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CdTe solar cells with efficiencies over 15%

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Abstract

High efficiency CdTe/CdS thin film solar cells have been prepared on SnO_2 coated borosilicate glass substrates. The CdS films are deposited by the Chemical Bath Deposition (CBD) technique from an aqueous solution containing cadmium acetate, ammonium acetate, ammonia and thiourea in the temperature range of 80–90°C. The CdTe films are deposited by the Close Spaced Sublimation (CSS) technique from CdTe powder of 99.999% purity. Doped graphite paste is used as the ohmic contact to the CdTe and indium is used as the contact to the SnO_2. Conversion efficiencies of over 15% have been achieved as a result of optimization of a number of processing steps.

1. Introduction

Cadmium telluride has been long recognized as a leading thin film photovoltaic material due to its near optimum bandgap of 1.44 eV and high absorption coefficient. CdTe absorbs over 90% of available photons ($h\nu > 1.44$ eV) in a 1 μm thickness, so that films of only 1–3 μm are sufficient for thin film solar cells. Several types of CdTe solar cells such as MIS, Schottky barrier, homojunction, heterojunction, and p-i-n have been investigated. The most successful types have been the heterojunctions where a wide bandgap semiconductor is used as the heterojunction partner or "window". Cadmium sulfide has been the most extensively studied and most suitable window material for CdTe solar cells to date.

Recent progress in the development of CdTe thin film solar cells resulted in significant improvements in small area conversion efficiencies. Several techniques

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such as atomic layer epitaxy [1], spraying [2], electrodeposition [3], and close spaced sublimation [4] have been used for the fabrication of CdTe/CdS thin film solar cells with efficiencies of over 12%. Even though important distinctions exist, the performances achieved are independent to processing demonstrating the versatility of CdTe and its advanced status in the photovoltaic technologies.

The CSS technique is particularly attractive for the deposition of CdTe films since it offers high deposition rates and can be easily scaled up for manufacturing purposes. The CBD technique is currently being used extensively for the deposition of CdS films for thin film solar cell applications due to its simplicity, low cost, and good quality of films.

In this work we report on CdTe/CdS solar cells prepared by the above two techniques that exhibited conversion efficiencies greater than 15%. The effects of processing parameters on the properties of the CdS and CdTe films and the electrical characteristics of the CdTe/CdS solar cells are discussed.

2. Experimental

CdTe/CdS solar cells are typically of the superstrate configuration as shown in Fig. 1. In this work a layer of tin oxide (SnO_2) was deposited on Corning 7059 glass by MOCVD. The sheet resistance of the SnO_2 films was in the range of 7–10 $(\Omega)/\square$, for a film thickness of 1–2 μm. The CdS films were deposited by the CBD technique to a thickness of 600–1000 Å. Following an in-situ annealing of the CdS film in H_2, a CdTe film was deposited by CSS to a thickness of 4–8 μm. After a post deposition heat treatment at 400°C, the surface of the structure was chemically treated to achieve a Te-rich CdTe surface. The back contact to the CdTe was formed by applying doped graphite paste. After isolation of the cells by scribing, indium was soldered on the SnO_2 to improve current collection. Magnesium fluoride was deposited on the glass side of the devices as an antireflection coating.

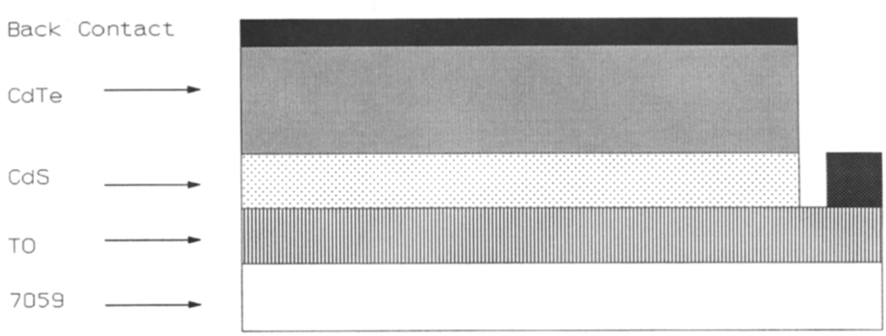

Fig. 1. The structure of CdTe/CdS thin film solar cells.

3. Experimental results and discussion

3.1. Cadmium sulfide films

The CdS films were deposited on the SnO_2 coated glass substrates by the CBD process. Two groups of salts, the acetates and chlorides were used in the temperature range of 70–90°C. The solution was stirred vigorously to facilitate the diffusion of the cadmium and sulfur ions to the substrate surface. Table 1 provides a summary of the range of deposition conditions used. The rate of formation of CdS depends on the composition and temperature of the solution [5]. For example the rate of formation of CdS depends on the concentration of sulfur ions (S^-) from the hydrolysis of thiourea. The rate of hydrolysis of thiourea depends on the pH and the solution temperature. Therefore the deposition rate of the CdS films can be controlled by the composition and the temperature of the solution. The formation of CdS can take place heterogeneously on the SnO_2 substrate surface or homogeneously in the solution resulting in a CdS precipitate. The presence of CdS powder in the solution as a result of the homogeneous reaction is undesirable since adsorption of the CdS particles on the substrate surface results in powdery and inhomogeneous films. Often this type of films contain pinholes when the CdS -powder is removed during a post deposition cleaning of the substrates.

In order to enhance the blue response of the CdTe/CdS solar cells it is necessary that the CdS films are sufficiently thin (400–600 Å) and pinhole free to avoid the formation of shunting paths. The formation of CdS powder in the solution was minimized by adjusting the solution composition and separately titrating thiourea to result in lower deposition rates. After the reaction was completed virtually no precipitate was present in the solution. Deposition rates were typically in the range of 10–15 Å/min. The maximum film thickness that could be achieved over the range of conditions used appeared to be limited to about 1200 Å. Thicker films could be obtained by multiple depositions.

Fig. 2 shows the spectral response of a number of CdTe/CdS solar cells with CdS of different thicknesses. In addition to the improved blue response, the use of a thin CdS layer also resulted in a reduction in the open-circuit voltage and fill factor by 20–50 mV and 5–10%, respectively. The illuminated diode quality factor also increased suggesting a degradation of the electrical properties of the junction at small CdS thicknesses.

Annealing of the CdS films at 400°C in H_2, prior to the CdTe deposition has been found to enhance device performance through reduction in the interface

Table 1
Summary of deposition conditions used for the deposition of the CdS films by the CBD technique

Cadmium acetate (chloride)	$0.5\text{–}2.0 \times 10^{-3}$ M
Ammonium acetate (chloride)	$8\text{–}12 \times 10^{-3}$ M
Thiourea	$1\text{–}4 \times 10^{-3}$ M
Ammonia	0.2–0.5 M

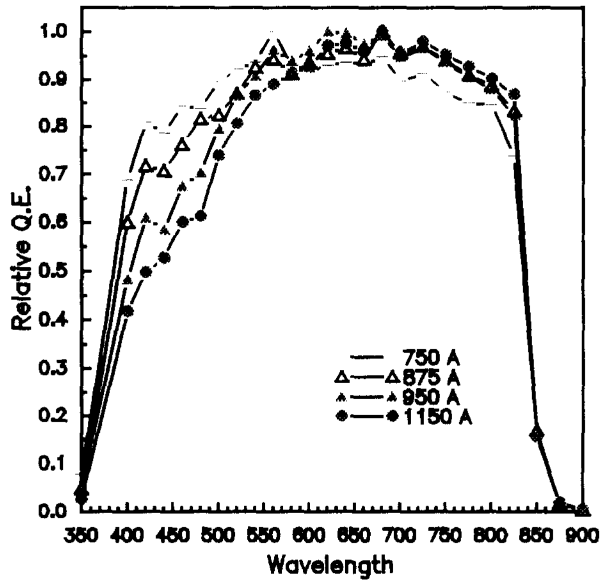

Fig. 2. The relative QE of CdTe/CdS solar cells as a function of the CdS thickness.

states [6]. Annealing in H_2 has also been found to leave the surface of the films Cd-rich [7]. In this work it was found that in-situ annealing of the CdS films in H_2 resulted in an increase in the depletion width from 1 μm for as deposited CdS films to 3–4 μm for annealed films. As the thickness of the CdS was reduced the H_2 heat treatment had to be modified. Thinner CdS films required longer annealing times or higher temperatures. Fig. 3 shows the effect of the CdS thickness on the illuminated diode quality factor for different annealing times. Diode quality factors close to 2.0 were typically accompanied by fill factors greater than 70%.

3.2. Cadmium telluride films

The CdTe films were deposited by the CSS technique to a thickness of 4–8 μm. Fig. 4 shows a schematic of the CSS reactor. The important process parameters of the CSS process are the substrate and source temperatures, the total reactor pressure, and the source-substrate spacing. The effect of the above parameters on the deposition rate has been well documented [8]. Table 2 provides a summary of the range of deposition conditions used for the deposition of the CdTe films.

The substrate temperature used for the deposition of the CdTe films is a very important parameter. Even though low temperatures are desirable to allow the use of inexpensive soda lime glass substrates, high temperatures are believed to be important in the formation of a mixed $Cd_xS_{1-x}Te$ layer that results in reduced interface states [9]. In this work the substrate temperature was varied in the range

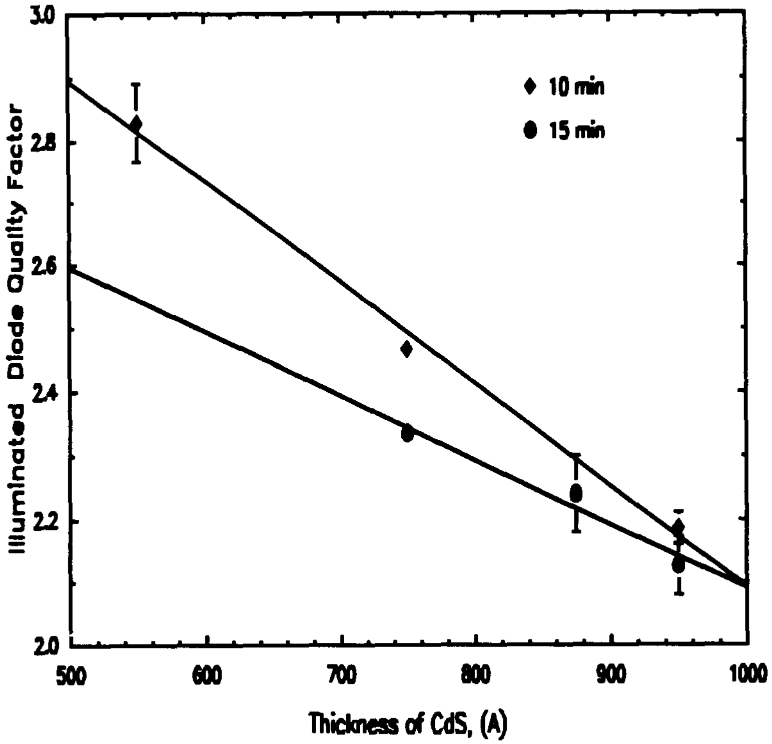

Fig. 3. The illuminated diode quality factor as s function of the CdS thickness and annealing time.

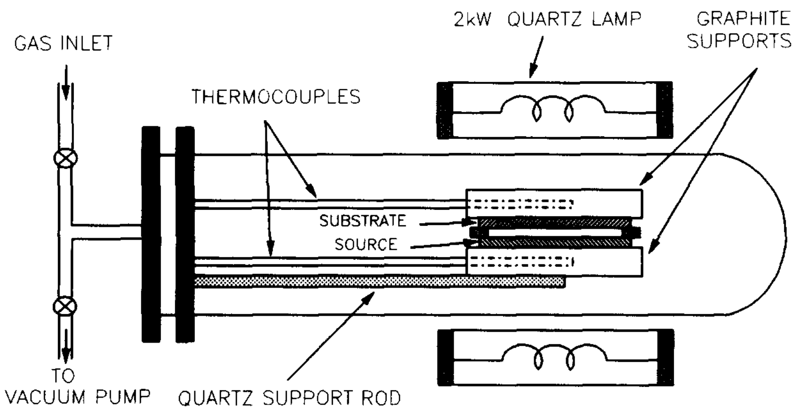

Fig. 4. Schematic diagram of the CSS reactor.

Table 2
Summary of deposition conditions used for the CSS preparation of the CdTe films

Substrate temperature	450–625°C
Source temperature	600–700°C
Pressure	1–30 Torr
Spacing	0.2–1.0 cm

of 450–625°C. The source temperature, the total pressure, and spacing were adjusted to result in deposition rates of 1.0–5.0 μm/min.

Fig. 5 shows the X-ray diffraction spectra of a number of CdTe films prepared at different temperatures. Films deposited at substrate temperatures of 575–600°C exhibited preferential orientation along the (111) direction as indicated by X-ray diffraction studies. Decreasing the substrate temperature to 550°C resulted in films with random orientation. Further decrease of the substrate temperature produced films with preferential orientation along the (200) axis. The grain size decreases with decreasing temperature from about 5 μm at 600°C to 1 μm at 500°C. The density of the films is also greatly affected by the substrate temperature. In general, film density decreases with decreasing substrate temperature.

The high conversion efficiencies obtained from CSS CdTe films have been attributed to the high substrate temperature [4]. The use of high substrate temperatures is believed to promote the interface reaction between the CdS and CdTe. The formation of a $Cd_xS_{1-x}Te$ mixed crystal layer shifts the electrical

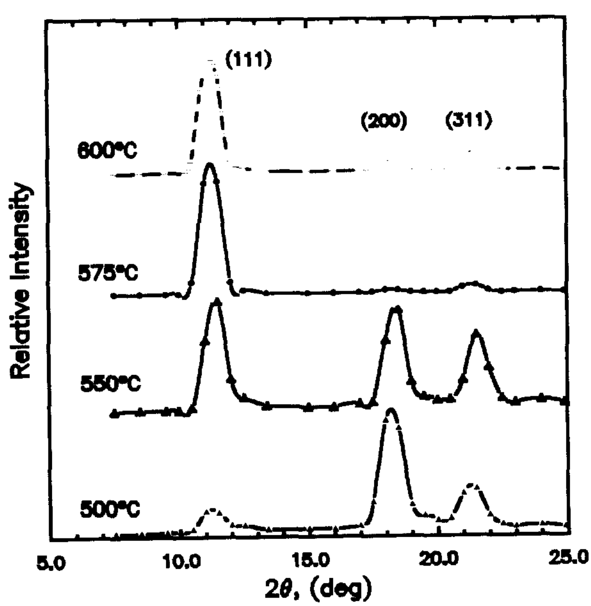

Fig. 5. X-ray diffraction spectra of CSS CdTe films deposited at different substrate temperatures.

Table 3
The effect of the CSS substrate temperature and the CdS thickness on solar cell performance

T_{SUB} (°C)	t_{CdS} (Å)	J_{SC} (mA/cm^2)	V_{OC}		
625	700	25.09	843	0.74	15.8
620	750	24.02	853	0.76	15.5
600	1150	23.4	853	0.75	14.9
570	1100	23.24	854	0.73	14.5

junction into the CdTe improving the electrical and photovoltaic characteristics of the junction. The saturation current density and diode quality factor increased with decreasing substrate temperature from 3×10^{-12} A/cm^2 and 1.48, respectively, for 600°C, to 1×10^{-8} A/cm^2 and 2.6 for 520°C. The open-circuit voltage was in the range of 840–850 mV and appeared to be relatively independent of the substrate temperature in the range of 540–625°C. However, the fill factor decreases rapidly for temperatures below 570°C resulting in reduced conversion efficiencies.

3.3. CdTe / CdS solar cells

CdTe/CdS solar cells have been prepared by the successive deposition of CdS and CdTe films on SnO_2 coated glass substrates. In order to improve the photocurrent of the devices the CdS film thickness was decreased gradually from over 1000 Å to 650–700 Å. Following a heat treatment of the CdS layer in H_2, a CdTe layer of 4–6 μm was deposited by the CSS process. After deposition of the CdTe film the structures were subjected to a standard post-deposition heat treatment at 400°C [10]. The back ohmic contact to the CdTe was formed by chemically treating the surface in a solution such as 0.1% Br_2 in methanol, or HNO_3:H_3PO_4:H_2O (1.25 : 100 : 40) followed by the application of a doped graphite paste. Table 3 lists the photovoltaic properties for a number of CdTe/CdS solar cells prepared at different substrate temperatures and utilizing CdS of several thicknesses. The best device exhibited a conversion efficiency of 15.8%. The devices were measured at the National Renewable Energy Laboratory under AM1.5 conditions.

4. Conclusion

Thin film CdTe/CdS solar cells with conversion efficiencies over 15% have been fabricated. The devices utilized a thin CdS layer deposited by the CBD technique and a CdTe layer deposited by the CSS. Low deposition rates during the CBD process can result in homogeneous and pinhole free thin CdS films. The annealing of CdS in H_2 prior to the CdTe deposition results in improved photovoltaic characteristics in particular for devices with a thin CdS layer. High substrate temperatures during the CSS process resulted in higher conversion efficiencies mainly due to higher fill factors. The open-circuit voltage is relatively independent of the substrate temperature in the range of 540–625°C. Further work is needed in order to reduce the substrate temperature and maintain high efficiencies.

Acknowledgement

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