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CHARACTERIZATION AND ANNEALING OF CdTe THIN FILM PREPARED BY VAPOR TRANSPORT DEPOSITION

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Polycrystalline CdTe thin film preparation for CdTe solar cell devices are typically established as the basis for this market-leading solar cell technology. The effects of substrate temperature and atmosphere of deposition and annealing on polycrystalline CdTe thin film prepared by vapor transport deposition (VTD) have been investigated. In order to analyze CdTe-borosilicate single layer structured, X-ray diffraction (XRD), Photoluminescence (PL) and Raman characteristics have been measured. The results show that increasing of substrate temperature can passivate grain boundary and improve grain integrity effectively. The addition of O_2 can promote the integrity of crystallization, but high O_2 partial pressure can inhibit grain growth. Annealing in O_2 ambience is more advantageous to CdTe thin films on preferred (111) orientation crystal plane. As a result of elevated $CdCl_2$-annealed temperature, the peak intensity at 1.27 eV decreased, because of the decrease of the concentration of structural defects in the Cd sublattice. Annealing at 450 °C has caused the oxides of cadmium and tellurium such as CdO, TeO_x and $CdTe_yO_x$.

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Keywords: CdTe, vapor transport deposition, X-ray diffraction, Raman spectroscopy, Photoluminescence

1. Introduction

The photovoltaic properties of CdS/CdTe hetero-junction based solar cells greatly depend on the deposition of CdTe. VTD process is originally proposed for solar cell[1, 2]. During VTD process, saturated source vapor is delivered to the space above substrate, which makes it maintain lower substrate temperature than close-spaced sublimation (CSS) method, and results in high-throughput and scalable processes. It has higher deposition rate compared with CSS process as well as better film quality[3]. It is also feasible to control substrate temperature regardless of deposition rate in VTD process. In this paper, we report the crystallinity and luminescence properties of polycrystalline CdTe film prepared by VTD method.

Recombination property of polycrystalline CdTe thin film absorption layer depends on the deposition and doping processes, which is closely related with film composition and structure. PL and Raman spectroscopy are employed to characterize the photon-generated carrier radiative recombination in polycrystalline CdTe. PL and Raman spectroscopy studies of CdTe thin

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film can reveal radiative states due to different impurities and are capable of explaining their roles in solar cell performance. This paper describes the work aimed at correlating the XRD, Raman and PL spectroscopy characteristics of CdTe thin film to most important deposition parameters such as substrate temperature and ambience during deposition, ambience and temperature during annealing.

2. Experimental

Polycrystalline CdTe films were prepared on 600 mm×450 mm borosilicate glass by VTD process. For the deposition process, CdTe powder with purity of 99.99% was fed into a graphite boat. CdTe was deposited in pure Ar, or Ar:O_2 mixed ambience at substrate temperature in the range of 400–520 °C and room temperature(RT).The chamber pressure was fixed to be 5 Pa. The thickness of prepared CdTe thin films is ~5-7 um. Thereafter, CdTe films were annealed in the presence of $CdCl_2$, under pure nitrogen or nitrogen mixed with a certain percentage of oxygen.

As listed in Table 1, the samples were deposited at substrate temperature from 400 ℃ to 520 ℃, under atmosphere of varied oxygen and argon partial pressure. Then the samples were annealed under $CdCl_2$, at temperature from 350 °C to 400 °C.

The PL (FLS980, Edinburgh Instrument) measurements were carried out using laser pulse wavelength of 655 nm as the excitation light with maximum output power of 5 mW, with the emission wavelength measurement range of 800 ~ 1600 nm, performed at room temperature. The crystallinity of thin films was measured by X-ray diffraction (XRD-DX-2600, Dandong, China) using Cu Kα radiation ($\lambda = 1.5404$ Å). The Raman spectroscopy (Andor Shamrock SR-303i-B, EU) measurements were carried out using laser pulse wavelength of 532 nm as the excitation light. The sample temperature was 79 K in Raman spectroscopy measurements.

Table1.Deposition and annealing conditions of CdTe thin film

Experiments	Substrate temperature(°C)	Ambience Ar:O_2(sccm)	Annealing temperature(°C)	Annealing Ambience N_2:O_2	Annealing time(min)
I Substrate temperature	520	10:2			
	460	10:2			
	400	10:2			
	RT	10:2			
II Deposition ambience	520	O_2-free			
	520	10:2			
	520	10:10			
III Annealing ambience	520	10:2	400	O_2-free	20
	520	10:2	400	4:1	20
IV Annealing temperature	520	10:2	350	4:1	20
	520	10:2	400	4:1	20
	520	10:2	450	4:1	20

3. Result and discussion

3.1 Effects of deposition substrate temperature

For polycrystalline CdTe thin film preparation, the substrate temperature is a key parameter that relates to the film growth rate, crystallinity, composition and thin film properties like absorption coefficient, light and dark conductivity and band-gap. With different substrate temperature, the thin film may be single-crystalline, polycrystalline or amorphous.

This experiment set up four groups of substrate temperature at room temperature, 400 °C, 460 °C and 520 °C, respectively, to observe its influence on the polycrystalline CdTe thin film structures and properties. Four groups of samples deposited under the Ar:O_2 mixed ambience with the same O_2 partial pressure of 0.6 Pa (12% O_2).

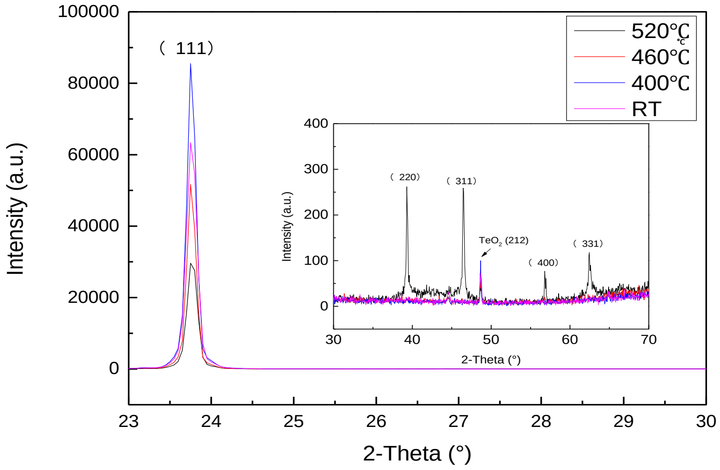


Fig. 1 The XRD pattern of as-grown samples deposited under different substrate temperature.

CdTe thin film deposited at all set substrate temperature were of cubic sphalerite polycrystalline structure, with highly oriented direction to (111) plane, as shown in Fig.1. As the substrate temperature was elevated, the (111) diffraction peak intensity decreased. Furthermore, it is clear that deposition at 520 °C led to (220), (311), (400) and (331) diffraction peaks of CdTe. Therefore, this indicates that deposition at 520 °C has enhanced the grain growth of polycrystalline CdTe during this processing step. This kind of polycrystalline orientation contributes to the performance of CdTe solar cells[4]. However, the peak of TeO_2 (212) which belongs to the tetragonal crystal system, can be found in the 2-theta from 44.523 ° to 48.585 ° in the results of the three samples at prepared which RT, 400 °C and 460 °C. It is because that at low temperature, the gas phase transported CdTe was decomposed into Te and Cd, then TeO_2 was formed under the O_2 ambience.

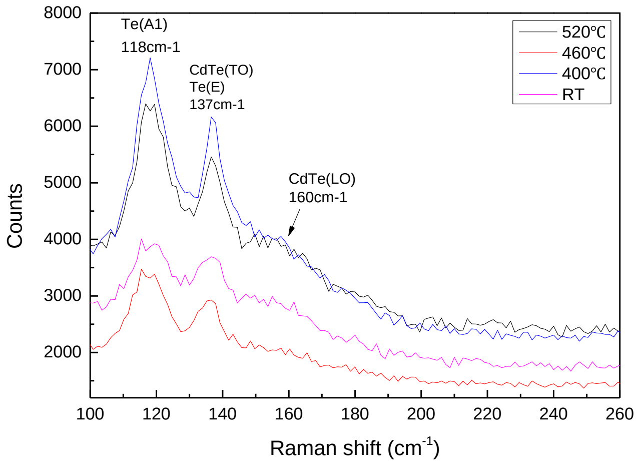


Fig.2 Raman spectra of samples deposited at varied substrate temperature, measured at 79 K. The laser wavelength is 532 nm

The general Raman peaks of CdTe transverse optical mode (TO) and longitudinal optical mode (LO) are at 141 cm^{-1} and 169 cm^{-1}, respectively. The full width of half maximum (FWHM) of the two peaks is usually about 3 cm^{-1}[5]. As shown in Fig. 2 that both TO and LO peaks have red shift, probably due to the absorption of oxygen and other impurities.

It can be seen that as deposited at substrate temperature of 400 °C and 520 °C, CdTe Raman scattering light was absorbed by Te 118 cm^{-1} strongly, which led to enhanced Raman peaks of Te. As the thin film deposited at room temperature and 460 °C had obvious drop of the peak of Te (A1) 118 cm^{-1} and (E) 137 cm^{-1} modes, soat these two substrate temperature, the amount of Te in CdTe film was smaller. The results indicated that as the growth temperature increases, CdTe becomes more Te-rich.

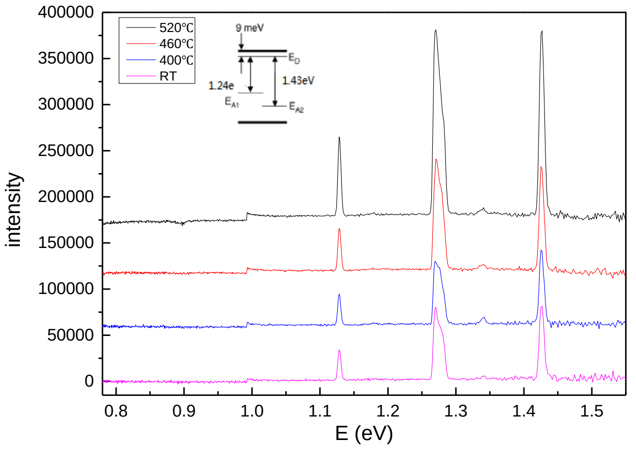


Fig. 3 The PL spectra of as-grown samples deposited at different substrate. temperature. The laser wavelength is 655nm with maximum output power of 5 mW.

The room temperature PL spectrum obtained by exciting the CdTe samples for which the CdTe film was deposited in Ar:O_2 ambient consists of two bands with maximum intensities located at 1.27 eV and 1.43 eV, as shown in Fig. 3. The 1.43 eV peak corresponds to the wavelength of 869 nm. This peak was caused by a variety of impurities or defects, and it is a manifestation of the comprehensive characteristic, which is difficult to distinguish the role of each transition. A related research claimed that, the peak near 1.43 eV associates with Cd containing complexes such as Cd vacancy and Te interstitial atoms, or Cd and surface defects[6]. The second PL band with maximum intensity at 1.27 eV is a characteristic of a D–A transition[7]. These results can be explained by presuming that both the 1.43 eV and 1.27 eV bands are results of electron recombination via the same donor level (E_D) with the holes localized at two acceptor levels (E_{A1} and E_{A2})[8] as shown in the inset of Fig. 3. The 1.13 eV band may be the result of coefficient of many impurities.

Summarizing the results from related literature, untreated CdTe is given priority to defects associated with Cd. The samples that deposited at room temperature have smaller grain size compared with other higher temperature of the substrate. With the increasing of substrate temperature, the PL intensity of samples increased significantly. It indicates that the increasing of substrate temperature can passivate grain boundary and improve grain integrity and crystalline quality effectively, which may boost the radiative recombination.

3.2 CdTe deposited under varied O_2 ambience

In the CdTe thin film deposition process, oxygen showed significant influence on film property. Oxygen can increase the acceptor concentrations in CdTe thin film, avoid the deep homogeneous junction formation[9]. The addition of oxygen can also affect the early stage of the CdTe thin film nucleation, directly reflecting the influence on film uniformity, compactness, and microstructure. The literatures have reported that oxygen has a beneficial impact on CdTe film quality as it increases charge carrier mobility and lifetime in the absorber layer of CdTe-based devices. Three groups of samples deposited under varied O_2 partial pressure 0%, 12% and 41% (0, 0.6 Pa and 2.05 Pa) respectively, and at the same substrate temperature of 520°C.

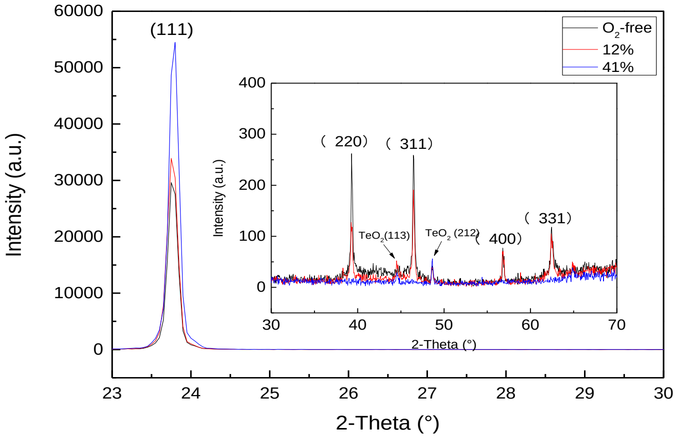
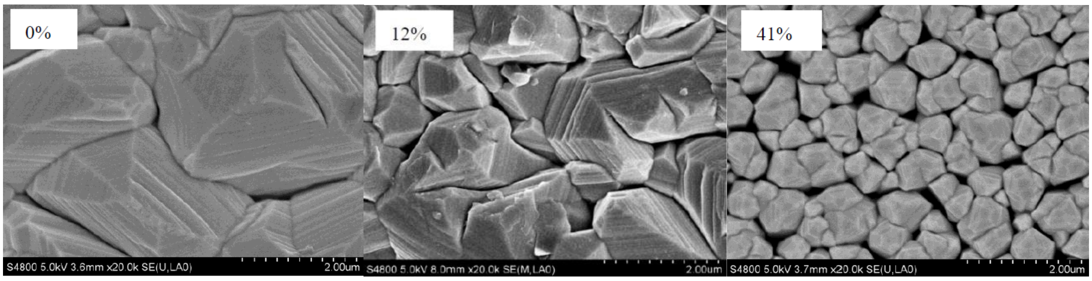


Fig. 4 The XRD pattern of as-grown samples deposited under Ar:O_2 ambience with different O_2 partial pressure

The XRD figure shows that CdTe thin films deposited in different O_2 partial pressures are cubic sphalerite polycrystalline structure. All the samples have shown highly preferred (111) oriented crystal plane. In the XRD results of samples deposited under O_2-free and 12%-O_2 ambience four low-intensity peaks which oriented to (220), (311), (400) and (331) appeared respectively. When oxygen partial pressure was increased to 41% (2.05 Pa), only CdTe (111) diffraction peak could be found. The preferred orientation degree (σ) is reduced when oxygen partial pressure was 12%, while the film has the highest preferred orientation when oxygen partial pressure was increases to 41%.



(a) (b) (c)

Fig. 5 SEM images of as-grown CdTe films deposited under ambience with (a) 0%, (b) 12%, (c) 41% O_2 partial presslure.

Image in Fig. 5 indicate that with the increase of oxygen partial pressure the grain size decreases. The average lateral grain length of 3um, 2um and 0.5um, corresponding to the CdTe film grown under 0%, 12% and 41% O_2 partial pressure respectively, shows that higher oxygen partial pressure yields smaller CdTe grain size. Higher oxygen partial pressure may increase the nucleation density, possibly because of the activation of growth surface and reduced surface diffusion length of source atoms and molecules. From Fig. 5 (a), (b), (c), it can be deduced that high O_2 partial pressure may limit CdTe grain growth during deposition[9].

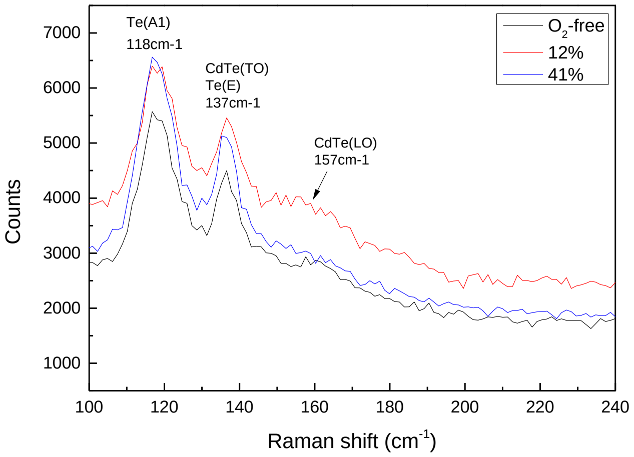


Fig. 6 Raman spectra of as-grown samples deposited under varied O_2 partial pressure, measured at 79 K

In Fig. 6, both TO and LO Raman peaks of the CdTe samples had redshift, which moved to 157 cm^{-1} and 137 cm^{-1} respectively. We can observe an A1 peak of Te at 118 cm^{-1} that prove the existence of Te segregation. At the same time another vibration mode E of Te generally appeared in the Raman peak around 139 cm^{-1} as oxygen was added. The CdTe LO mode (137 cm^{-1}) Raman peak and the 139 cm^{-1} peak are very close to each other. So the Raman peak near 137 cm^{-1} can be regarded as a joint contribution which consists of vibration pattern E of Te and TO of CdTe.

The intensity of LO peak at 157 cm^{-1} of CdTe thin film increased as it was deposited in Ar:O_2 ambience with O_2 partial pressure of 12%. This can indicate that the quality of CdTe thin film has been improved most in the Ar:O_2 ambience with O_2 percentage of 12%, compared with other atmosphere gas composition.

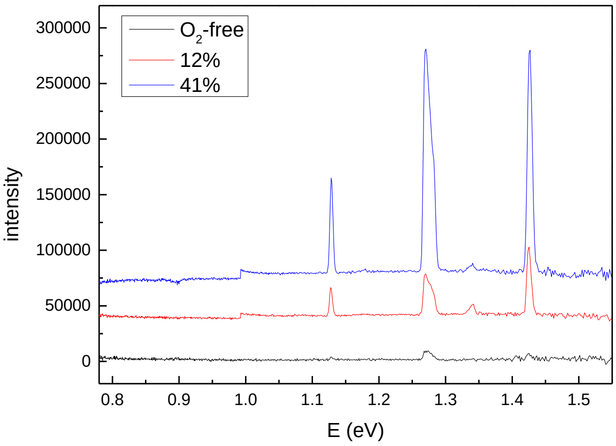


Fig. 7 The PL spectra of as-grown samples deposited under varied O_2 partial pressure

The room temperature PL was performed by exciting the samples deposited under varied O_2 partial pressure, which consists of two bands with maximum intensity located at 1.268 eV and 1.423 eV, as shown in Fig. 7. The bands at 1.423 eV and 1.268 eV have high intensity of samples deposited in 41% and 12% O_2 partial pressure. S. Vatavu et al. have correlated ~1.268 eV band to the presence of O_2 in CdTe[10]. However, as can be seen in Fig. 7, this band is also present in CdTe layers grown in O_2-free ambient, but with only a trace of a signal.

The oxygen may have a passivating effect regarding defects at the grain boundary[11]. Combined with the XRD and SEM results, it shows that the addition of O_2 can promote the integrity and the uniformity of plane orientation of the crystallization, but high O_2 partial pressure can inhibit grain growth by elevating nucleation density and limiting the grain size[12]. The samples deposited under atmosphere with 12% O_2 partial pressure showed better performance such as high open circuit voltage and minority carrier lifetime. Furthermore, in other experiments (data not shown), it was observed that generally higher performance in CdTe PV device was achieved with ~6% oxygen during the growth of CdTe film.

3.3 CdTe annealing ambience

Generally, it was claimed that the $CdCl_2$ treatment in the presence of oxygen produces better devices. The inclusion of oxygen in the material and device structure should be examined in a systematic way in order to understand this processing step. Therefore this sample group contains as-grown one and annealed ones under oxygen mixed ambience.

CdTe samples were annealed in the presence of $CdCl_2$, under the ambience of nitrogen mixed with a certain percentage of oxygen. In order to know the influence of the presence of oxygen in the annealing ambience, CdTe thin films annealed under O_2 added and O_2-free conditions were prepared.

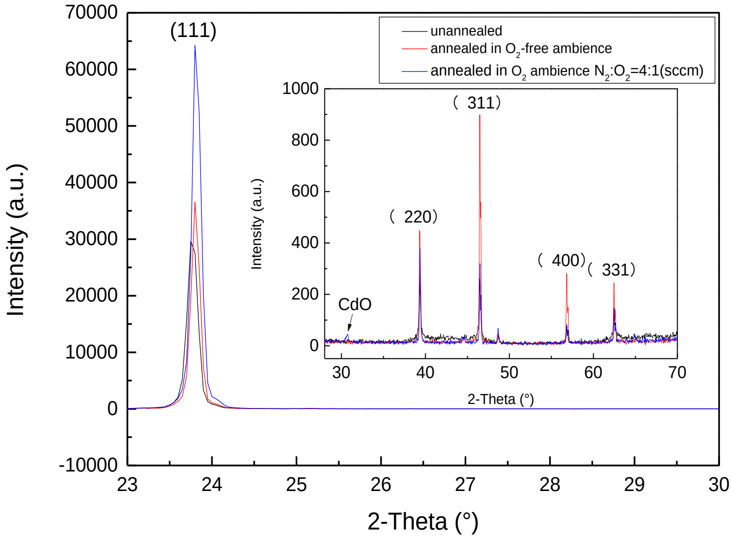


Fig. 8 The XRD patterns of as-grown sample and samples annealed under the ambience with and without O_2

The position of XRD peaks of all the as-grown and annealed samples are almost the same, corresponding to the CdTe planes of (111), (220), (311), (400), and (331). It is may be because that O_2 had been introduced to as-deposited CdTe samples. The peak intensity of (111) which annealed in O_2 ambience was twice higher than O_2-free and not annealed samples. It is clear that the peak intensity of (111) was oxygen sensitive. However, the other low-intensity peaks which oriented to (220), (311), (400) and (331) were quite different. The peak intensity of the sample which was annealed under pure nitrogen was higher than that annealed under O_2 mixed ambience and the not annealed, especially the (311) plane. The preferred orientation degrees(σ) for untreated, annealed in O_2-free and O_2 added ambience are 1.653, 1.272 and 1.786, respectively. It can indicate that annealed in O_2 ambience is more advantageous to CdTe thin films to form (111) crystal plane orientation[4].

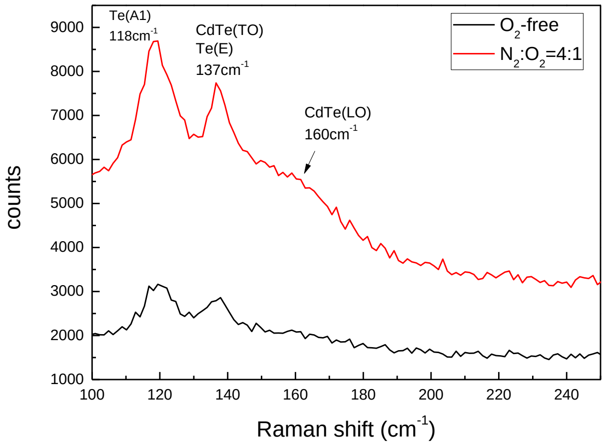


Fig. 9 Raman spectra of samples annealed under the ambience with and without O_2, measured at 79 K. The laser wavelength is 532 nm

Annealing with the presence of O_2 resulted in significant changes in the Raman spectra. As annealed under the conditions of N_2:O_2 ambience, the peak intensity of elemental Te at 118 cm^{-1} is about two times higher than the O_2-free sample. The 137 cm^{-1} peak is attributed to the contribution from both of Te (E) and CdTe (LO). It is likely correlated to the reduced amount of separated elemental Te. The CdTe peak around 160 cm^{-1} is not able to be observed in the curve of the sample annealed under O_2-free condition, while it extended broadly and its intensity also was enhanced dramatically in the result of the sample annealed under O_2-present atmosphere. It is clear that as the O_2 was mixed, the CdTe became Te richer and better recrystallized.

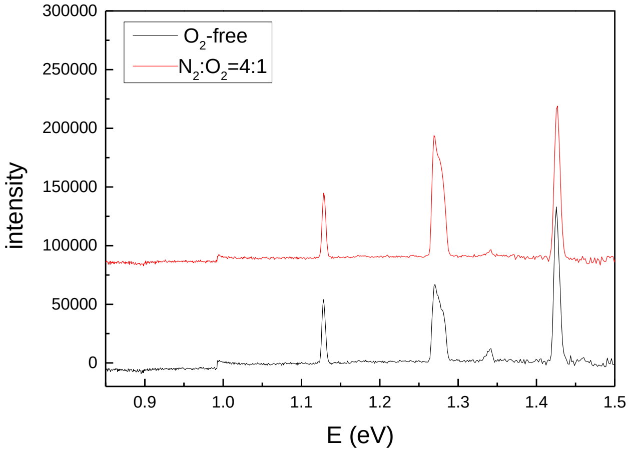


Fig. 10. PL spectra of samples annealed under the ambience with and without O_2

The room temperature PL spectra obtained by exciting the samples which were annealed under different O_2 ambience are shown in Fig. 10. The band with peak energy at 1.427 eV has no obvious change in PL spectrum. It can be explained that the origin of the 1.427 eV band appeared in annealed sample is attributed to some structural defects characteristics for CdTe only and it is most probably attributed to Cd vacancies[13]. However, the band with peak energy at 1.269 eV has been enhanced by annealing in O_2 containing ambience. It can correlate to the presence of O_2 during annealing.

Therefore, $CdCl_2$ thermal treatment in the presence of O_2 seems to be a better condition in our works. O_2 may introduce CdO into CdTe layers, and completely change the impurity level, recrystallization or electrical properties of these layers. CdO is known to have n-type conduction and almost similar bandgap (2.20 eV) to CdS (2.42 eV) and hence could introduce helpful advantages results to the device[14].

3.4 CdTe annealed at different temperature

The most common processing step in the fabrication of CdTe solar cells is a thermal treatment carried out with the presence of $CdCl_2$. During the early stages of development, this process involved applying $CdCl_2$ directly onto the CdTe surface and subjecting the entire structure to a heat treatment in air for approximately 30 minutes. All CdTe samples were annealed with the presence of $CdCl_2$, under the ambience of nitrogen mixed with a certain percentage of oxygen.

In this paper another way was employed. The quartz glass was coated with $CdCl_2$ solution. Then $CdCl_2$ which coated on quartz glass was transported to as-deposited CdTe surface using the mixture gas of O_2 and N_2. At the same time the CdTe thin films were annealed at different temperature at 350 °C, 400 °C and 450 °C for 20 minutes.

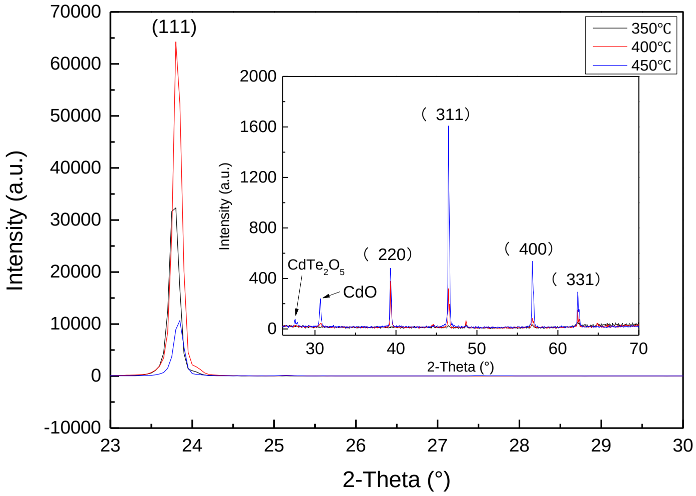


Fig. 11 The XRD pattern of samples annealed at different temperature

All the samples annealed at different temperature in the presence of $CdCl_2$ show cubic sphalerite polycrystalline structure, and a highly preferred orientation to (111) direction. When the samples were annealed above 400 °C, (220), (311), (400) and (331) diffraction peaks can be observed, compared with the sample annealed at 350 °C which only showed the peak of CdTe (111) plane. The sample annealed at 350 °C didn't show the other diffraction peaks indicates that the recrystallization process at 350 °C is different from that at 400 °C and 450 °C. The annealing at higher temperature may be promote better grain growth by maintaining the preference for the (111) plane and the other diffraction peaks. However, if the annealing temperature is too high at 450 °C for example, the oxygen would oxidize Te and Cd by forming oxides of cadmium and tellurium such as CdO, TeO_x and $CdTe_yO_x$. These oxides are evident as we can see from the XRD patterns in

Fig. 8 and Fig. 10. In the cases of samples annealed at 350 °C and 400 °C the oxide peaks were not observed.

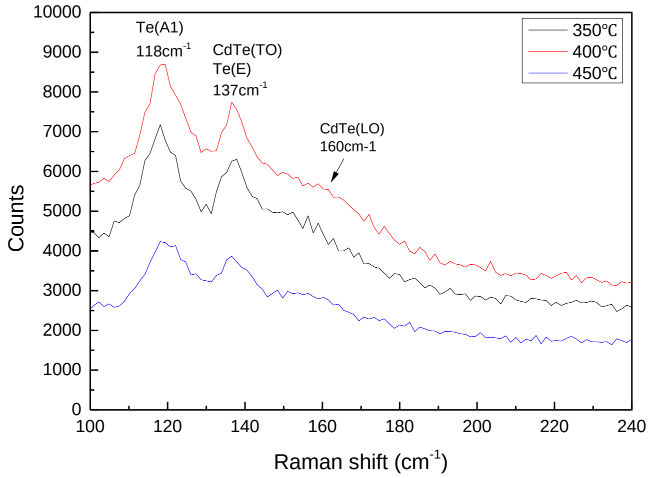


Fig. 12 Raman spectra of samples annealed under different temperature at 79 K. The laser wavelength is 532nm

As shown in Fig. 12 that CdTe annealed at 400 °C and 350 °C, the Raman peak intensity of elemental Te is quite high, comparing with the sample annealed at 450 °C. It indicates that the content of elemental Te has decreased with increasing annealing temperature. The peaks around 160 cm^{-1} are consistent with the phonon dispersion curves obtained by inelastic neutron scattering in CdTe[15]. According to Refs[16, 17], the possibility that the low frequency mode at 156.5 cm^{-1} is associated with Te segregation or TeO_2 modes should be discarded.

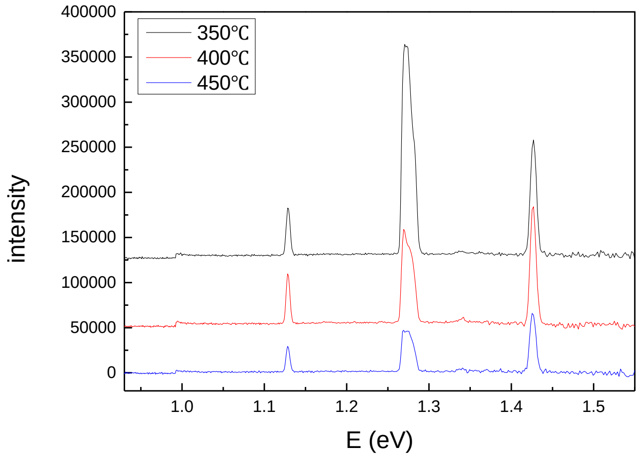


Fig. 13 The PL spectra of samples annealed at different temperature

Annealing in the presence of $CdCl_2$ under different temperatures results in significant changes in the PL spectra measured from CdTe. Fig. 13 shows the PL spectra of CdTe that the band with peak energy at 1.27 eV has increased drastically, comparing with 1.427 eV PL band. Thermal annealing of the CdTe structures in $CdCl_2$ results in decrease of the concentration of the states localized in CdTe surface layer which are screening the electron–hole bonds[18]. As a result of elevated $CdCl_2$-annealing temperature along with the decrease of the density of structural defects in the Cd sublattice, intensity of all the PL peaks decreased.

4. Conclusions

In this work we studied the effect of substrate temperature and ambience during deposition, annealing atmosphere and temperature on structural, Raman spectroscopy and photoluminescence properties of CdTe polycrystalline single layer prepared by VTD technique. The increasing of substrate temperature can passivate grain boundary and improve grain integrity effectively, along with boosted radiative recombination. The addition of O_2 can promote the integrity of the crystallization, but too high O_2 partial pressure can limit the grain growth, greatly increase the probability of recombination. Annealed under O_2-free and O_2 containing ambience led to no significant change in PL spectrum, but annealing in O_2 ambience is more advantageous to CdTe thin films to form preferred (111) plane orientation better and cause more Te-rich and better recrystallization. As a result of $CdCl_2$-annealing temperature was elevated, the intensity of all the three PL peaks became smaller, because of the decrease of the density of structural defects in Cd sublattice. Annealing at 450 °C has formed the oxides of cadmium and tellurium such as CdO, TeO_x and $CdTe_yO_x$, while they have not been observed in the samples annealed at 350 °C and 400 °C.

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