The research of post-treatment on Cd$_{1-x}$Mg$_x$Te thin films and CdTe solar cells

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Abstract. As for its higher band gap, Cd$_{1-x}$Mg$_x$Te (CMT) material has been taken into consideration to improve the open-circuit voltage of CdTe solar cells as an electron reflector layer. An essential step in the development of this new interlayer is the passivation process. X-ray Diffraction (XRD) and scanning electron microscope (SEM) results give us the suitable annealing temperature range of CMT thin films from 350°C to 400°C, and suggest that the annealing process is beneficial to grain growth and recrystallization. The concentration of CdCl$_2$ solution has an influence on the crystallinity of the thin films and coating method would contribute to electrical performance of the devices. The CMT/CdTe cells which underwent the two-step annealing procedure at high purity nitrogen atmosphere showed the significant improvements in device performance. Furthermore, the CdTe solar cells with the CdTe cap layer and Te/Cu back contacts also demonstrated higher performance.

Keywords: Cd$_{1-x}$Mg$_x$Te, Passivation, Annealing process

1. Introduction
Cadmium telluride (CdTe) is a photovoltaic material with great development prospects over recent decades and is attracting the interest of many researchers in the area of thin film solar cells due to the incredible progress achieved by First Solar in pushing the efficiency reached 22.1%, but it still lags behind that of c-Si and GaAs solar cells [1]. Despite the records, laboratory CdS/CdTe solar cell efficiencies are still below the theoretical limits, primarily due to the poor current, fill factor and low open-circuit voltage [2]. K. Hsiao and T. Coutts [3, 4] have proposed the new ideas that develop a tandem structure or an electron reflector layer into the devices to improve the open-circuit voltage. So the Cd$_{1-x}$Mg$_x$Te (CMT) material has been taken into consideration because its higher band gap and can be easily varied by changing the Mg/(Cd+Mg) fraction. CMT can be used as the absorber in higher band gap top cells in tandem junction devices and as a higher band gap layer to make the needed conduction band barrier in electron reflector (ER) structures [5]. In order to gain an in-depth understanding of CMT, researchers have carried out a series of studies. R. Dhare [6] showed the growth of CMT thin films by co-sublimation method, R. Palomera [7] did some research of the Mg incorporation and the related material properties. Furthermore, P. Kobyakov [8] discussed the passivation treatment effects on CMT thin films and found that CdCl$_2$ passivation is crucial to improve performance of CdTe solar cells which has improved device efficiency from ~1% to ~13% at Colorado State University.

We deposited CMT thin films by the co-evaporation technique and investigated the effects of annealing temperature and concentration of CdCl$_2$ solution on the properties of thin films in this study. Finally, we made some research on the post-treatment of the CdS/CdTe/CMT solar cells to find optimal passivation conditions and obtain better photovoltaic characteristics.

2. Experimental
2.1. Film fabrication

CMT thin films were prepared by co-evaporation method in this study and the Mg content is been controlled in 0.18 [9]. Substrate temperature was held at approximately 350°C and the base pressure in vacuum chamber was held below 10⁻³ Pa during deposition. The structure of CdTe/CMT thin film solar cells was glass/SnO₂: F(FTO)/CdS/CdTe/CMT/BC/Au, in which CdS window layer was deposited by chemical bath deposition method and CdTe absorber layer was deposited by vapour transport deposition method. A 80-nm-thick CMT was deposited on the back of CdTe thin films and then annealing five minutes in tubular annealing furnace after the CdCl₂ treatment [8]. Finally, a layer of back contact, ZnTe: Cu or Te/Cu, was deposited and Au was used as the back electrode.

2.2. Characterization

Structural characterization was performed using a DX-2600 X-ray diffractometer with Cu-Kα radiation scanning in the 10°−70° configuration and a Hitachi S-4800 field emission scanning electron microscopy (SEM) was used for imaging. The cells were analyzed by current density-voltage (J-V) characteristics used ABET technologies Sun 2000 solar light simulator under simulated AM1.5 illumination.

3. Results and discussion

3.1 The exploration of annealing temperature on CMT thin films

In order to study the effect of different annealing temperatures on the properties of the thin films, the samples were prepared under the same condition with the thickness of about 300 nm. The X-ray diffraction patterns (figure 1) indicate that the annealing temperature does not change the preferential orientation of the films and the (111) peak location [10]. However, the intensity of the (111) peak increases first and then decreases with increasing the temperature. The increase of the annealing temperature has made the grain crystallized and the preferential orientation tends to be obviously. But higher annealing temperature can damage grain growth, which degrades the film quality. As can be clearly seen from figure 2, the shape and size of the grain does not change significantly and the annealing process has no effect on the film structure when the film are annealed at 300°C~350°C. The grain boundary gradually becomes inconspicuous with the appearance of the pores until the temperature rises up to 400°C. As the temperature continue raising, it is obvious that the pores are dwindling and the grains become visible again due to the recrystallization of the grains during this temperature process. The experimental results show that the phenomenon of grain growth and recrystallization of the thin films is beneficial to the reduction of the grain boundary recombination. However, the film surface structure has been damaged under 500°C annealing temperature and the presence of grains was invisible at this time. Combine the analysis with figure 1, it is presumed that the optimum annealing temperature should be between 350°C and 450°C.

![Figure 1. XRD patterns of the Cd₃₋ₓMgₓTe thin films annealed at various temperatures.](image-url)
3.2 The CdCl$_2$ post-processing of CMT thin films

It can be seen from the figure 3 that the films only have a strong diffraction peak at 23.75$^\circ$ without the CdCl$_2$ treatment, which corresponds to CdTe (111) planes. On the contrast, the relatively weak diffraction peaks appeared at 27.6$^\circ$ and 38.4$^\circ$, which are also from CdTe thin films after annealing at 350$^\circ$C. Then the 39.4$^\circ$ and 49.5$^\circ$ peaks are originated from Te (154) or Te (152) diffractions when the annealing temperature increased up to 400$^\circ$C. However, the films without CdCl$_2$ treatment have no diffraction peak at these 20 positions as shown in the JCPDS card (15-0770), indicated that CdCl$_2$ treatment is beneficial to grain recrystallization. In addition, it is also observed that the (111) peak intensity is not strong at the lower CdCl$_2$ solution (0.03 and 0.06 mol/L) treatment. But it becomes stronger with the increase of the CdCl$_2$ concentration and the diffraction peak intensity is approximately the same as that of the films without the CdCl$_2$ treatment, which indicates that the post-treatment has an effect on the crystallinity of the thin films. In a certain range, the greater the concentration of CdCl$_2$ solution, the higher the crystallinity of the thin films.

3.3 Current-voltage (J-V) characteristics of CdTe solar cells after post-treatments

In this part of the experiment, the same color of the box chart represents the nearly identical configuration cell. When CMT deposited on the back of CdTe absorber thin films, the CdCl$_2$ treatment need to be carried out before the cell annealing. Firstly, we made a comparison of two CdCl$_2$ processing methods, as the red box chart shown. The cell that has been coated with CdCl$_2$ has better J-V
performance while the spraying method exhibits breakdown characteristics of PN junction and its J-V curve is almost linear. The possible reason for this phenomenon is that the CMT is a kind of material which is easily oxidized, the film surface in the air during the spraying procedure while the solution coated on surface of the film make the isolation environment from the air to a certain extent. In order to reduce CMT oxidation, the addition of a thin CdTe cap layer was introduced into the back of the CMT thin films corresponding to the orange box chart as shown in figure 4 [11]. Another kind of protection method is to deposit a thicker CMT layer and then etching the oxidized part before the back contact deposition. It can be seen that two methods have their pros and cons. The latter technique exhibits the optional J-V performance in the efficiency and fill factor while the other prevails in the open-circuit voltage. For CdTe cap, the fill factor is reduced due to the increased series resistance and the presence of oxygen contamination in the film during the reheating which form an extra oxide layer between CMT and CdTe. Meanwhile, the addition of CdTe cap in the open circuit voltage improvement is a worthy consideration [12].

ZnTe:Cu is a mature back contact material in CdTe solar cells. To some content, Te/Cu back contact also shows the better side. The green box chart show the effect of two back contacts on the CMT solar cells. It can be seen that the Te/Cu back contact show the better J-V performance, this is probable that the CMT material can form a larger valence band offset (VBO) blocking the holes and reducing the fill factor of the device, a back contact with a higher electron affinity and doping is needed to minimize the VBO formation and the tellurium is a potentially ideal contact for CMT cells. It is theorized that the holes may diffuse from the tellurium layer into the CMT layer moving the bands and minimizing the VBO [13, 14].

Then, we explored the effect of two annealing process: one-step procedure and two-step procedure. CdCl₂ annealing treatment before the deposition of CMT can promote the recrystallization and the diffusion processes of sulfur from the CdS [15]. Then CdCl₂ dealt with the cell again after the preparation of CMT aimed as passivating the grainboundary and facilitating the carrier separation. For this count, two-step annealing procedure enhanced the higher cell performance which shown by the blue in figure 4. Pink box deliver the point that high purity nitrogen atmosphere would build a better environment than low vacuum condition during the annealing process. In addition, we can also choose the other inert gases, such as argon to act as protective gases to prevent the external environment from affecting the cell performance during this procedure.

Figure 4. Photovoltaic parameters of CMT solar cells after the various post-treatments: CdCl₂ spraying and coating (red box), annealing mode (blue box), different back contact materials (green box), the atmosphere in the annealing process (pink box), different CdTe caps (orange box).
4. Conclusion
Based on the research of the CMT thin-film post-treatment process, the following conclusions have been drawn. The optimum annealing temperature of CMT films was obtained between 350°C and 450°C. The CdCl$_2$ treatment could promote the grain recrystallization during the annealing process and it had an appropriate concentration in order to obtain the higher crystallinity of the CMT thin films. A post-treatment using two-step annealing at high purity nitrogen atmosphere is an alternative passivation for CdTe based photovoltaic cells. It is also found that the CdCl$_2$ coating process can obtain better performance in the devices. Furthermore, the CMT/CdTe cells with a CdTe cap layer and Te/Cu back contact show significant improvement in device performance.

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References
[1] Green M A, Y Hishikawa, E D Dunlop, D H Levi, J Hohl-Ebinger 2018 Progress in Photovoltaics: Research & Applications 26 3-12
[2] Morales-Acevedo 2006 Sol. Energy 80 675-681
[3] Coutts T J, J S Ward, D L Young, K A Emery, T A Gessert 2003 Progress in Photovoltaics Research & Applications 11 359-375
[4] Hsiao K J, J R Sites 2012 Progress in Photovoltaics: Research & Applications 20 486-489
[5] Hsiao K J, J R Sites 2009 IEEE 34th Phot. Spec. Conf. (Pvsc) 1846-1850
[6] Dhene R, K Ramanathan, J Scharf, D Young 2007 Mrs Proceedings 1012
[7] Palomera R C, O S Martinez, J Pantoja-Enriquez, X Mathew 2017 Appl. Therm. Eng. 114 1169-1175
[8] Kobyakov P S, D E Swanson, J Drayton, J M Raguse, K L Barth, W S Sampath 2013 IEEE 39th Phot. Spec. Conf. (Pvsc) 386-391
[9] Kobyakov P S, A Moore, J M Raguse, D E Swanson, W S Sampath 2014 J. Vac. Sci. Technol. A. 32 021511-021517
[10] Shimp T M, J M Kephart, D E Swanson, A H Munshi, W S Sampath 2016 J. Vac. Sci. Technol. A. 34 051202
[11] Reich C, D Swanson, T Shimp, J Drayton, A Munshi 2016 IEEE Phot. Spec. Conf. (Pvsc) 487-491
[12] Sites J, A Munshi, J Kephart, D Swanson, W S Sampath 2016 IEEE Phot. Spec. Conf. (Pvsc) 3632-3635
[13] Swanson D E, A Abbas, A H Munshi, J A Drayton, J M Raguse 2015 Mrs Proceedings 1771 133-138
[14] Zhao Y, M Boccard, S Liu, J Becker, X-H Zhao 2016 Nature Energy 1 16067
[15] McCandless B E, L V Moulton, R W Birkmire 1997 Prog. Photovoltaics 5 249-260