High efficiency CSS CdTe solar cells

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Abstract

Cadmium telluride (CdTe) has long been recognized as a strong candidate for thin film solar cell applications. It has a bandgap of 1.45 eV, which is nearly ideal for photovoltaic energy conversion. Due to its high optical absorption coefficient essentially all incident radiation with energy above its band-gap is absorbed within 1–2 μm from the surface. Thin film CdTe solar cells are typically heterojunctions, with cadmium sulfide (CdS) being the n-type junction partner. Small area efficiencies have reached the 16.0% level and considerable efforts are underway to commercialize this technology. This paper will present work carried out at the University South Florida sponsored by the National Renewable Energy Laboratory of the United States Department of Energy, on CdTe/CdS solar cells fabricated using the close spaced sublimation (CSS) process. The CSS technology has attractive features for large area applications such as high deposition rates and efficient material utilization. The structural and optical properties of CSS CdTe and CdS films and junctions will be presented and the influence of some important CSS process parameters will be discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: CdTe; CdS; Thin films; High efficiency

1. Introduction

Cadmium telluride is one of the leading thin film materials for solar cell applications. Small area laboratory devices have demonstrated efficiencies of 16.0% [1,2] while large area modules have exceeded the 9.0% level [3]. The fact that a variety of deposition technologies can be used to fabricate efficient CdTe solar cells demonstrates the flexibility of this material with regards to the method of fabrication, and sets it apart from other thin film technologies. The close spaced sublimation (CSS) is one of various technologies with large area manufacturing potential due to its high throughput and efficient material utilization. This paper discusses the influence of certain CSS process parameters on the structural and optical properties of films and junctions, and identifies parameters that are important to achieving high efficiencies. Films and junctions were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL), dark and light *I–V*, and spectral response (SR) measurements.

2. Experimental

Thin film CdTe/CdS solar cells are typically of the superstrate configuration, which is shown in Fig. 1. For all devices discussed in this paper two types of substrates were used. Borosilicate glass substrates (Corning 7059) and Libbey Owens Ford (LOF) SnO_2 coated soda lime glass. The 7059 substrates were briefly etched in dilute hydrofluoric acid prior to being coated with a bi-layer SnO_2 (high ρ/low ρ), which was deposited by metalorganic chemical vapor deposition (MOCVD). The thickness of the SnO_2 films was 0.7–1.0 μm and their sheet resistance (R_{SH}) was 8–10 Ω. The LOF substrates were also coated with a SnO_2 bi-layer to reduce their R_{SH} from 15–20 to less than 10 Ω. CSS or chemical bath deposition (CBD) was used for the deposition of the CdS films. The thickness of CdS was in the range of 600–1000 Å. After a heat treatment of the CdS, the CdTe was deposited by CSS to a thickness of 4–8 μm. After the CdTe deposition the structures were subjected to a heat treatment in the presence of $CdCl_2$ which is used by essentially all CdTe groups. Prior to the formation of the back contact the CdTe surface was chemically treated in a bromine methanol solution (approx. 0.1% by vol.). The back contact was formed by the application of doped graphite paste or the deposition of a Cu_xTe/Mo followed by a heat treatment. Table 1 provides an outline of the fabrication sequence and processing details. Film properties were studied using PL, XRD and SEM. Solar cells were characterized using dark and light *J–V, J–V–T*, spectral response, and PL measurements.

2.1. Close spaced sublimation

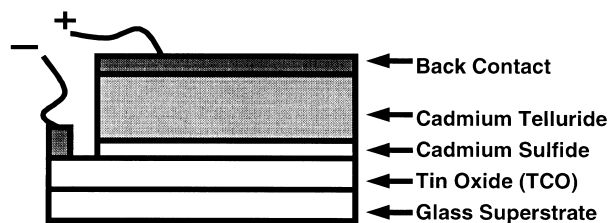The CSS of both CdS and CdTe films was carried out in a

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Fig. 1. The typical CdTe/CdS superstrate configuration.

Fig. 2. Schematic diagram of CSS deposition chamber.

simple reactor, a schematic of which is shown in Fig. 2. The source material, typically 5N CdS or CdTe powder, was placed in a silicon carbide (SiC) coated graphite boat. The substrate which was supported by a second SiC coated graphite plate, was kept in close proximity to the source material. Quartz spacers were used to separate the source from the substrate. Thermocouples were inserted into the graphite plates to monitor and control the temperature. The graphite plates were heated independently using two 2-kW tungsten halogen lamps. A gas inlet and an evacuation port were used to evacuate the deposition chamber and introduce the appropriate amounts of gases. All films were deposited in a stationary ambient. The important process parameters are source temperature, substrate temperature, source/substrate spacing, pressure, and ambient. For this work the spacing was kept constant at 2 mm for the CdTe depositions and varied between 3–6 mm for CdS. Emphasis was placed on understanding the effect of the substrate and source temperatures as well as the effect of the ambient on solar cell performance and not necessarily on completely
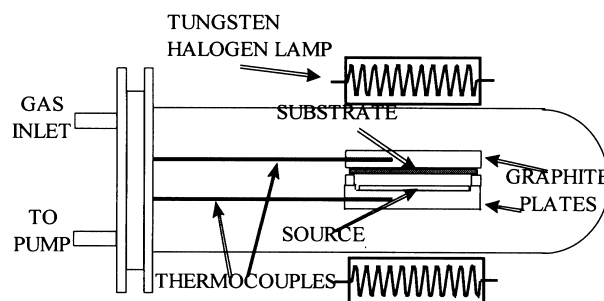
characterizing the CSS process. A range of the deposition parameters is included in Table 1.

2.2. CSS CdS films

One of the important CdTe technology issues is the fabrication of CdTe/CdS solar cells using thin (<1000 Å) CdS films. The energy gap of CdS is 2.42 eV. Based on AM1.5 data (1000 W/m^2) this layer absorbs the equivalent of about 7 mA/cm^2 out of a maximum theoretical of approximately 30 [5]. Since the process of carrier collection in CdS is very inefficient and essentially all photo-generated carriers are lost, it is necessary to use thin CdS in order to increase the number of incident photons that reach the CdTe. Thin CdS films can lead to higher J_{SC}'s and therefore higher efficiencies. However, as the thickness of CdS is decreased the films can become discontinuous leading to the formation of localized CdTe/SnO$_2$ junctions, which lead to excessive shunting and therefore lower the solar cell efficiency. The deposition of pinhole free CdS films is critical in achieving high solar cell efficiencies.

One of the CSS process parameters studied in this work was the ambient and in particular the use of O$_2$. This was due to the fact that solar cells fabricated with CdS films prepared in O$_2$ ambient exhibited higher efficiencies than devices fabricated with CdS films deposited in inert ambient (solar cell results are included in a later section). The use of O$_2$ is known to play an important role in preparing device quality II–VI compounds [6]. It has been found to behave as an acceptor in CdTe, ZnS, and CdS [7]. In order to study the effect of O$_2$ on CSS CdS films, a He/O$_2$ gas mixture was introduced into the deposition chamber. The amount of oxygen was varied from 0 to 100%. It was found that the presence of O$_2$ leads to a drastic decrease in the deposition rate. In order to maintain reasonably high deposition rates when O$_2$ was used during the deposition, higher source temperatures were required. The presence of O$_2$ also influenced the grain size of the CdS films. Fig. 3 shows the SEM micrographs of two films prepared in He and He:O$_2$ ambient (all other process parameters were held constant). The grain size for the O$_2$ film is considerably smaller than that of the films deposited in inert ambient, and also appear much denser. The film thicknesses were 2040, and 1900 Å for (a) and (b), respectively. The results shown in Fig. 3 were typical for all films deposited in a He/O$_2$ ambient and were

Table 1
Fabrication sequence and process description

|	Material	Process description
1		Glass cleaning: borosilicate (dilute HF); LOF (soap solution)
2	SnO$_2$:F/SnO$_2$	MOCVD: T_{sub} > 450°C. precursors: tetramethytin, oxygen, halocarbon 13B1 (fluorine source)
3	CdS	Chemical bath deposition: cadmium and ammonium acetate, thiourea, ammonium hydroxide; $T \approx 90°C$. [4]
4		Close spaced sublimation; 5N CdS powder; $T_{sub} \approx 500$–550°C; ambient He or He/O$_2$; pressure ≈ 10 Torr
5		Heat treatment: H$_2$/400°C; CdCl$_2$/400°C
6	CdTe	CSS: $T_{sub} \approx 400$—630°C; ambient: He, or He/O$_2$; pressure ≈ 1–50 Torr
7		Heat treatment: $T_{sub} \approx 400°C$; CdCl$_2$ (O$_2$)
8	Back contact	Surface preparation: bromine/methanol; doped graphite; Cu$_x$Te, heat treatment
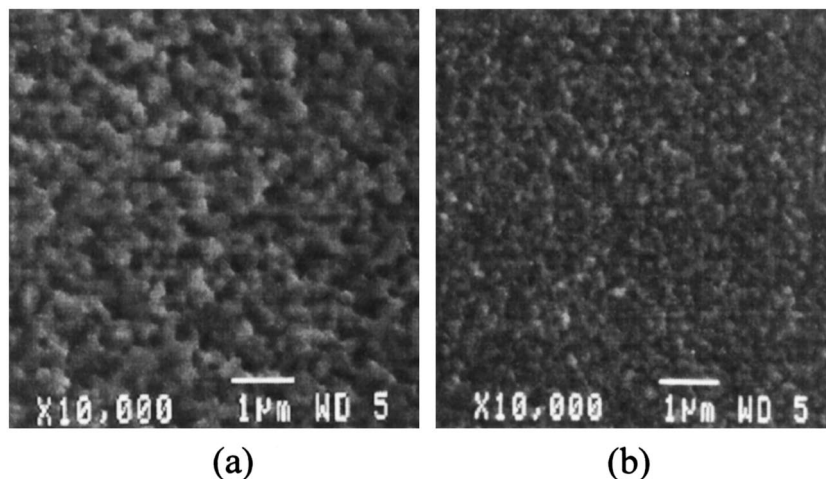
Fig. 3. SEM images of CSS CdS films deposited in (a) He and (b) He/O$_2$ ambient.

essentially independent of the amount. It appears that O$_2$ affects the nucleation process resulting in an increase in the number of nucleation sites and attaining denser films. This is critical in particular when these films are deposited to small thicknesses.

The CSS CdS films were also characterized using XRD. The XRD spectra were acquired with a Philips/Norelco diffractometer using Cu K$_\alpha$ radiation. CdS, CdO, SnO$_2$, SnO, and CdSnO$_4$ standards were used to index the peaks. All films were found to be of hexagonal structure, which is believed to be the stable phase for CdS films prepared at high temperatures [4]. Fig. 4 shows high resolution XRD scans in the 30–40° (two theta) range for films prepared in He (top) and He/O$_2$ (50%) ambient (bottom). The spectrum of the CdS films prepared in ambient containing more than 50% oxygen indicated that a second phase was present. The reflections at 32.95 and 38.2° are associated with CdO. Reflections at 55.25 and 65.9° (not shown in Fig. 4) were
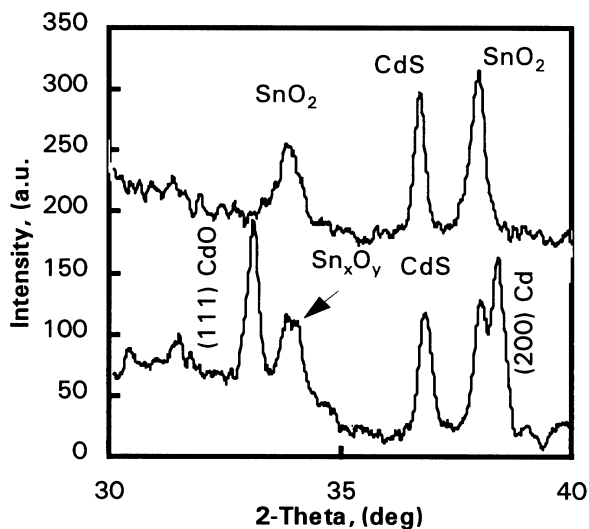
also observed. The formation of the CdO phase did not appear to have a detrimental effect on solar cell performance, however, most depositions were carried out with less than 50% O$_2$ in the ambient where deposition rates were faster.

The effect of O$_2$ on the properties of CSS CdS films was also studied using PL measurements at 77 K. Fig. 5 shows the PL spectra of several CdS films prepared under various O$_2$ concentrations: 0, 10, and 50%. Three deep level emission bands are present at 1.94 eV (630 nm), 1.46 eV (840m) and 1.24 eV (1000 nm). As shown in Fig. 5 the intensity of the 1.94 eV transition decreases as the amount of O$_2$ present during the deposition increases, however the intensity of the 1.46 eV band increases with the amount of O$_2$. A model has been proposed that suggests that oxygen incorporation in CdS leads to a reduction in the concentration of sulfur vacancies [8]. It is therefore suggested that if the previously proposed model is correct, the 1.94 eV transition is associated with a sulfur vacancy complex while the 1.46 eV transition is due to an O$_2$ complex.

2.3. CSS CdTe films   One of the critical device regions in CdTe solar cells is the CdTe/CdS interface. It has been shown by various groups that ternary compounds form as a result of interdiffusion between CdTe and CdS: a sulfur-rich layer of CdTe$_y$S$_{1-y}$ and a Te-rich layer of CdS$_x$Te$_{1-x}$ [9–13]. The formation of these two ternary compounds is believed to be important in that it reduces the concentration of recombination centers that would otherwise be present due to the lattice mismatch (10%) between CdTe and CdS. The extent of interdiffusion between the two semiconductors depends on various process parameters. However, the most important ones are the CdTe deposition temperature (junction formation temperature) and the heat treatment in the presence of CdCl$_2$. It is believed that the high substrate temperature used during the CSS CdTe deposition is one of the main reasons that CSS CdTe/CdS solar cells have reached
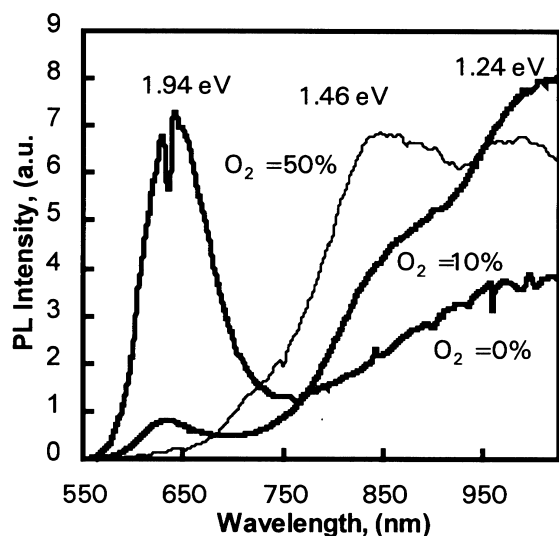

Fig. 4. XRD spectra of CSS CdS films deposited with (bottom) and with out (top) O$_2$ in the ambient.

Fig. 5. PL spectra of CSS CdS films deposited in He/O$_2$ ambient.

Fig. 7. XRD spectra of CSS-CdTe films deposited at temperatures in the range 500–600°C.

efficiencies of 16.0%. It should be noted that all three groups that demonstrated these efficiencies [1,2,14] use the CSS process for the CdTe deposition. In this section some of the structural properties of CSS CdTe films are presented as well as PL measurements of CdTe and the CdTe/CdS.

The grain size and density of the CdTe films are also important cell parameters. The CSS technology is known to produce films with large grains as compared to processes such as sputtering, electrodeposition, physical vapor deposition etc. Fig. 6 shows SEM micrographs of CSS CdTe films prepared at two substrate temperatures (a) 600 and (b) 500°C. The film deposited at 600°C consists of grains 3–4 μm in size and is dense. However, the film deposited at 500°C consists of grains approximately 1 μm in size and appears to contain many voids. Solar cells fabricated using films such as the one shown in Fig. 6b exhibited considerable shunting which limited their performance. However, it
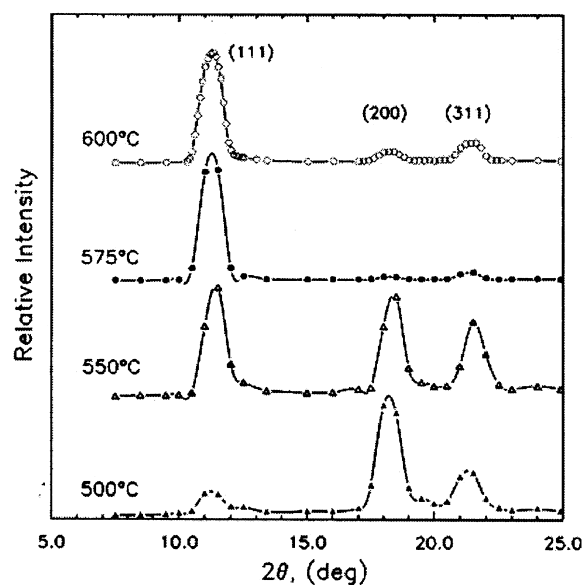
should be noted that if large thicknesses were used (>10 μm) the amount of shunting was considerably reduced. It is believed that the increased shunting observed for these devices is associated with excess dopant diffusing along the grain boundaries during the back contact formation process. The XRD spectra of a series of CSS-CdTe films deposited at temperatures in the 500–600°C are shown in Fig. 7. As these results suggest films deposited at high temperatures are highly oriented along the (111) direction. However, at temperatures below 550°C the films become randomly oriented, and at 500°C the (200) direction dominates. The above films were deposited in the presence of O$_2$: the reason O$_2$ was considered for the deposition of CdTe films is because as previously mentioned it can enhance the p-type characteristics of II–VI semiconductors. The above
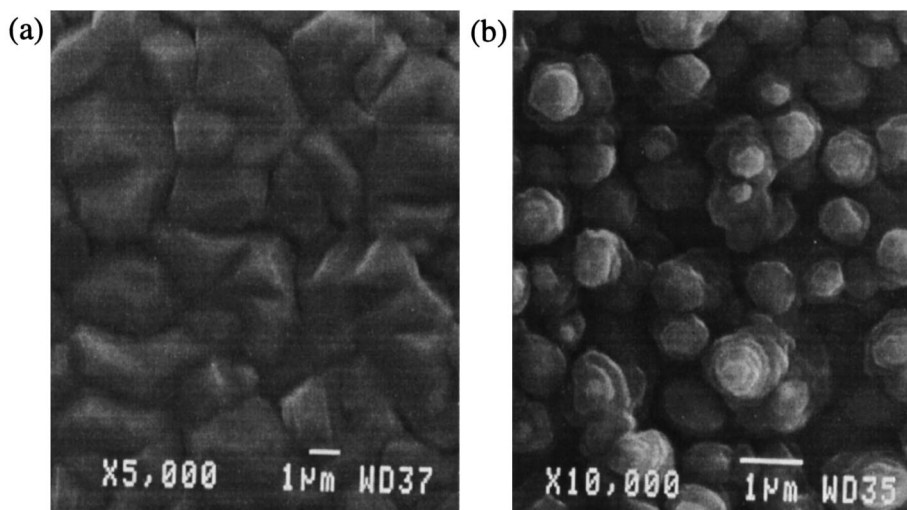

Fig. 6. SEM images of CSS-CdTe films deposited at (a) 600 and (b) 500°C.

results exemplify the significant impact the CSS process parameters can have on the film properties.

It is possible however, to deposit quality device CSS–CdTe films at low temperatures. Fig. 8 shows SEM micrographs of a series of CSS–CdTe films deposited at substrate temperatures of 420, 440, and 460°C, respectively. The grain size of these films appears to increase with the deposition temperature, as one should expect, since the surface mobility of the depositing species increases leading to less nucleation sites and therefore larger grains. Solar cells fabricated with films such as the ones depicted in Fig. 8, have to date reached a performance level within 80–90% of state-of-the-art devices fabricated with CSS-CdTe films deposited at high temperatures (~600°C).

As previously mentioned the CdTe/CdS junction is a critical part of the device and two of the most influential process parameters are the CdTe deposition temperature and the $CdCl_2$ heat treatment. The PL (4 K) spectra for several CdTe films and junctions are shown in Fig. 9. The spectra were obtained from glass/SnO_2/CdS/CdTe structures. In some cases the optical excitation (488 nm line of Ar ion laser) was shined directly onto the CdTe surface, i.e. the PL signal emanates from CdTe, and in others it was shined thorough the glass, i.e. the signal emanates from the CdTe near the junction or the junction itself. Table 2 summarizes the processing and measurement conditions for the various samples of Fig. 9. It should be noted that 'CdTe' implies that the sample was excited at the free CdTe surface, while CdTe/CdS implies that the sample was excited at the junction, i.e. through the glass.

Spectra A and C in Fig. 9a are nearly identical with the exception of a deep band at 1025 nm only present in spectrum C. This suggests that at low junction formation temperatures the interaction between CdTe and CdS is minimal. After heat treating the sample with spectrum A, spectrum B is obtained which contains a major PL band at 830 nm, which is believed to be associated with a V_{Cd}–Cl complex. Spectrum D is obtained after heat treating the sample with spectrum C. The new PL signal contains two major bands located at 820 and 920 nm and is believed to be emanating from the junction, i.e. CdSTe alloy, and not the CdTe. The band at 820 nm is believed to be associated with the CdS_xTe_{1-x} compound. Small amounts of S in CdTe lead to a decrease in its energy gap [15] (band to band PL (4 K) transitions for CdTe occur at 778 nm). The origin of the band at 920 nm is currently unknown. Spectrum A in Fig. 9b is that of the CdTe/CdS interface for an As-deposited structure but for which the junction formation temperature was higher (600 vs. 400°C) compared to the sample with Fig. 9a spectrum. The similarity between Fig. 9a(D) and Fig. 9b(A) suggests that when the CdTe is deposited at low temperatures a heat treatment is necessary to cause interdiffusion at the interface, while for high junction formation temperatures the interdiffusion occurs during the CdTe deposition. Spectrum Fig. 9b(B) is that of a junction prepared at 550°C. A broad band is present at 900–910 nm. A small shoulder at 820 nm indicates that the band previously assigned to the CdS_xTe_{1-x} compound may also be present. After heat-treating this sample (Fig. 9b(C)) the PL signal is similar to Fig. 9a(D) and Fig. 9b(A) suggesting formation of the CdS_xTe_{1-x} alloy. Although the preceding discussion is qualitative, it clearly demonstrates the effect of high CdTe deposition temperatures and post-deposition heat treatment. To obtain a better understanding of this critical device region additional studies are necessary to completely quantify the influence of processing on the CdTe/CdS interface and on device performance.

2.4. CdTe/CdS solar cells

As mentioned in a previous section one of the major issues in thin film CdTe solar cells is the utilization of thin CdS films (<1000 Å). Although the use of thin CdS can lead to increased photocurrents, it also leads to lower open-circuit voltages and FF's. Fig. 10 shows
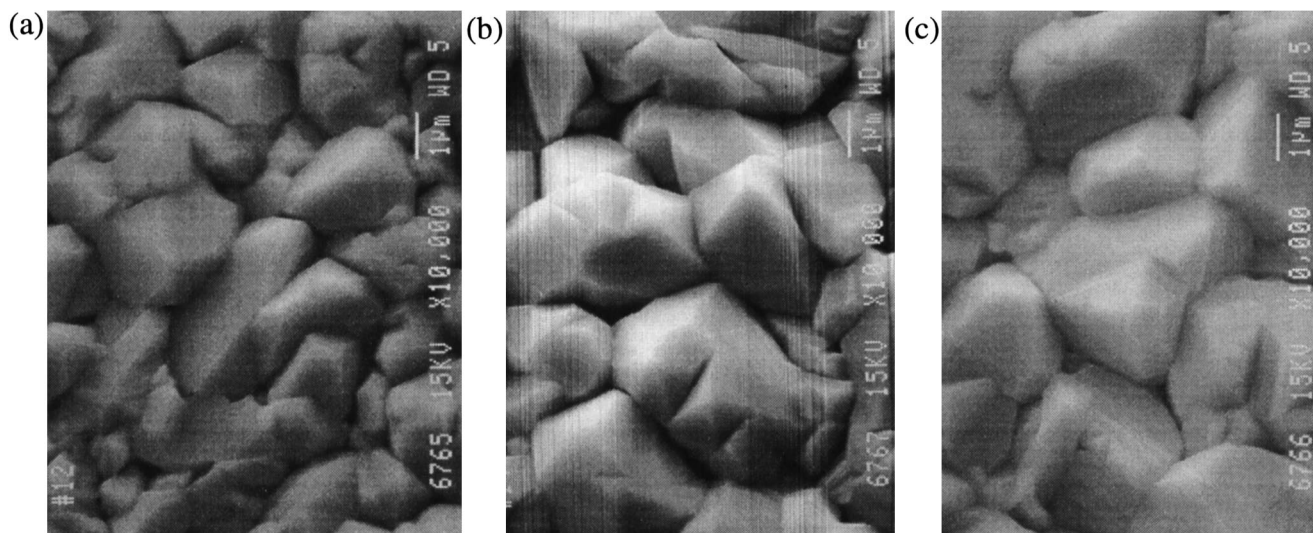

Fig. 8. SEM micrographs of CSS-CdTe films deposited at low substrate temperatures: (a) 420; (b) 440 and (c) 460°C.
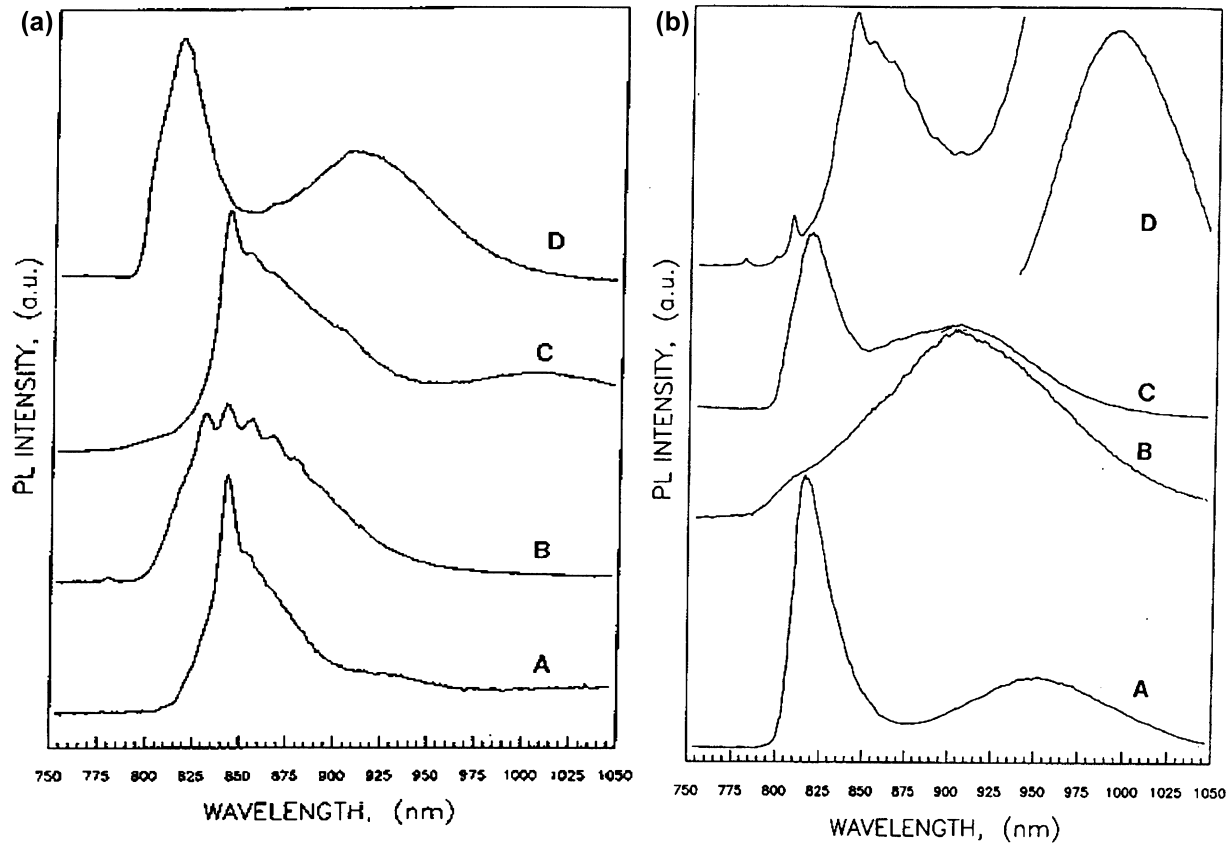
Fig. 9. PL spectra of As-deposited and heat-treated CdTe films and CdTe/CdS junctions.

the effect of the CdS thickness on solar cell performance. The CdS thickness in a finished solar cell is not the same as the starting CdS thickness since some of the CdS is consumed as a result of the interdiffusion that takes place at the interface. As a measure of the CdS thickness in a finished solar cell (1-QE @ 450 nm) is used instead. Fig. 10 includes data for all-CSS CdTe/CdS solar cells. When CdS prepared in inert ambient (He) is used, the impact of its decreasing thickness on solar cell performance is dramatic. However, when CdS prepared in the presence of O_2 is used, the overall solar cell performance improves, and the decrease on V_{OC} and FF is more gradual. These results

demonstrate the effect of the small CdS thickness and the important role of O_2 during the CSS process. Table 3 lists important device results achieved at the University of South Florida and verified at the National Renewable Energy Laboratory. All devices listed in Table 3 were fabricated

Table 2
Description of samples shown in Fig. 9

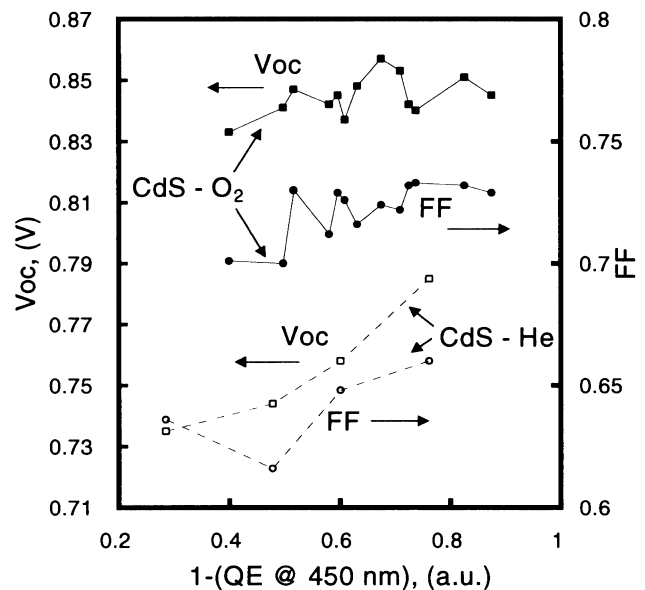| (a) Low (400°C) junction formation temperature	(b) High (>550°C) junction formation temperature
A: CdTe – As-deposited	A: CdTe/CdS – As-deposited at 600°C
B: CdTe – CdCl$_2$ heat treated	B: CdTe/CdS – As-deposited at 550°C
C: CdTe/CdS – As-deposited	C: B after the CdCl$_2$ heat treatment
D: CdTe/CdS – CdCl$_2$ heat treated	D: CdTe – As-deposited

Fig. 10. The effect of CdS thickness on V_{OC} and FF.

Table 3
CdTe/CdS solar cells fabricated at USF and measured at NREL

Substrate	CdS	CdTe	Back contact	Efficiency (%)
Corning 7059	CBD	CSS – high T_{sub}	Doped graphite	15.8
Corning 7059	CSS – low T_{sub}	CSS – low T_{sub}	Doped graphite	15.0
Soda lime	CSS – low T_{sub}	CSS – low T_{sub}	Doped graphite	14.3
Corning 7059	CSS – low T_{sub}	CSS – high T_{sub}	Cu_xTe	15.1

using CdTe deposited by CSS. The V_{OC}'s and FF's for these devices are in the range of 840–850 mV and 73–75% respectively. The performance variations are attributed almost entirely to variations in J_{SC}. The J_{SC} of the 15.8% device was 25.09 mA/cm^2. The two devices fabricated with CSS–CdS (on borosilicate glass) exhibited slightly lower J_{SC}'s (24.16 and 24.09 mA/cm^2). This is due to the larger thickness of CSS–CdS as compared with CBD–CdS. It is typically easier to deposit thin and continuous CdS by CBD due to differences in nucleation between the two processes. The device fabricated on soda lime glass exhibited a J_{SC} of 23.11 mA/cm^2. The poor optical properties of soda lime glass result in a J_{SC} loss of about 2 mA/cm^2 as compared with borosilicate glass.

3. Summary

The close spaced sublimation process is a strong candidate for manufacturing applications. Dense, device quality, polycrystalline CdS and CdTe films can be deposited at high deposition rates. The use of oxygen during the CSS of CdS and CdTe influences the nucleation process by increasing the number of nucleation sites. Photoluminescence measurements of CSS CdS films indicated that O_2 incorporation leads to a reduction in the concentration of sulfur vacancies. More importantly the use of O_2 for the CSS deposition of CdS yields pinhole free thin (<1000 Å) films. Cadmium telluride films are highly oriented when deposited at high temperatures (600°C) in the presence of O_2. At temperatures below 550°C the films become porous and randomly oriented. Eliminating O_2 from the ambient increases the density of low temperature CSS CdTe films considerably. PL measurements provided qualitative evidence on the role of the junction formation temperatures as well as the CdCl$_2$ heat treatment. The high temperatures used for the deposition of the CSS CdTe films lead to interdiffusion at the CdTe/CdS interface, which is important in achieving high quality junctions. For junctions formed at lower temperatures ($\approx$400°C) the CdCl$_2$ heat treatment is necessary to cause interdiffusion at the junction. Solar cell performance in particular for devices fabricated with thin CdS films, is enhanced when O_2 is used for the deposition of the CSS CdS films. The most obvious reason for this improvement is presumably the elimination in the pinhole density in these films. The impact of O_2 incorporation on device performance is not well understood at this time. It is important to note that understanding the effect of process parameters such as O_2 will require additional studies in order to develop material and device models that can adequately account for the improvements/changes observed.

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