size with increasing sintering temperature because the microstructure shown in Fig. 3 shows otherwise.

Secondly, sintering temperatures above 625° C cause the formation of a second phase on the exposed

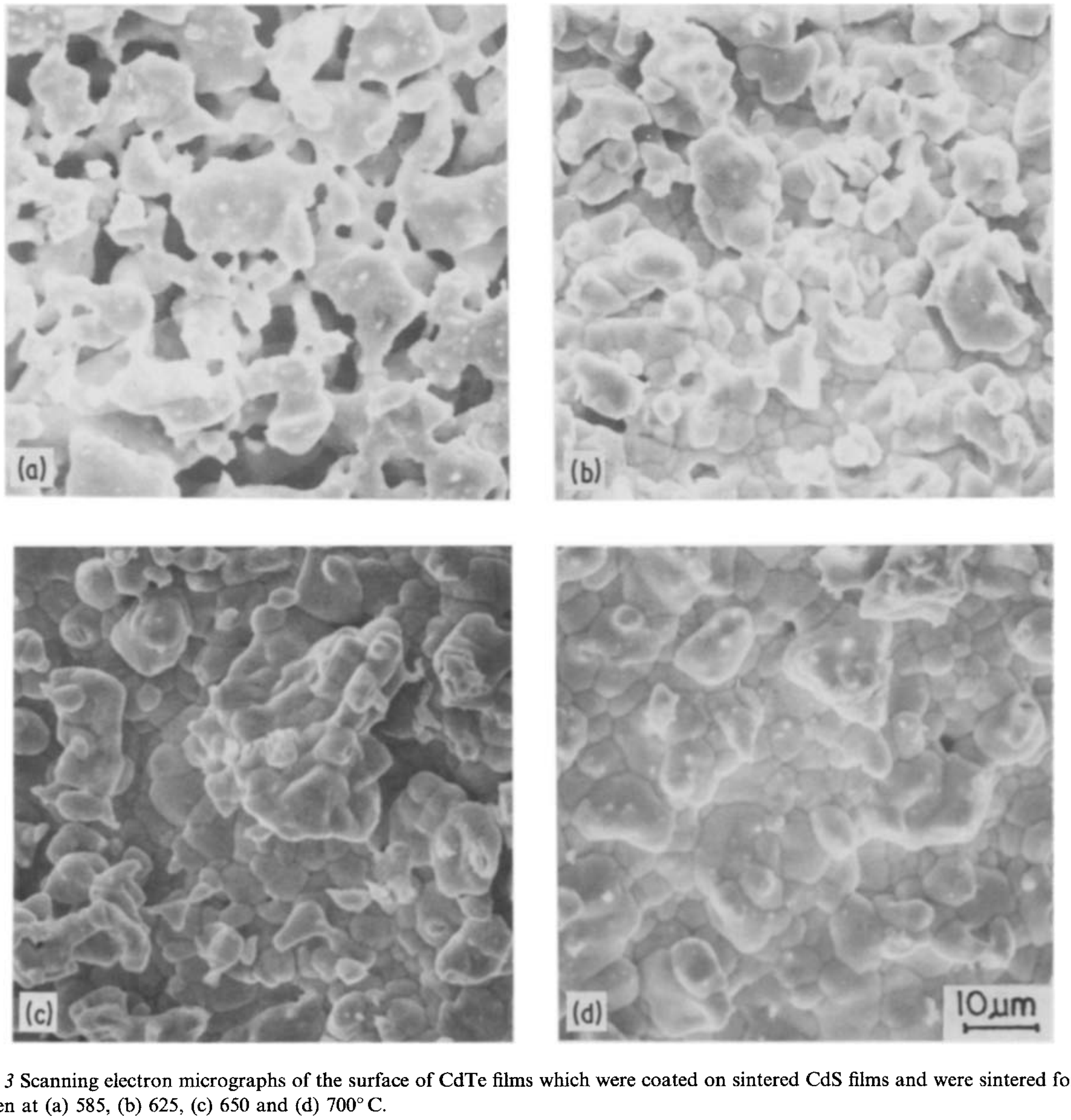

Figure 3 Scanning electron micrographs of the surface of CdTe films which were coated on sintered CdS films and were sintered for 1 h in nitrogen at (a) 585, (b) 625, (c) 650 and (d) 700° C.

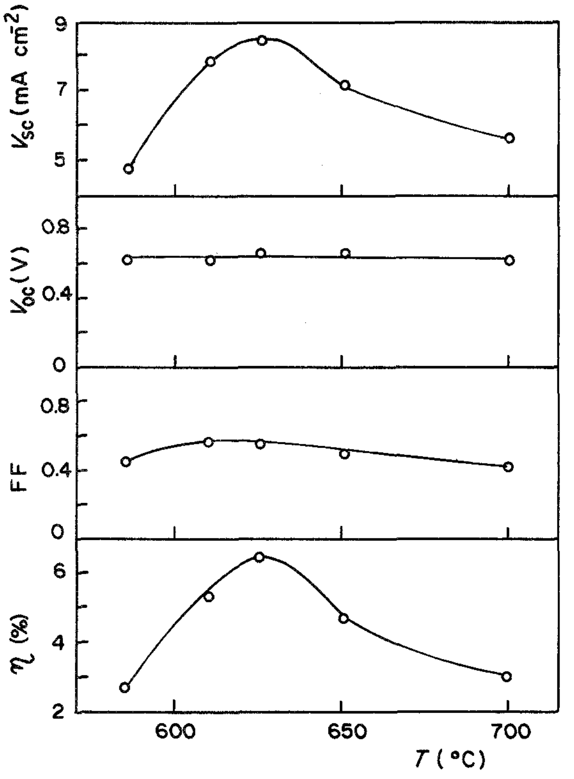

Figure 4 Cell parameters of sintered CdS/CdTe solar cells as a function of sintering temperature of CdS/CdTe films.

surface of the CdS films, where the indium contacts were to be placed later, as shown in Fig. 6. Analysis of energy dispersive analysis of X-ray (EDAX) scans indicated that the second phase consisted of $CdCl_2$ and CdTe. This second phase, and possibly a thin layer of $CdS_{1-x}Te_x$ solid solution which was formed by the condensation of the evaporated $CdCl_2$ and CdTe on to the exposed area of the CdS, increase the contact resistance and the sheet resistance of the CdS layer resulting in an increase of the total series resistance. For the specimen which was sintered at 625° C, the sheet resistance of the CdS layer increased from 245 to 261 Ω/□. For the specimen which was sintered at 700° C the sheet resistance increased from 255 to 856 Ω/□, and the series resistance was increased from 14 to 37 $\Omega\,cm^2$ causing the decrease in the fill factor from 0.573 to 0.438.

Thirdly, the sintering process also causes the formation of $CdS_{1-x}Te_x$ solid solution due to the interdiffusion of sulphur and tellurium at the compositional interface as well as the formation of a p–n junction near the metallurgical interface due to the diffusion of donor impurity from the CdS layer to the CdTe layer. The p–n junction should be formed in the CdTe layer since the donor concentration in the CdS is $10^{18}\,cm^{-3}$ [8] and the acceptor concentration in the CdTe is approximately $10^{13}\,cm^{-3}$ [10]. To understand the decrease in J_{sc} with increasing sintering temperature above 625° C, spectral responses of the solar cells which were fabricated by sintering at 625 and 700° C were measured. Fig. 7 shows the normalized spectral response of these cells. It can be seen that the spectral response of the cell whose junction was formed at 625° C is similar to that of a heterojunction solar cell. Thus it can be said that the sintering of the CdTe layer and the junction formation conditions of 625° C for 1 h do not cause significant interdiffusion of either sulphur and tellurium or the donor impurity atoms across the interface.

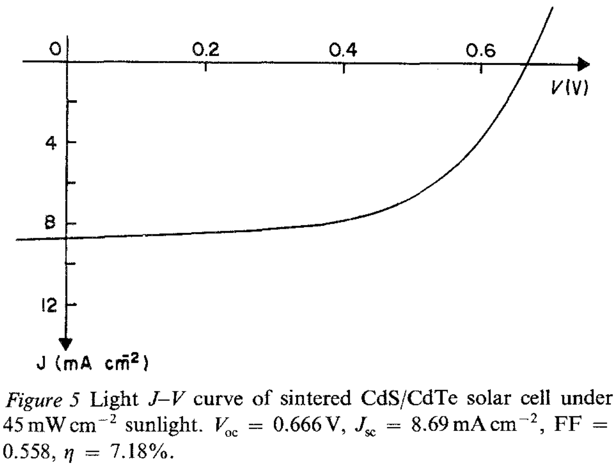

Figure 5 Light *J–V* curve of sintered CdS/CdTe solar cell under 45 $mW\,cm^{-2}$ sunlight. $V_{oc} = 0.666\,V$, $J_{sc} = 8.69\,mA\,cm^{-2}$, FF = 0.558, $\eta = 7.18\%$.

On the other hand, the spectral response of the cell that was formed at 700° C is similar to that of a solar cell with a buried homojunction, and is similar to that observed by Nakayama *et al.* [5] in gallium-doped CdS/CdTe solar cells. This type of spectral response, i.e. poor response in the short wavelength region ($\lambda < 700\,nm$), is also possible if the thickness of the $CdS_{1-x}Te_x$ solid solution at the interface is large. It is worthwhile to note that the spectral response of the solar cell that was formed at 700° C is also shifted to the longer wavelength side by 30 nm (0.05 eV). This shift can hardly be explained in terms of a buried homojunction model. Considering the phase diagram for the binary system of CdS–CdTe reported by Ohata *et al.* [11] and the reported energy band gaps for the compositions in $CdS_{1-x}Te_x$ solid solution by Ohata *et al.* [12], it appears that the response shift of 30 nm is caused by the thick layer of the solid solution formed at the interface. However, since the diffusion length of chlorine in CdTe is 3 μm [13] for the junction formation condition (700° C, for 1 h), the depth of the p–n junction may also be about 3 μm. Thus the poor response in the short wavelength region observed in the solar cell that was formed at 700° C and the decrease in J_{sc} with increasing formation temperature above 625° C (Fig. 4) could be due to the combined effects of $CdS_{1-x}Te_x$ solid solution at the interface, which absorbs the short wavelength radiation before it reaches the region within the carrier diffusion length from the p–n junction, and large p–n junction depth from the interface.

4. Conclusions

The microstructures and properties of sintered CdS films on glass substrates and sintered CdTe films on polycrystal CdS substrates were studied. A polycrystal CdS film which is to be used as a window layer of a CdS/CdTe solar cell must have high optical transparency and low sheet resistance, and a polycrystal CdTe film which is to be used as an absorber layer of the CdS/CdTe solar cell must have a dense microstructure with average grain size larger than 5 μm. The CdS films which contained 9 wt % $CdCl_2$ as a sintering aid and were sintered at 650° C for 1 h in nitrogen, are

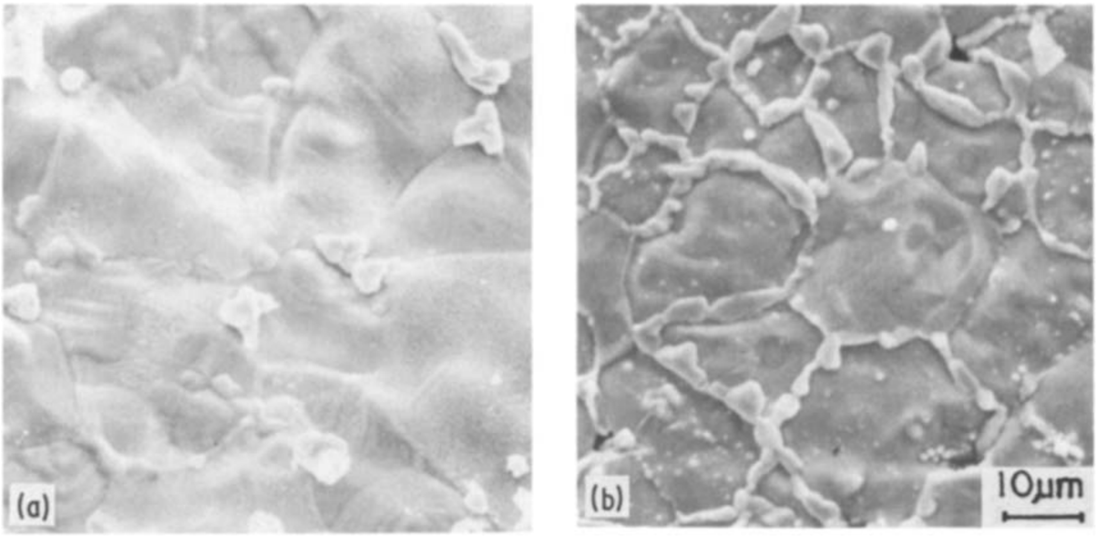

Figure 6 Scanning electron micrographs of the exposed area of CdS in CdS/CdTe films sintered at (a) 625 and (b) 700° C.

transparent provided that the films have been sintered in a boat with a controlled opening to retard the evaporation of $CdCl_2$ during sintering. These sintered CdS films have an average grain size of 15 μm and electrical resistivity less than 0.5 Ωcm. The CdTe films with 1 wt % $CdCl_2$, which were coated on the sintered CdS substrate and were sintered in a quartz ampoule with controlled opening, above 610° C for 1 h in nitrogen atmosphere, have a dense structure with an average grain size of larger than 5 μm.

All polycrystal CdS/CdTe solar cells have been fabricated by coating CdTe slurry on the sintered CdS films and by subsequent sintering of the composite layers of glass–CdS–CdTe films at temperatures ranging from 585 to 700° C. Compositional interfaces and p–n junctions are formed during the sintering of the composite layer. A fabrication temperature below 610° C resulted in poor solar cell efficiency due to the porous structure of the CdTe films and above 650° C also resulted in poor efficiency due to the formation of a $CdS_{1-x}Te_x$ layer at the interface and large p–n junction depth. The highest solar cell efficiency (7.18%) was found in a solar cell which was fabricated by sintering at 625° C for 1 h.

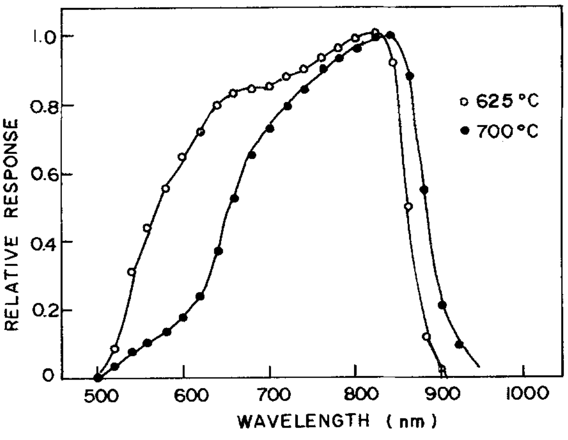

Figure 7 Spectral response for two different sintered CdS/CdTe solar cells with sintering temperature of CdS/CdTe films indicated on the figure.

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