

THE PL SPECTROSCOPY OF CdTe POLYCRYSTALLINE THIN FILMS BY VAPOR TRANSPORT DEPOSITION

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CdTe thin films on CdS coated FTO glasses were prepared by vapor transport deposition (VTD). The photoluminescence spectra excited both from CdTe film side and the glass side were investigated in order to study the effect of deposition parameters in VTD process such as substrate temperature, pressure and atmosphere on the defects in CdTe films. The results show that the substrate temperature and the atmosphere w/o oxygen have great influence on the number and variety of defects in CdTe films as well as at CdTe/CdS interface, which leads to significant difference in CdTe film properties and device performances. The effect of the pressure in this paper is identical to the effect of the substrate surface temperature. During the VTD deposition process, the real substrate temperature and the oxygen in atmosphere are the first two important parameters to control.

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1. Introduction

Cadmium telluride thin film solar cells have been studied because of its low cost and high conversion efficiency. And the maximum conversion efficiency for small area device has reached 22.1% up to now [1, 2]. Cadmium telluride polycrystalline thin film was usually deposited using high temperature technology, such as close spaced sublimation (CSS) [3] or vapor transportation deposition (VTD) [4]. The parameters of VTD process are easily controlled compared with CSS technology. In fact, six devices in nine record CdTe solar cells have been fabricated using VTD technology since 2011 [5]. However, there are only three groups (University of Delaware [6], Sichuan University [7, 8] and First Solar Inc. [4]) to develop VTD technology compared with lots of groups studying CdTe solar cells by CSS technology. G. M. Hanket et al. reported the design of a VTD process and the analysis of preparation process of VTD [6]. But First Solar Inc. has never reported any details about the VTD process due to commercial reasons. S Cao et al. and H Gu et al. in our group reported the influence of oxygen and substrate temperature on film property and device performance [7, 8].

For CdTe solar cells defects are the key factors to limit the efficiency because of the lattice mismatch of up to 11% between CdS and CdTe and many grain boundaries in CdTe films [9, 10]. Fortunately, the lattice mismatch can be passivated through interdiffusion during a high-temperature process such as CSS and VTD [10]. But much higher temperature will result in poor heterojunction. Therefore, it is very important to balance between lattice mismatch and heterojunction quality. Photoluminescence spectroscopy (PL) as a non-destructive characterization technique has been widely used in the preparation of optoelectronic devices such as LEDs and detectors and yielded some valuable results in radiative recombination defects characterization of chalcogenide photovoltaic devices [11-16]. M Tuteja et al. studied the low temperature PL spectra on sputter deposited CdS/CdTe junctions and solar cells [11]. S Vatavu et al. reported the PL

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spectra of CdTe films and junctions prepared under various deposition conditions of CSS process and chloride treatment [12]. DP Halliday et al. reported the PL spectra of as-grown CdTe films, air-annealed and CdCl₂-treated CdTe films, in which CdTe films were prepared by CSS [13]. CJ Bridge et al. reported the PL spectra CdTe thin films which was prepared by CSS annealed at different temperatures [14]. D Kuciauskas et al. reported the PL spectra of Cu-doped CdTe films prepared by VTD [15, 16].

In this paper, CdTe polycrystalline thin films prepared by VTD were characterized by PL and the corresponding devices were fabricated. We tried to find out the relationship between VTD parameters (e.g. substrate temperature, pressure and deposition atmosphere) and the defects in CdTe films and to analyze the effect of defects on device performances.

2. Experimental

2.1 Preparation

In this study, CdS thin films were grown on FTO coated glasses (Pilkington Tec10) by chemical bath deposition (CBD) with the thickness of about 80 nm [17]. Then the CdTe layers were deposited on CdS substrates by VTD under different substrate temperatures, deposition pressures and atmospheres. The detailed deposition parameters of CdTe thin films are listed in table 1. The source temperature of CdTe for all films is 680 °C. The preparation details of CdTe thin films by VTD can be found in ref. [7]. PL and scanning electron microscope(SEM) measurement was performed on as-deposited CdTe films. After PL characterization, a CdCl₂ treatment was carried out by applying a water solution of CdCl₂ with concentration of 0.1 mol/L and subsequently annealing at 385 °C for 30 min. Then the surface of CdTe thin films was etched by Br₂-methanol solution with volume ratio of 0.8% for 8s. Gold was finally coated as electrode by evaporation.

Table 1 The preparation conditions of CdTe samples.

serial	substrate temperature	deposition pressure	atmosphere
	°C	Pa	
1	520	800	Ar with 6% O ₂
2	580	800	Ar with 6% O ₂
3	610	800	Ar with 6% O ₂
4	640	800	Ar with 6% O ₂
5	610	500	Ar with 6% O ₂
6	610	1000	Ar with 6% O ₂
7	610	800	He

6% is the volume ratio of O₂ in Ar.

During analyzing the effect of substrate temperature, deposition pressure and atmosphere, we found these parameters are not independent and the surface temperature of the substrate is one of the fundamental factors to influence the growth of CdTe film. For example, the real temperature on the substrate surface did vary with the pressure although the monitoring temperature of the substrate heating part was kept constant. In order to understand how the three parameters influence the surface temperature of the substrate, we carried out a test on the substrate surface temperature under different parameters. The thermocouple was placed at the center of the substrate surface to test the surface temperature. Fig.1 shows the result of the test. It can be seen that the substrate surface temperature increases with the increasing substrate heating temperature and pressure. This shows that both the substrate temperature and the pressure have obvious influence on the substrate surface temperature while oxygen has little effect on it, which is important to analyze the following results.

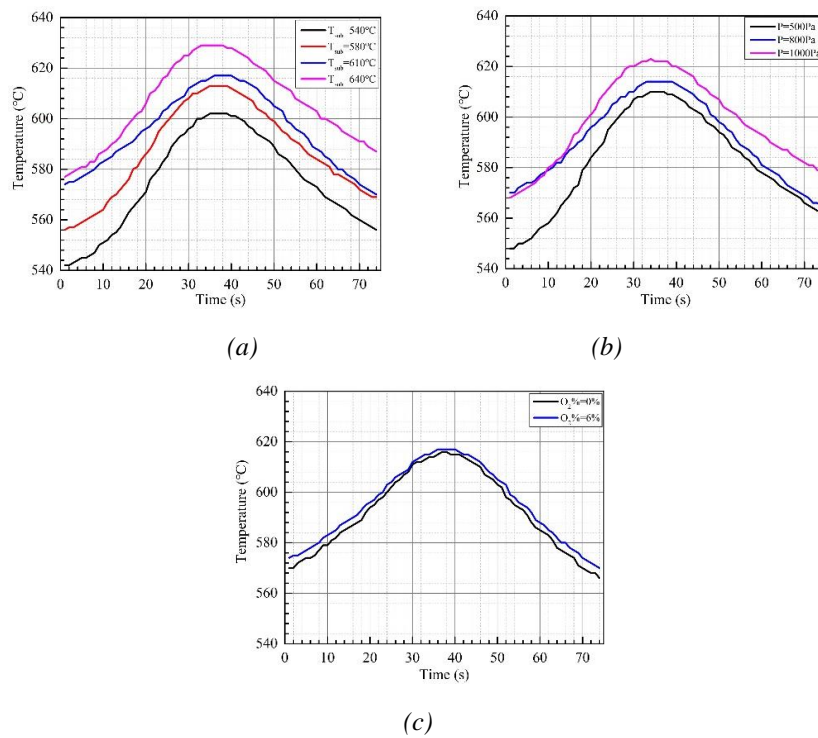


Fig. 1. The dependence of the substrate surface temperature on (a) the substrate heating temperature, (b) the deposition pressure and (c) the atmosphere with or without O₂

2.2 Characterization

The surface morphology of CdTe thin films was performed by the Hatachi-4300 scanning electron microscope. The PL measurement of CdTe films was characterized by photoluminescence spectroscopy (FLS980, Edinburgh Instruments Ltd). The samples were put on a low-temperature sample holder and illuminated by an EPL-655 laser light source with 655 nm wavelength and 5 mW power. The signal of PL was detected by an AR5509-73 NIR detector (Hamamatsu, Japan) which was cooled by a Liquid nitrogen system (Hamamatsu, Japan) (<-80 °C). The low-temperature sample holder was cooled by a liquid helium circulation system (ARS, USA), and the temperature was measured by a Lake Shore 335 temperature controller. To avoid the effect of temperature on the PL spectroscopy, the temperature of CdTe samples was set at 30 K. The laser light illuminated not only from the surface of CdTe but also from the glass side so that we can get the information both from CdTe films and CdTe/CdS interface, respectively. The photovoltaic measuring system with the light source conformed to AM1.5 was used to obtain light *J-V* characteristics of solar cells.

3. Results and discussion

3.1 The PL spectra of CdTe thin films deposited at different substrate temperatures

Fig. 2(a) is the PL spectra excited from CdTe film side of sample 1, 2, 3 and 4 at 30 K, corresponding to the substrate temperature of 520 °C, 580 °C, 610 °C and 640 °C, respectively.

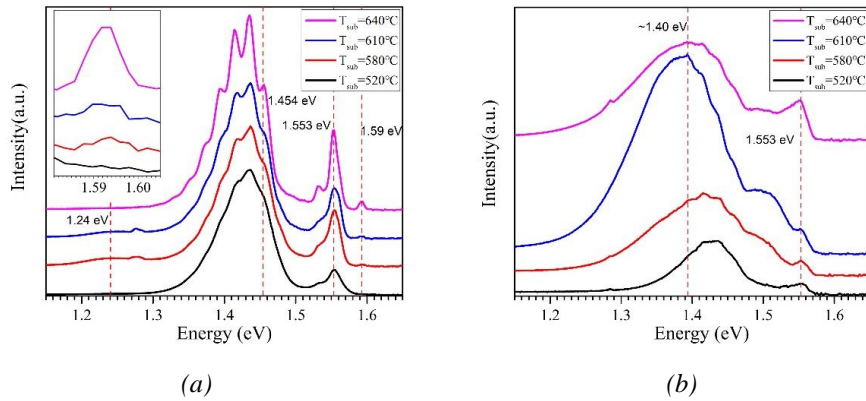


Fig. 2 The PL spectra from CdTe film-side excitation (a) and glass-side excitation (b) of CdTe/CdS films deposited at different substrate temperatures by VTD

The strongest peak of all PL spectra is ~ 1.43 eV, and it can be divided into several equidistant emission peaks, with the energy difference of about 20 meV. Some researchers reported the same phenomenon and explain that these emission peaks are associated with the LO phonon and the zero-phonon line at 1.453 eV (the energy of LO phonon of CdTe is 21 meV [18]) [14, 15, 19]. The emission peak of 1.453 eV is associated with donor-acceptor pair transition [20], and this emission is composed of shallow level defects caused by V_{Cd} and Te_i [21, 22]. The distinction of phonon replica is more obvious with the increased substrate temperature, which suggests that films deposited at low substrate temperature have more complex defects than films at high temperature. The reason is that low substrate temperature results in small grains and lots of grain boundaries in films which leads to more complex defects.

The second strongest peak is the peak near 1.55 eV and it is possibly composed of 1.53eV, 1.551eV and 1.559eV peaks [19]. These peaks converge together in Fig. 2(a) because photoluminescence signals from many small grains and grain boundaries were detected simultaneously since the laser spot is much larger than the grains. Many researchers considered that these near 1.55 eV emission peaks are generated by donor-acceptor transition of cadmium vacancies (V_{Cd}) [21, 23] or O_2 [24, 25]. The mechanism of the O_2 effect on the transition is not clear. One of the possible reasons is that O_2 could occupy position of tellurium (O_{Te}) to form a shallow substitutional defect or TeO_2 , leading to the formation of tellurium vacancies (V_{Te}) and cadmium interstitial atoms (Cd_i) [22, 25, 26]. The emission peak of 1.55 eV was heightened with the increased substrate temperature, indicates a low rate of nonluminescent recombination [19].

By amplifying the PL spectra, a low intensity emission peak at 1.59 eV was found. It becomes more pronounced with the increased substrate temperature. This peak is very close to the energy band gap of CdTe (1.60 eV at 30 K) and it has been attributed to acceptor bound exciton transition [22]. Since excitonic luminescence can only be detected at high quality films, the films which have this emission peak should have high crystallinity and large grain size [13]. Fig. 3 is the SEM photographs of CdTe surface for sample 1, 2, 3 and 4. It demonstrates that the grain size increases with the substrate temperature, which is in accord with PL results.

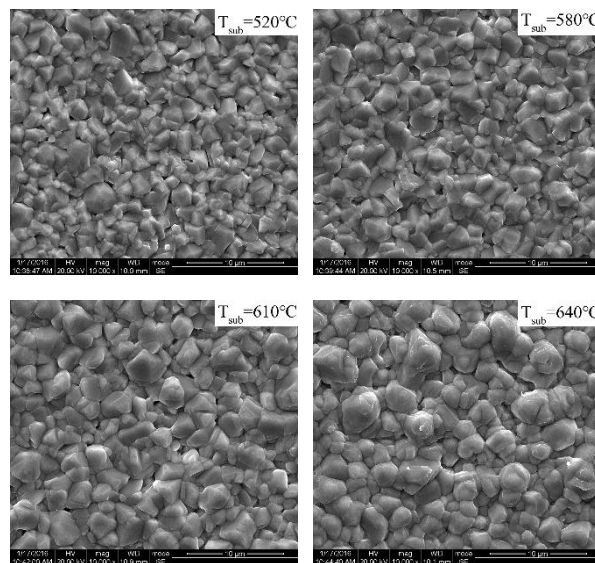


Fig. 3 SEM micrograph of CdTe thin films deposited at different substrate temperature.

Fig. 2(b) is the PL spectra as a result of glass-side excitation of the sample 1, 2, 3 and 4 at 30 K. The main difference between the film-side and glass-side excitation is that the glass-side spectra have a broad emission band around 1.40 eV extending near 1.25 eV. Currently, there are two reasons which are generally accepted for this phenomenon: a) $\text{CdS}_x\text{Te}_{1-x}$ alloy layer forms at the interface area leading to the change of the band gap [15]; b) high defect concentration and low crystallinity results in many emission lines superimposed on each other, thereby leading to broadened emission peak. It is found that the peak position for different samples shifts a bit with the increased substrate temperature. This phenomenon could be explained that $\text{CdS}_x\text{Te}_{1-x}$ alloys with different composition has formed at CdTe/CdS interface due to the different substrate temperatures [27]. In addition, the x value in $\text{CdS}_x\text{Te}_{1-x}$ affects the performance of solar cell devices [28]. The emission peak at 1.55eV has the same origins with 1.55eV peak in fig.2(a). It increases with the substrate temperature, too.

3.2 The PL spectra of CdTe thin films deposited at varied pressures

Fig. 4 is the PL spectra obtained from the film-side and the glass-side excitation for sample 5, 3 and 6 at 30K, corresponding to deposition pressure of 500 Pa, 800 Pa and 1000 Pa, respectively.

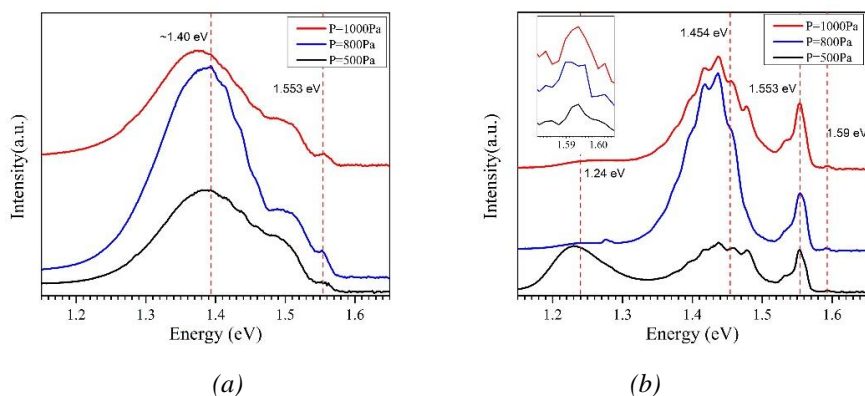


Fig. 4 The PL spectra excited from film-side(a) and glass-side (b) of CdTe thin films deposited at varied pressures

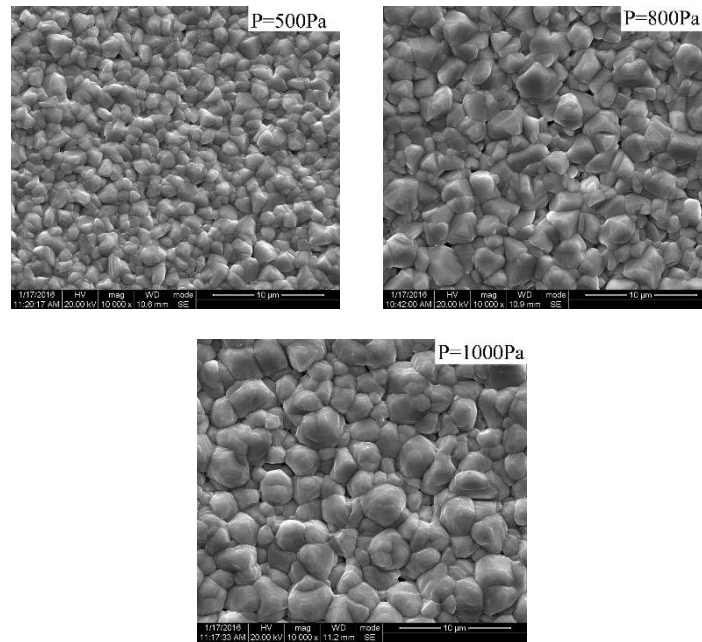


Fig. 5. SEM micrograph of CdTe thin films deposited at varied pressures.

The most obvious influence of deposition pressure is that the intensity of emission peak of 1.24 eV is reduced when the deposition pressure increases from 500 Pa to 800 Pa. The emission peak of 1.24 eV is associated with donor-acceptor pair (DAP) transition, and this peak is related to O_2 [12]. This phenomenon is more obvious in the film-side PL spectra of CdTe thin films deposited in different atmospheres. (Further analysis is shown in section 3.3)

The emission peak of 1.59 eV, which is due to acceptor bound exciton transition, appears in the spectra of 800 Pa and 1000 Pa films. The emission peak of 1.55 eV, which is associated with donor-acceptor transition, heightens with the increased pressure. This suggests that the CdTe films deposited under relatively high pressures has larger grain size and better crystallinity. SEM surface photos of sample 5, 3 and 6 shown in Fig.5 demonstrate that the grain size of CdTe film increases with the pressure. Temperature test from fig.1 shows that the deposition pressure would basically influence the substrate surface temperature. Therefore, high pressure corresponds to high substrate surface temperature and it results in larger grain size and better crystallinity.

~1.40 eV emission band in glass-side PL spectra shifts a bit with the change of deposition pressure. It is inferred that the chemical composition of CdS_xTe_{1-x} alloy at interface is different for different samples since pressure will influence the substrate surface temperature where CdTe film grows.

3.3 The PL spectroscopy of CdTe thin films deposited in atmosphere with and without oxygen

Fig. 6(a) is the film-side PL spectra of sample 3 and 7 in 30 K with and without oxygen (6%). The emission peak at 1.28 eV is Raman peak which is beyond the scope of this article.

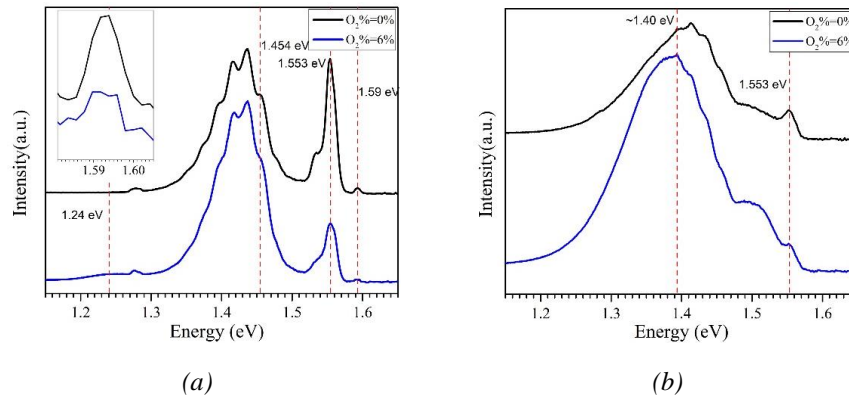


Fig. 4. The PL spectra excited from film-side(a) and glass-side (b) of CdTe thin films deposited in atmosphere with or without oxygen

At present, there is no definite explanation for the role of oxygen in CdTe films. Therefore, we only focus on the comparison of PL spectra for CdTe films deposited in atmosphere with or without oxygen. The emission peak of 1.24 eV does not appear in the PL spectra of the film grown in an oxygen-free atmosphere, demonstrating that the formation of this peak is related to oxygen which is in accord with S Vatavu et al[12, 29]. This emission peak is associated with DAP transition and this DAP transition is linked to the V_{Te} [30].

A high emission peak was observed at 1.55 eV and 1.59 eV, indicating that the film quality was relatively high. Fig. 7 is the SEM pictures of sample 3 and 7 which were deposited in atmosphere with and without oxygen. It is apparent that the oxygen-free film has a larger grain size, which is consistent with the higher intensity of the emission peak at 1.55 eV.

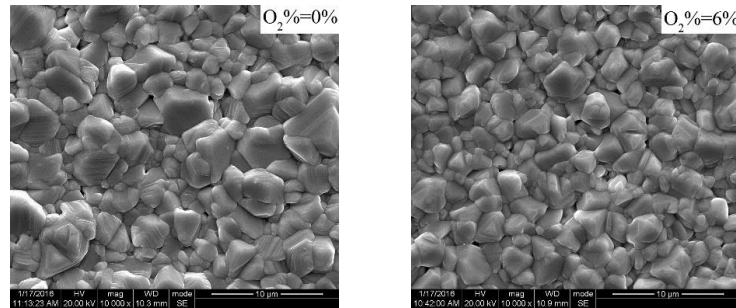


Fig. 7. SEM photos of CdTe thin films deposited with(left) and without(right) oxygen

Fig. 6(b) is the glass-side excited PL spectra of CdTe films with and without oxygen at 30 K. Two emission peaks are observed at 1.55 eV and 1.40 eV. With the addition of oxygen, the center of the peak at ~1.40 eV shifts from 1.415 eV to 1.391 eV. This phenomenon can be explained that oxygen leads to an increase of the number and variety of recombination centers which results in the peak shift. Moreover, the addition of oxygen would increase the density of shallow acceptor level defects in CdTe such as: O_{Te} [25]. Because the shallow acceptor level is effective p-type dopant, the addition of oxygen has a positive effect on the performance of CdTe solar cells.

3.4 The solar cells performances

The J - V parameters for each kind of solar cell are the average results of 3~5 small solar cells with 0.24 cm^2 area.

Table 2. The *J-V* characteristics of the presented samples

serial	substrate temperature	deposition pressure	atmosphere	<i>FF</i>	<i>J_{sc}</i>	<i>V_{oc}</i>	<i>Eff</i>
	°C	Pa	-	%	mA/cm ²	mV	%
1	520	800	He-O ₂ (6%)	59	24.6	0.702	10.2
2	580	800	He-O ₂ (6%)	58	24.4	0.729	10.3
3	610	800	He-O ₂ (6%)	61	24.0	0.771	11.3
4	640	800	He-O ₂ (6%)	56	23.0	0.726	9.4
5	610	500	He-O ₂ (6%)	43	24.1	0.745	7.7
6	610	1000	He-O ₂ (6%)	56	23.9	0.469	6.3
7	610	800	He	39	13.2	0.617	3.2

The devices with Au/CdTe/CdS/SnO₂ structure were fabricated after PL measurements. Table 2 gives a list of *J-V* characteristics of these solar cells. From the results of Table 2, it can be seen that with the increase of substrate temperature, the open circuit voltage and filling factor increase first and then decrease and reach the highest value when the substrate temperature is 610 °C while the short-circuit current density changes little. This result suggests that with the increase of substrate temperature, the grain size becomes larger and the nonradiative recombination defect of grain boundary decreases, which is beneficial to the improvement of solar cell performance. However, when the substrate temperature is too high (640 °C), the defects formed at the CdTe/CdS interface are not beneficial to the performance of the solar cells. With the increase of deposition pressure, the open circuit voltage and filling factor increase first and then decrease. This is consistent with the effect of substrate temperature on the *J-V* characteristics, which confirms that the effect of the pressure is the sum of the temperature and the pressure. In order to distinct the two factors, we deposited CdTe films at different pressures while carefully keeping the sample surface temperature to be consistent and characterized light *J-V* performance of devices. The result shows that the pressure has little effect on device performance. The addition of O₂ during the deposition process can increase the short-circuit current density, open circuit voltage and fill factor significantly. This indicates that oxygen can help form an effective p-type doping increasing carrier concentration and improving device performance.

4. Conclusions

In this paper, PL spectra of CdTe thin films prepared by VTD were investigated. The relationship between the film quality and the process parameters (substrate temperature, pressure and atmosphere) was analyzed by low temperature PL spectroscopy as well as SEM. PL spectra obtained from CdTe film side shows that the emission peak at 1.43 eV is composed of emission peak of 1.453 eV and its phonon replica. This peak is composed of shallow level defects which are influenced by deposition temperatures. The emission peaks at 1.55 eV and 1.59 eV reflect the crystalline quality of CdTe films. A significant emission band close to 1.40 eV in PL spectra excited from glass-side shifts with different deposition temperatures and oxygen content in deposition atmosphere.

In conclusion, the substrate temperature and atmosphere w/o oxygen have great influence on the number and variety of defects in CdTe films as well as at CdTe/CdS interface, which leads

to significant difference on CdTe film property and device performance. The effect of the pressure is basically identical to the effect of the substrate surface temperature. If the surface temperature is maintained, the pressure in the range of 500Pa~1000Pa would have little effect on CdTe film deposition. During the VTD deposition process, the substrate surface temperature and the oxygen in atmosphere are the two important factors to control.

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References

- [1] O Zelaya, F Sánchez-Sinencio, JG Mendoza-Alvarez, MH Farías, L Cota-Araiza, G Hirata-Flores. *Journal of Applied Physics* **63**, 410 (1988).
- [2] <http://investor.firstsolar.com/releasedetail.cfm?ReleaseID=956479>
- [3] TC Anthony, AL Fahrenbruch, RH Bube. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2**, 1296 (1984).
- [4] R.P. D. Rose, U. Jayamaha, M. Maltby, D. Giolando, A. McMaster, K. Kormanyos, G. Faykosh, J. Klopping, G. Dorer. *Proceedings of the 28th IEEE Photovoltaic Specialists Conference*: 428 (2000).
- [5] http://www.nrel.gov/ncpv/images/efficiency_chart.jpg
- [6] GM Hanket, BE McCandless, WA Buchanan, S Fields, RW Birkmire. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **24**, 1695 (2006).
- [7] H Gu, A Ren, J Zhang, et al. *Journal of Materials Science: Materials in Electronics* **28**, 9442 (2017).
- [8] W-L Cao Sheng, Feng Liang-Huan, Wang Wen-Wu, Zhang Jing-Quan, Yu Xiao-Qi, Li Xin-Xin, Li Wei, Li Bing, *Journal of Inorganic Materials* **31**, 141 (2016).
- [9] S.H. Wei, S.B. Zhang, A Zunger. *Journal of Applied Physics* **87**, 1304 (2000).
- [10] R.G. Dhere, D.S. Albin, DH Rose, et al. *Mrs Online Proceeding Library* 426 (2011).
- [11] M. Tuteja, P. Koirala, J Soares, R Collins, A Rockett. *Journal of Materials Research* **31**, 186 (2016).
- [12] S. Vatavu, H. Zhao, V. Padma, et al. *Thin Solid Films* **515**, 6107 (2007).
- [13] D.P. Halliday, J.M. Eggleston, K. Durose. *J Cryst Growth* **186**, 543 (1998).
- [14] C.J. Bridge, P. Dawson, P.D. Buckle, M.E. Ozsan. *Semicond Sci Tech* **15**, 975 (2000).
- [15] D. Kuciauskas, P. Dippo, Z. Zhao, et al. *IEEE Journal of Photovoltaics* 6: 313 (2016).
- [16] D. Kuciauskas, P. Dippo, A. Kanevce, et al. *Applied Physics Letters* 107: 243906 (2015).
- [17] M.L.A. Aguilera, J.M.F. Márquez, M.A.G. Trujillo, Y.M. Kuwahara, G.R. Morales, O.V. Galán, *Energy Procedia* **44**, 111 (2014).
- [18] W. Stadler, D.M. Hofmann, H.C. Alt, et al. *Physical Review B Condensed Matter* **51**, 10619 (1995).
- [19] C. Kraft, H. Metzner, M. Hädrich, et al. *Journal of Applied Physics* **108**, 124503 (2010).

- [20] T. Taguchi, J. Shirafuji, Y. Inuishi Japanese Journal of Applied Physics **12**, 1558 (1973).
- [21] J.M. Figueroa, F. Sanchez - Sinencio, J.G. Mendoza - Alvarez, O. Zelaya, C. Vazquez - Lopez, J.S. Helman, Journal of Applied Physics **60**, 452 (1986).
- [22] J. Van Gheluwe, J. Versluys, D. Poelman, P. Clauws. Thin Solid Films **480-481**, 264 (2005).
- [23] D. Grecu, A.D. Compaan, M. Young, U. Jayamaha, D.H. Rose. Journal of Applied Physics **88**, 2490 (2000).
- [24] M.A. Hernández-Fenollosa, D.P. Halliday, K. Durose, M.D. Campo, J. Beier. Thin Solid Films **431-432**, 176 (2003).
- [25] K. Akimoto, H. Okuyama, M. Ikeda, Y. Mori. Applied Physics Letters **60**, 91 (1992).
- [26] K. Yokota, T. Yoshikawa, S. Inano, T. Morioka, S. Katayama. Applied Physics Letters **56**, 866 (1990).
- [27] J.D. Poplawsky, N.R. Paudel, C. Li, et al. Advanced Energy Materials **4**, n/a (2014).
- [28] C. Li, J. Poplawsky, N. Paudel, et al. IEEE Journal of Photovoltaics **4**, 1636 (2014).
- [29] S. Vatavu, H. Zhao, I. Caraman, P. Gasin, C. Ferekides. Thin Solid Films **519**, 7176 (2011).
- [30] P.J. Roland, N.R. Paudel, C. Xiao, Y. Yan, R.J. Ellingson. Photovoltaic Specialist Conference, (2014)