

Research Article

Characterization of $\text{Cu}_{1.4}\text{Te}$ Thin Films for CdTe Solar Cells

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The copper telluride thin films were prepared by a coevaporation technique. The single-phase $\text{Cu}_{1.4}\text{Te}$ thin films could be obtained after annealing, and annealing temperature higher than 220°C could induce the presence of cuprous telluride coexisting phase. $\text{Cu}_{1.4}\text{Te}$ thin films also demonstrate the high carrier concentration and high reflectance for potential photovoltaic applications from the UV-visible-IR transmittance and reflectance spectra, and Hall measurements. With contacts such as $\text{Cu}_{1.4}\text{Te}$ and $\text{Cu}_{1.4}\text{Te}/\text{CuTe}$, cell efficiencies comparable to those with conventional back contacts have been achieved. Temperature cycle tests show that the $\text{Cu}_{1.4}\text{Te}$ contact buffer has also improved cell stability.

1. Introduction

Copper chalcogenides have attracted much interest because of their potential applications in thermoelectric devices [1] and in heterojunction structures [2–7]. Cusano [3] prepared a CdTe solar cell with an efficiency of 7.5% in which cuprous telluride (Cu_2Te) was used as a *p*-type partner to the *n*-type CdTe semiconductor. To further improve device performance of CdTe solar cells, Cu_2Te is commonly used as a *p*-type back contact layer to facilitate low resistance contact formation [4, 5]. However, due to the fast diffusivity of Cu in CdTe and the apparent instability of Cu_2Te ($\text{Cu}_2\text{Te} \rightarrow \text{CuTe} + \text{Cu}$, $\text{Cu}_2\text{Te} \rightarrow 2\text{Cu} + \alpha\text{Te} + 1/2(1-\alpha)\text{Te}_2$ [8, 9]), copper is suspected to be responsible for changes in cell performance and stability with exposure to light [10–12]. Since this particular element plays a key role in cell performance and characteristics, it is important to minimize the Cu supply while maintaining the ohmic characteristics of p^+CdTe contact. Thus, an extensive investigation of the properties of copper tellurides (Cu_xTe) and stability of CdTe-based solar cells with Cu_xTe has been carried out [13]. It has been found that Cu_xTe shows bistability with energy minimum at $x \approx 1.25$ and $x \approx 1.75$ [13]. These results using first-principles calculations are consistent with experimental observations, which find stable Cu_xTe structures at two different Cu concentrations (i.e., $1.30 < x < 1.43$ and $x \approx 2$ [6, 7]). The calculated minimum

energy concentrations are slightly smaller than experimental observations due to the fact that strain and temperature effects are not included in the calculation. Therefore, in our work, Cu_xTe thin films at low x ($x = 1.4$) were prepared by vacuum coevaporation. The properties of Cu_xTe thin films at low x were studied and performance of CdTe solar cells with Cu_xTe was investigated and also monitored with the temperature cycle test.

2. Experimental Details

$\text{Cu}_{1.4}\text{Te}$ thin films were deposited on a simultaneous evaporation system DM-400 to a thickness of ~ 200 nm at room temperature. Cu foil (99.999% purity) and Te powder (99.999% purity) were evaporated on substrates from two independent sources, respectively. The deposition rate and the thickness of thin films were monitored by two-thickness monitors (LHC-2, Huazhao Industrial Ltd., China). After deposition, a posttreatment was performed at different temperatures in N_2 ambient. X-ray diffraction (XRD) (DX-2600, Dandong Fangyuan Instrumental Ltd., China) measurements were used to study the copper telluride structure. The transmittance and reflectance spectra were used to investigate the optical properties of materials. The four-probe Van der Pauw method was used to carry out the Hall measurements to

determine the Hall coefficient, mobility, and carrier concentration.

Solar cells were fabricated in a superstrate configuration typical of CdTe devices, that is, glass/TCO/CdS/CdTe/back contact. CdS thin films were deposited by a chemical bath deposition technique to a thickness of 180 nm onto the glass substrate coated with SnO₂:F. CdTe thin films were subsequently prepared in argon and oxygen ambient by close-spaced sublimation to a thickness of $\sim 5 \mu\text{m}$. Following the heat treatment of the samples in CdCl₂, the CdTe surface was etched in a bromine/methanol solution (0.05% vol.). The back contact, Cu_{1.4}Te (~ 100 nm), was deposited on the etched CdTe surface by coevaporation. And then samples were treated in a pure N₂ ambient in the 180°C~220°C range. Finally, Ni thin films (~ 300 nm) prepared by electron beam evaporation were used as a back electrode to complete the back contacts processing. The photovoltaic devices were characterized using dark *J-V* measurement (4155C, Agilent, USA) and light *J-V* measurement (XJCM-9, Gsolar, China) under simulated AM1.5 illumination (100 mW/cm²). The device stability was performed using the high- and low-temperature cycle tests. As shown in Figure 1 one cycle was the process of the cycling through two temperature extremes (i.e., 85°C and -40°C).

3. Results and Discussion

3.1. Structural, Optical, and Electronic Properties of Cu_{1.4}Te Thin Films. Copper telluride thin films were deposited by coevaporation at room temperature on glass substrates as shown in Figure 2. The thin films as-deposited were an amorphous structure. There are no changes in the phase for copper telluride thin films with annealing temperature up to 170°C. Then the thin films were annealed at 180°C in N₂ ambient. Copper telluride thin films annealed had some diffraction peaks. The peaks at about 2θ of 11.393°, 14.461°, 23.516°, 26.586°, 26.667°, 29.159°, 44.415°, 55.078°, and 60.501° correspond to the (021), (002), (051), (052), (004), (006), (204), and (176) planes of Cu_{1.4}Te, respectively. The results also indicate that the Cu_{1.4}Te thin films are single-phase hexagonal structure with random orientations when annealed at a higher temperature, that is, 200°C. Figure 2 shows XRD pattern of Cu_{1.4}Te thin films annealed at 220°C. The intensity of these diffraction peaks for the thin films increased with annealing temperature. And there are remarkable differences among these two samples annealed at 200°C and 220°C. The peak at 2θ of 12.9°, corresponding to the lattice spacing of 6.8487 Å, was indexed as the 1st order diffraction of the cupric telluride (CuTe). So, the peak positions of the (002), (003), and (004) planes at 2θ of 25.8°, 40°, and 52.8° were the 2nd, 3rd, and 4th order diffraction of CuTe. The presence of other X-ray diffraction peaks associated with a CuTe phase indicated that the coexisting phase had occurred. It is obvious that annealing to 220°C results in the formation of coexisting phase for copper telluride thin films, which may have a strong influence on the stability of the CdTe-based solar cells. Therefore, the devices for this work were

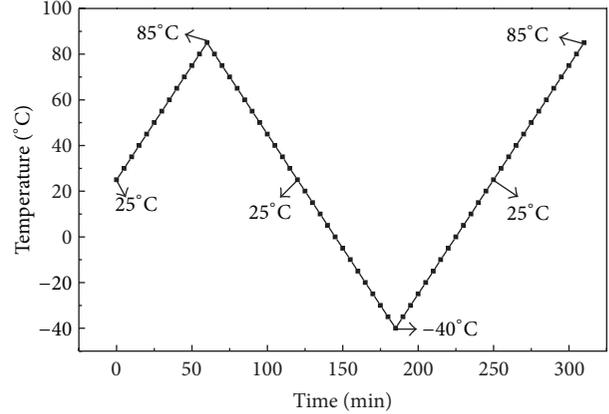


FIGURE 1: The high- and low-temperature cycle testing curve.

postannealed at 180°C~220°C, whose results will be discussed in Section 3.2.

The optical properties of Cu_{1.4}Te thin films with a single-phase hexagonal structure were studied using the UV-Visible-IR transmittance and reflectance spectra as shown in Figure 3. The transmittance of no more than 30% for Cu_{1.4}Te thin films in the range of 300~900 nm was observed. While the reflectance for the thin films increased up to $\sim 50\%$ in the range from 500 to 900 nm, which may reflect the photons in this range to p-n junction. It can be inferred that the thickness of the absorption layer, CdTe, can be reduced in the CdTe solar cells due to the incorporation of the thin films, Cu_{1.4}Te, as the back contact. From the optical properties of Cu_{1.4}Te thin films we suggest that it may be a kind of good photovoltaic materials in CdS/CdTe heterojunction solar cells.

The electronic properties of single-phase Cu_{1.4}Te thin films from the Hall measurements were also investigated. Table 1 shows the parameters for Cu_{1.4}Te thin films such as the mobility, Hall coefficient, and carrier concentration. The results show that Cu_{1.4}Te thin films were *p*-type semiconductor compounds and had high carrier concentration, $\sim 10^{21} \text{ cm}^{-3}$. The high carrier concentration means high conductivity which can reduce series resistance of the solar cells with a Cu_{1.4}Te layer and thus improve remarkably the device performance. Table 1 also shows that the mobility of Cu_{1.4}Te thin films is very low. The carrier mobility has the following relation:

$$\mu_p = \frac{q\tau_p}{m_p}, \quad (1)$$

where q is the elementary charge, τ_p is the relaxation time, and m_p is the effective mass. Because the carrier effective mass did not alter much, it is deduced that the increase of the mobility is due to the decrease of the relaxation time, which inverses to the scattering probability. Therefore, further improvement in the thin films, such as less defects, small strain, and large grain sizes, for practical use can be made.

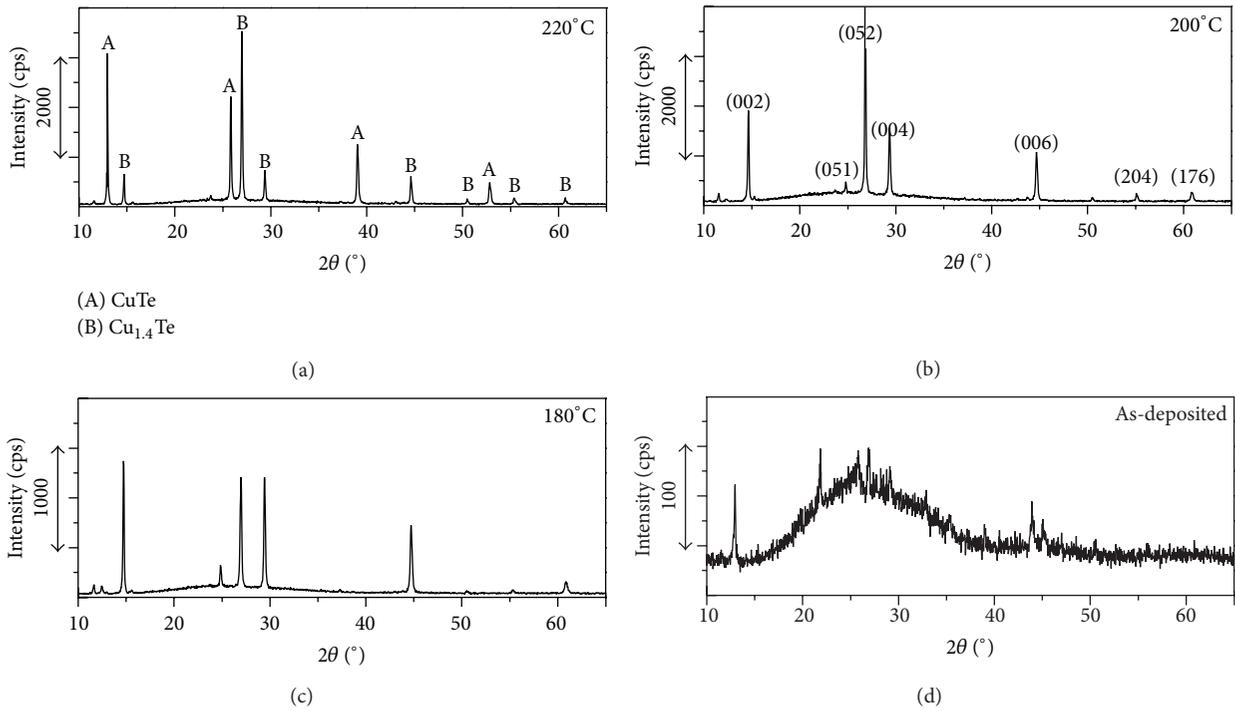


FIGURE 2: XRD patterns of copper telluride thin films as deposited and annealed at different temperatures.

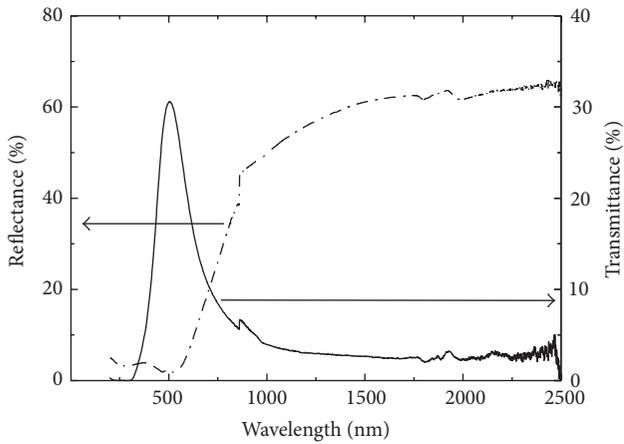


FIGURE 3: Transmittance and reflectance spectra for $Cu_{1.4}Te$ thin films.

TABLE 1: Parameters for $Cu_{1.4}Te$ thin films.

Sample	Mobility ($cm^2/V \cdot s$)	Hall coefficient (cm^3/Cb)	Carrier concentration (cm^{-3})
$Cu_{1.4}Te$	13.82	0.0042	1.48×10^{21}

3.2. *CdTe Solar Cells with $Cu_{1.4}Te$ Thin Films.* In this work, the device configuration consisted of a glass/ SnO_2 / CdS / $CdTe$ /back contact/ Ni structure, where back contact was $Cu_{1.4}Te$ thin films. After chemical etching, the $Cu_{1.4}Te$ thin films were deposited on the $CdTe$ thin films and annealed in N_2 ambient. Figure 4 shows the XRD pattern of $CdTe$

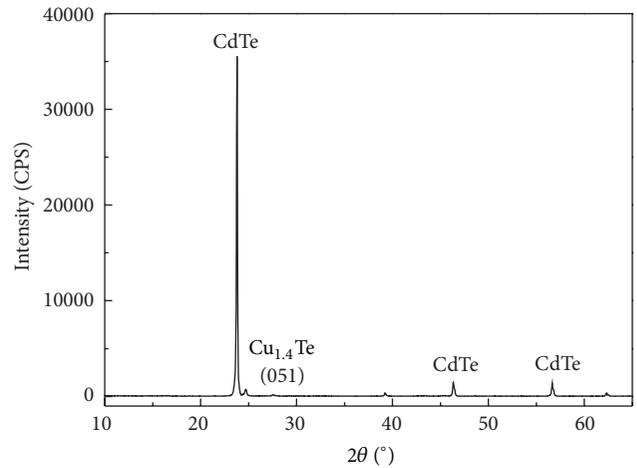


FIGURE 4: XRD pattern of $Cu_{1.4}Te$ thin films deposited on the $CdTe$ thin films.

solar cells with a $Cu_{1.4}Te$ layer annealed at $200^\circ C$ before metallization. Besides the diffraction peaks of $CdTe$, the XRD pattern demonstrates the other phase with weak diffraction intensity, which can be indexed to (051) planes of $Cu_{1.4}Te$ thin films.

To investigate the effect of $Cu_{1.4}Te$ thin films on back contact formation and device performance, device characterization was performed on $CdTe$ devices. Table 2 shows the device parameters for $CdTe$ solar cells with or without $Cu_{1.4}Te$ thin films annealed at different temperatures in N_2 ambient. One can see that $CdTe$ solar cells made with a

TABLE 2: Device parameters for CdTe solar cells with or without Cu_{1.4}Te thin films.

T (°C)	V_{oc} (mV)	J_{sc} (mA/cm ²)	E_{ff} (%)	FF (%)	Area (cm ²)
nbc*	667	20.5	7.6	55	0.0707
180	721	22.7	9.7	57	0.19625
200	736	23.6	11.6	67	0.0707
220	788	21.0	9.5	57	0.19625

*nbc denotes the cells without back contacts.

TABLE 3: Evolution of device parameters for CdTe solar cells with the temperature cycling.

Day and cycle	nbc				Cu _{1.4} Te			
	V_{oc} (mV)	FF (%)	J_{sc} (mA/cm ²)	E_{ff} (%)	V_{oc} (mV)	FF (%)	J_{sc} (mA/cm ²)	E_{ff} (%)
Initial	695	55.9	21.45	8.33	732	67.4	23.81	11.75
30d3c*	676	46.4	19.33	6.74	709	58.4	22.95	9.50
90d9c	495	—	17.81	—	712	58.2	23.07	9.56
180d12c					708	57.0	22.56	9.10
420d42c					707	50.5	21.24	7.58

*30d3c denotes 3 cycles after 30 days in the period of testing.

Cu_{1.4}Te layer have better performance than those without Cu_{1.4}Te back-contact. that is, the short circuit current (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and conversion efficiency (E_{ff}) increased for CdTe solar cells made with a Cu_{1.4}Te layer. Annealing at high temperatures is commonly used in the back contact formation process for the diffusion and dopant activation [14]. In this work, higher V_{oc} was obtained when the cells were annealed at a higher temperature. This may be attributed to the increase of the acceptors. It can be seen that the device performance of CdTe solar cells with single-phase Cu_{1.4}Te thin films annealed at 200°C is superior to that of the solar cells with coexisting phase copper telluride thin films at 220°C. We suggest that the single-phase Cu_{1.4}Te thin films annealed at 200°C are more suitable for forming p -type back contacts between CdTe and the electrodes than coexisting phase thin films.

Dark J - V characteristic of solar cells (Figure 5) can be expressed by Shockley diode equation:

$$J = J_0 \left[\exp\left(\frac{qV}{AKT}\right) - 1 \right], \quad (2)$$

where J stands for the diode current, J_0 denotes the dark saturation current, A is the diode ideality factor. From the dark J - V characteristic curve (Figure 5), one can obtain a dark saturation current $J_0 = 1.67 \times 10^{-6}$ mA/cm², and a diode quality factor $A = 2.23$, which is consistent with the results reported by Wu et al. [6], for CdTe solar cells with a single-phase Cu_{1.4}Te layer annealed at 200°C. The illuminated J - V curve (see also Figure 5) compared to the dark J - V curve shows that the crossover is eliminated effectively due to the incorporation of the Cu_{1.4}Te back contact.

The stability of the solar cells with Cu_{1.4}Te back contacts was evaluated with the temperature cycle tests. Table 3 shows the evolution of the photovoltaic parameters for the CdTe solar cells with Cu_{1.4}Te. Under this environmental stress condition, some parameters of the device have quite random values as a function of stress time, which is similar to other

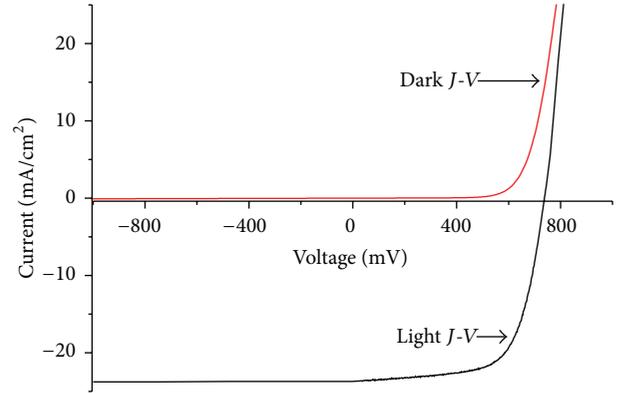


FIGURE 5: Dark and light J - V curves for a CdS/CdTe/Cu_{1.4}Te solar cell.

environmental stress tests [12]. This may be evidence of the existence of traps within the absorber CdTe layers. The CdTe cell without Cu_{1.4}Te degraded rapidly in cell efficiency from 8.33% to zero after 90 days and 9 cycles, whereas the CdTe cell with Cu_{1.4}Te showed much improved stability with efficiency loss from 11.75% to 7.58% even after 420 days and 42 cycles. The degradation may be attributed in part to the unencapsulated cells in the laboratory and the back electrodes with exposure to moist air.

4. Conclusions

Copper telluride thin films were prepared by using the vacuum coevaporation method. At low temperature, the copper telluride thin films were an amorphous structure. In the temperatures ranging between 180 and 220°C, the copper telluride thin films indicate the form of the single-phase Cu_{1.4}Te structure, whereas with annealing temperature higher than 220°C, the coexisting phase for the thin films

occurs. With a $\text{Cu}_{1.4}\text{Te}$ as a back contact layer, efficient and stable CdTe solar cells can be obtained.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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