Eur. Phys. J. Appl. Phys. **45**, 20304 (2009)
DOI: 10.1051/epjap/2009006

THE EUROPEAN PHYSICAL JOURNAL APPLIED PHYSICS

The study of properties of CdTe thin films deposited in Ar/O_2 atmosphere*

Y. Li[1], B. Li[1,a], L. Feng[1], J. Zheng[1], and W. Li[1]

College of Materials Science and Engineering, Sichuan University, 610064 Chengdu, P.R. China

Received: 29 September 2008 / Accepted: 4 December 2008
Published online: 31 January 2009 – © EDP Sciences

Abstract. The preparation and properties of CdTe thin films is of a primary interest for the CdTe thin film solar cells in both research and technology. In our work, polycrystalline CdTe thin films were deposited on pretreated glass substrates in Ar/O_2 atmosphere by closed-space sublimation (CSS) technology. Structural property was studied by X-ray diffraction (XRD), surface morphology was observed by scanning electron microscopy (SEM). The optical and electrical properties of CdTe films were investigated, as well as the effects of deposition temperatures, the ratio of gas (Ar/O_2) and post-treatment on the properties. The high quality CdTe layer was prepared based on the above studies. These layers were used to prepared CdS/CdTe/ZnTe:Cu solar cells. Efficiency of 13.38% and fill factor of 70.3% (0.501 cm^2 area) for CdTe solar cells have been achieved.

PACS. 68.35.Ct Interface structure and roughness – 78.20.-e Optical properties of bulk materials and thin films – 73.61.-r Electrical properties of specific thin films

1 Introduction

The fabrication and properties of CdTe layer are most important for the performance of CdTe thin film solar cells among their several function layers [1–3]. About ten methods of fabricating CdTe thin films of depositing in He/O_2 atmosphere have been developed [4,5]. The closed-space sublimation (CSS) is the only way to obtain high efficient records of small-area CdTe solar cells [6–8]. In order to decrease the cost of CdTe solar cells, we concern in development of Ar/O_2 atmosphere CSS method.

In order to obtain the high efficient CdTe thin film solar cells, the preparation of high quality CdTe thin films is one of the key factors, so the characterization of the structural properties, surface morphology, optical and electrical properties of CdTe films is especially important. However, it is impossible to study the properties of the CdTe films deposited on SnO_2 or CdS layers by electro-deposition or by CSS. In addition, it is difficult to obtain high quality CdTe films by CSS on a glass substrate because the density of crystal nuclei is very low on smooth surface [9,10]. So, a improved CSS method is proposed: the glass substrate is pretreated before the deposition of CdTe films.

In the paper, a glass substrate roughened with borax solution make the crystal nuclei of CdTe forming before growing films. Then, the continuous and dense CdTe polycrystalline films were obtained by CSS on the glass substrate of surface was pretreated. Not only the structural, optical and electrical properties of CdTe films deposited on a glass substrate in different O_2 fractional pressure were studied, but also the effects of post-treatment on the properties of CdTe films were investigated.

From the studies above, the high quality CdTe layer has been prepared. CdTe solar cells, SnO_2/n-CdS/p-CdTe/ZnTe/p+-ZnTe:Cu/Au, without anti-reflection layer have been fabricated. FF of 70.3% and efficiency of 13.38% have been demonstrated for a 0.501 cm^2 sized CdTe solar cell.

2 Experimental details

CdTe thin films were deposited by CSS in atmosphere of Ar/O_2. A diagram of the closed-space sublimation apparatus is shown in Figure 1. The fractional O_2 pressure varied from 0 to 15%. One kind of substrate was used: soda-lime glasses roughened with 0.05 mol L^{-1} borax solution. Substrate temperatures were 520 °C and 600 °C. CdS thin films were fabricated by chemical bath deposition (CBD), and ZnTe and ZnTe:Cu films were deposited by vacuum co-evaporation technology.

Thickness of CdTe thin films were measured with α-step 500 KLA Tencor. Structure and morphology of

* Project supported by the National High Technology Research and Development Program of China (Grant No. 2003AA513010) and the National Natural Science Foundation of China (Grant No. 60506004).

[a] Corresponding author: e-mail: libing70@126.com

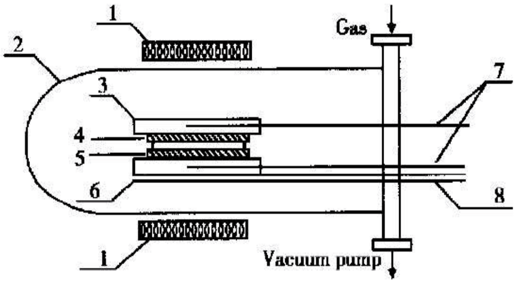

Fig. 1. Schematic of apparatus of CSS 1: Halogen tungsten lamp, 2: Quartz tube, 3: Upper graphite block, 4: Substrate, 5: CdTe source, 6: Lower graphite block, 7: Thermocouple, 8: Holding rod.

Table 1. The thickness dates of CdTe thin films deposited in glass substrate with different roughening times.

The number of samples	Average thickness (μm)	Standard deviation of thickness
1	5.5	3.240
2	5.6	2.736
3	5.6	1.790
4	5.6	1.005

CdTe films were determined with XRD (DX-1000, China) and SEM (S4800, Japan) respectively. Optical transmittance spectrum was recorded with Lambda 900 Perkin Elmer. The temperature dependence of dark conductivity was measured between 15 °C and 200 °C. The performance of CdTe solar cells was obtained by $I-V$ characteristic measurements.

3 Results and discussion

3.1 The structures of CdTe films

In order to investigate the structural properties of CdTe thin films on soda-lime glasses, the film thickness of four kinds above were measured. The samples are: (1) glass substrate without roughening; (2) glass substrate roughening 20 times; (3) glass substrate roughening 50 times; (4) glass substrate roughening 80 times. All of them were deposited at 600 °C. The thickness is shown in Table 1.

As shown in Table 1, the thickness of films is not much different. But the thickness of the Standard deviation of samples (3) and (4) are less than that of samples (1) and (2) obviously. It can be inferred that the CdTe polycrystalline thin films of samples (3) and (4) are more homogeneous than that of samples (1) and (2).

To confirm above inference, The XRD and SEM of the four kinds of samples were measured. The results of measurement were shown in Figures 2 and 3.

From Figure 2, it can be seen all the CdTe films of samples are polycrystalline thin films, and they have preferred orientation and cubic phase in (111) direction. The intensity of (111) peak decreases greatly with roughening times increasing, but the intensity of (220) peak increases.

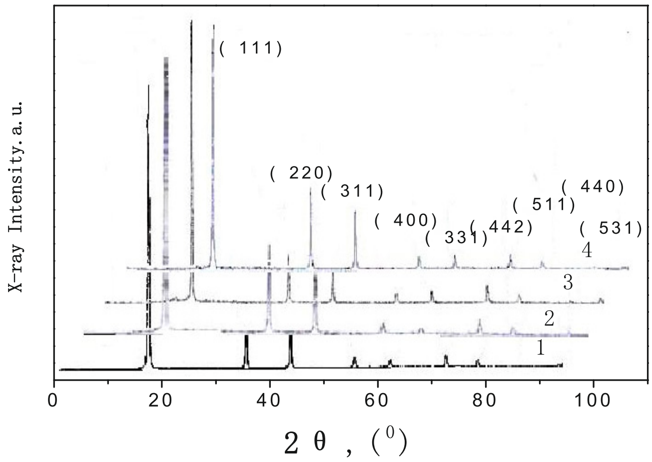

Fig. 2. XRD of CdTe films.

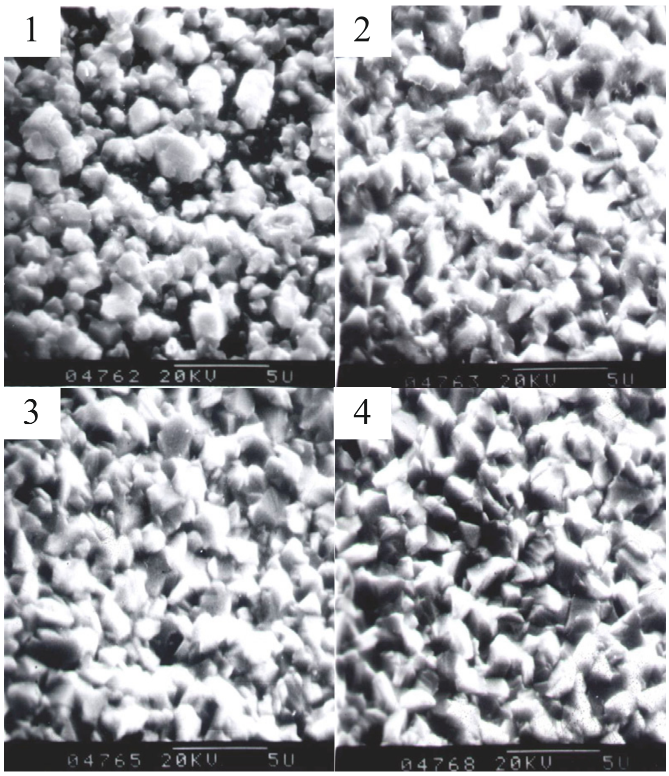

Fig. 3. SEM microphotographs of CdTe films.

This means the structures of films have changed by different roughening times. The polycrystalline orientation of CdTe thin films increases gradually with the roughening times.

The SEM shows the grains of the CdTe polycrystalline thin films are more continuous, homogeneous and higher compactness with roughening more times. The properties of thin films would be better with increasing of surface roughness. As shown as in Figure 3, this result is consistent with the XRD measurement.

3.2 Optical properties

The relationships between transmittance and wavelength of CdTe films deposited at two substrate temperatures have been observed:

$$(\alpha h\nu) = A(h\nu - E_g)^2. \quad (1)$$

According to equation (1) above for direct band gap semiconductors, E_g of CdTe films deposited in different O_2 fractional pressure has been obtained from the optical transmittance spectra and it is shown in Table 1. In fact, the values of different samples are identical nearly, which does not depend on the O_2 fractional pressure. When the deposition temperature is 600 °C, all E_g are 1.5 eV, and when the deposition temperature is 520 °C, E_g is 1.50–1.52 eV.

3.3 Electrical properties

σ_{dark} and the temperature dependence of σ_{dark} have been measured. For the polycrystalline semiconductor films the formula of dark conductivity as a temperature function is:

$$\sigma_{dark} = \sigma_0 KT \exp\left(\frac{-E_f}{KT}\right) \exp\left(\frac{-E_b}{KT}\right). \quad (2)$$

According to equation (2) above, the general activation energy is:

$$E_a = E_f + E_b. \quad (3)$$

See equation (3) above, E_f is Fermi Energy, E_b is the activation energy of carrier mobility and it is the average boundary barrier.

For all the samples, the experimental curves of $\ln(\sigma_{dark}/kT) \sim T$ are straight-line. From the curves, σ_{dark} and its activation energies have been calculated from equation (2) above. The results are shown in Table 2. We can see that σ_{dark} of the samples deposited at 600 °C is slightly higher than that at 520 °C for each O_2 fractional pressure. According to the results, the activation energies E_a, of dark conductivities for samples deposited at 600 °C are lower than that for the ones deposited at 520 °C. For the samples deposited at 600 °C, σ_{dark} is higher at some O_2 fractional pressure, such as 9% and 12%. A considerable thing is that σ_{dark} is the lowest and E_a highest for the samples deposited in no O_2 fractional pressure.

Table 2 shows that the effects of deposition temperature on the dark conductivity and its activation energies are not obvious. That is beyond our expectations. However, the annealing temperatures affect the electrical properties of CdTe films strongly.

Table 3 gives the data of σ_{dark} and E_a of CdTe samples deposited at 580 °C after annealing in air at 350 °C and 400 °C for 40 min. Table 4 shows that the annealing leads to the increase in σ_{dark} by around 2 or 3 degrees of magnitude, and to the relatively large decreases in E_a, for example, from 0.56 ∼ 0.62 eV to about 0.42 eV. We think that the decreases in E_a may include both decreases in E_f and E_b. As we know that the annealing likes a doped process [11], which can make E_f lower. And on the other hand, our previous work on PL of CdTe films has shown that an appropriate annealing, for example an annealing at 400 °C, can make the grain size larger and order extent higher, hence, the boundary barrier lower and more narrow. It can be understood that the lower conductivity activation energy of CdTe is useful to CdTe cells.

Table 2. Optical gap of CdTe polycrystalline thin films deposited in different O_2 fractional pressure.

O_2 Fractional Pressure	Optical Gap (eV)	Substrate Temperature (°C)
3%	1.52	520
3%	1.50	600
6%	1.50	520
6%	1.50	600
9%	1.51	520
9%	1.50	600
12%	1.51	520
12%	1.50	600
15%	1.50	520
15%	1.50	600

Table 3. Dark conductivity and its activation energy of CdTe polycrystalline thin films deposited in different O_2 fractional pressure.

O_2 Fractional Pressure	σ_{dark} (S cm^{-1})	E_a (eV)	Substrate Temperature (°C)
0%	1.7×10^{-6}	0.63	520
0%	4.9×10^{-5}	0.59	600
3%	2.2×10^{-6}	0.62	520
3%	5.0×10^{-5}	0.59	600
6%	6.8×10^{-6}	0.62	520
6%	5.7×10^{-5}	0.57	600
9%	3.5×10^{-5}	0.61	520
9%	9.7×10^{-5}	0.56	600
12%	6.8×10^{-5}	0.60	520
12%	8.5×10^{-5}	0.58	600
15%	2.3×10^{-5}	0.61	520
15%	4.7×10^{-5}	0.60	600

Table 4. Dark conductivity and its activation energy of CdTe polycrystalline thin films deposited in different O_2 fractional pressure and annealed in different conditions in air atmosphere.

O_2 Fractional Pressure	σ_{dark} (S cm^{-1})	E_a (eV)	Annealing Temperature (°C) and time (min)
3%	3.8×10^{-3}	0.47	350/40
3%	3.6×10^{-3}	0.45	400/40
6%	4.9×10^{-2}	0.43	350/40
6%	2.2×10^{-1}	0.37	400/40
12%	6.3×10^{-2}	0.42	350/40
12%	8.6×10^{-2}	0.40	400/40

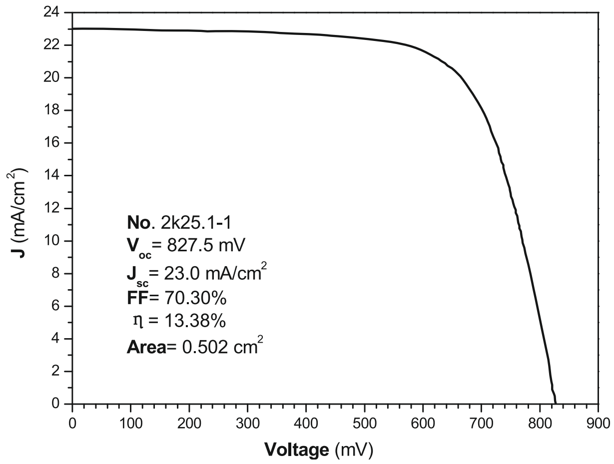

Fig. 4. $I-V$ curver of 0.501 cm^2 CdS/CdTe/ZnTe:Cu thin film solar cell.

3.4 CdTe thin film solar cells

The high quality CdTe layer have been prepared at 600 °C in 9% O_2 fractional pressure, and annealed at 400 °C for 40 min in air. The structure of CdTe thin film solar cells prepared in our laboratory is SnO_2:F/n-CdS/p-CdTe/p-ZnTe/p^+-ZnTe:Cu/Au. p-ZnTe/p^+-ZnTe:Cu is a complex back contact layer fabricated by co-evaporation, and its thickness is 30 nm/50 nm. Efficiency of 13.38% and fill factor of 70.3% have been demonstrated for CdTe solar cells with 0.501 cm^2 without an anti-reflection layer. The $I-V$ curve of the cell is shown in Figure 4.

4 Conclusions

(i) Quality CdTe polycrystalline films were obtained on glass substrate in Ar/O_2 atmosphere by CSS. The structure of CdTe films on glass substrate changes little by different roughening times. The polycrystalline thin films are more continuous, homogeneous and higher compactness with the increase of the roughening times.

(ii) The energy gaps are 1.5–1.52 eV at room temperature, and independent of the substrate temperature. The dark conductivities and their activation energies of as-deposited CdTe films are different from substrate temperature and O_2 fractional pressure. When the substrate temperature is 600 °C, the effect of O_2 fractional pressure on dark conductivities and their activation energies become obvious. Annealing in air makes the dark conductivities increased and their activation energies decreased, which is helpful to improve the performance of CdTe solar cells.

(iii) The high quality CdTe layer have been prepared at 600 °C in 9% O_2 fractional pressure, and annealed at 400 °C for 40 min in air.

(iv) 13.38% efficiency and 70.3% fill factor have been demonstrated for a 0.501 cm^2 sized CdTe solar cell without an anti-reflection layer.

The work has been supported by National High Technology Research and Development Program (863 Program) of China (No. 2004AA513010) and National Natural Science Foundation of China (No. 60506004). Figures 2 and 3 were tested by Analytical and Testing Center of Sichuan University.

References

1. R.W. Brikmire, in *Proc. 26th IEEE Conf. Recent Prog. Critical Issues in Thin Film Polycryst. Solar Cells and Mudules* (1999), p. 295
2. T.L. Chu, S.S. Chu, Solid State Electron. **38**, 533 (1995)
3. H.R. Moutinho, J. Vac. Sci. Technol. **13**, 2877 (1955)
4. J. Britt, Appl. Phys. Lett. **62**, 2851 (1993)
5. T. Aramoto, Jpn J. Appl. Phys. **36**, 6304 (1997)
6. X. Wu et al., in *Proc. 17th Eur. Sol. Energy Conf., Munich, Germany* (2001), p. 126
7. J. Zang, Acta Energiae Solaris Sinica **62**, (2003)
8. L. Feng, Acta Energiae Solaris Sinica **22**, 403 (2001)
9. R. Chakrabarti, J. Phys. D: Appl. Phys. **32**, 1258 (1999)
10. A.L. Fanrenbruch, *Fundamentals of Solar Cells* (Academic Press, 1983)
11. R. Brini, Eur. Phys. J. Appl. Phys. **30**, 153 (2007)