Effects of deposition temperature and CdCl₂ annealing on the CdS thin films prepared by pulsed laser deposition

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Abstract

Pulsed laser deposition (PLD) technique is suitable for the deposition of high-quality compound semiconductor thin films, and has been widely developed in recent years. However, pulsed laser deposition of CdS films has rarely been reported. In this work, we prepared CdS thin films using PLD. The effects of growth temperature on the PLD-CdS thin films were studied towards high-performance CdS/CdTe thin film solar cells. Results showed that the CdS film prepared at 400°C has the best crystallinity and optical transmittance, while 200°C is more suitable for the window layer of CdTe solar cells due to the highest energy conversion efficiency and the best short-wavelength response. CdCl₂ annealing treatment was also employed on the 200°C-deposited and 400°C-deposited PLD-CdS layer. Annealing treatment further enhanced crystallinity, and obviously enlarged the grain size. Optical transmittance spectra showed that the band gap of the CdS film increased after annealing. Fermi level of CdS films shifted closer to the conduction band from XPS analysis. CdTe solar cells with annealed windows obtained further improved performance, including higher short-circuit current, open-circuit voltage and energy conversion efficiency.

Key words: CdS, pulsed laser deposition, annealing, thin film, solar cell

Introduction

With a direct band gap of 1.46 eV and high absorption coefficient ($>10^5 \text{ cm}^{-1}$), CdTe is a promising semiconductor material for high-performance thin film solar cell [1]. The highest energy conversion efficiency of CdTe solar cell is predicted to be 28% [2]. N-type CdS is commonly utilized as window layer for p-type CdTe solar cell due to its wide band gap ($\sim 2.4 \text{ eV}$) [3, 4]. Generally, CdS polycrystalline thin film is deposited using chemical bath deposition (CBD) [5-8]. However, the CBD method

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has several disadvantages. For example, the deposition process is very slow, and it produces considerable liquid waste that needs to be recycled [9]. In this paper, we attempt to prepare CdS polycrystalline thin film using pulsed laser deposition (PLD).

PLD is a physical vapor deposition technique which has been widely developed in recent years. During the PLD process, a pulsed laser beam is focused to strike the target of a specific material, and the material is vaporized from the target (in a plasma plume) and deposited as thin film on a substrate. PLD technique has numbers of advantages. It doesn't generate waste by-product, compared to the CBD method. Another advantage of PLD for the growth of thin films is an extremely smooth film surface compared to films grown by close-space sublimation (CSS) and RF magnetron sputtering. In addition, the relatively higher kinetic energy of atoms in PLD generated plasma plume renders them higher mobility on substrate surface, enabling lateral growth at relatively lower substrate temperatures than other physical vapor deposition methods [10]. Also, the film thickness can be controlled to a single atomic layer by fine adjusting the pulse number. Those unique merits make PLD suitable for the deposition of various high-quality thin films [11]. However, PLD technique has rarely been reported on the preparation of CdS films. So we first investigated the influence of different deposition temperatures on the physical properties of PLD-CdS thin films, since the optical and structural properties of the thin films prepared by PLD have a strong correlation to the deposition temperature [12].

However, the as-deposited CdS polycrystalline thin films prepared by PLD were composed of nano-scaled grains, which severely affect the performance of CdS/CdTe solar cells [13]. A post anneal process in CdCl₂ was then applied to improve the crystalline quality through a recrystallization process. In fact, improved physical properties of CBD-CdS films were reported previously after the CdCl₂ annealing [13, 14]. A similar trend was observed on PLD-CdS films, and the annealed CdS film has a much lower density of defects, better crystalline and larger grain size. In this paper, we have studied the influence of annealing treatment on the properties of PLD-CdS films and the performances of CdTe solar cells with annealed CdS windows.

Experiment

CdS thin films were deposited in a vacuum chamber using 248 nm KrF excimer laser (Lambda Physic COMPEX201). A CdS target (purity 99.99%) was mounted on a rotating target stage. The substrates were 50mm×30mm commercial fluorine-doped tin oxide (FTO) glass.

Four CdS thin film samples were fabricated at room temperature, 200°C, 300°C and 400°C, respectively. The vacuum chamber pressure was maintained $\sim 10^{-6}$ Torr during the entire deposition process. The laser pulse energy and repetition rate were 90 mJ and 6 Hz, respectively. The thickness of these four samples was all 100 nm. X-ray diffraction (XRD) patterns were recorded with Dandong Fangyuan DX-2600 diffractometer using CuK α radiation and optical transmittance spectra were measured

using an UV/Vis spectrophotometer (Perkin Elmer-Lambda 950).

CdTe solar cells based on these four PLD-CdS layers were then fabricated by the following process. First the CdTe layers were prepared onto CdS window layers by close-space sublimation (CSS) under the mixture gases of Ar and O₂ at 500-600°C. During this process, the pressure (Ar+O₂) was maintained at 3kPa. About 2μm-thick CdTe polycrystalline layer was deposited. Then these four samples were annealed in CdCl₂ atmosphere at 385°C for 30 minutes and subsequently etched in bromine-methanol solution. The cells were completed with the evaporated Cu-doped ZnTe back contact layer and Au electrodes before characterization of the solar cell performance.

In addition, PLD-CdS thin films prepared at 200°C and 400°C were annealed with CdCl₂ to extract the effects of the CdCl₂ annealing on the physical properties of the window layer before deposition of the CdTe absorber layer. CdCl₂ was ultrasonic-sprayed onto the surface of CdS layer initially. Then CdS layer was annealed in a tube furnace at 400°C for 30 minutes with a flow of 20 sccm N₂ and 20 sccm O₂. The annealed CdS film samples were characterized by XRD, optical transmittance spectra, SEM and XPS. CdTe solar cells were then prepared on the annealed CdS window layer, followed with characterization of their current density-voltage (J-V) curves.

Results and Discussion

1. Effects of deposition temperature

The XRD spectra of four window layer samples made at different temperatures were depicted in Fig.1 together with that for FTO for comparison. All the CdS layers are in the hexagonal phase, which is desirable for the window layer of high efficiency CdS/CdTe solar cells. On CdS samples deposited at room temperature (red curve) and 200°C (blue curve), the three peaks located at 26.5°, 43.6° and 47.7° are respectively associated with the (002), (110), and (103) planes, and the others belong to the FTO substrate. When the temperature increases to 300°C (green curve) and 400°C (purple curve), the (110) peak is disappeared. Also, as the deposition temperature rises, the diffraction peaks become more intense and sharper, indicates better crystallinity in the CdS film. In addition, the volume portion of the (002) phase is much higher with the CdS growth temperature since the (002) peak intensity increases much more than other XRD peaks at higher deposition temperature.

Fig. 1 X-ray diffraction pattern of PLD-CdS films prepared at various temperatures together with the spectrum of FTO.

Fig. 2 shows the optical transmittance spectra of these four CdS samples which have the same thickness of 100 nm. The transmittance of CdS deposited at room temperature is poor ($\sim 60\%$) within the visible range. With increasing deposition temperature, the optical transmittance increases considerably, which is accompanied by the blue shift of the absorption edge, indicative of widened band gap. Among these four samples, the CdS prepared at 400°C hence has the best optical property as the window layer for a solar cell.

Fig. 2 Optical transmittance spectra of PLD-CdS films prepared at various temperatures

The performance of the CdTe solar cells was tested using a Solar Cell Tester (Gsolar XJCM-9) under AM1.5. Fig. 3 shows the box charts comparing the results of energy conversion efficiency, fill factor (FF), short-circuit current (J_{SC}) and

open-circuit voltage (V_{OC}) obtained from 15-20 dot cells of the four CdTe cell samples. Fig.4 provides the J-V curves of the dot cell with the best performance of each sample, and the associated performance parameters are summarized in Table 1. The overall performance of the CdTe solar cells with CdS layer prepared at 200°C is the best among these four samples, and the best dot of this sample obtains the highest Energy Conversion Efficiency (10.07%), as well as the highest short-circuit current J_{SC} (26.17mA/cm²). However, contrary to the best optical performance achieved on the CdS sample deposited at 400°C, the average efficiency of the CdTe solar cell with this window is the poorest among these four samples, mainly resulted from its lowest fill factor (FF). Since the same CdTe fabrication process and post annealing treatment on CdTe were applied to these four samples, we speculate the lowest FF is caused by a great deal of defects exist in the 400°C-prepared CdS layer. The atoms the plasma plume brings to the substrate from the target have relatively higher kinetic energy, leading to the high mobility on the surface. Thus the crystallization and growth of CdS film merely need relatively low temperature. However, when the substrate temperature rises, CdS grains are prone to agglomerate (can be observed in the SEM image, Fig. 9c), which damages crystalline structure and generates a large number of defects as a consequence. Those defects increase the recombination of photon-generated carriers and retard the migration of carriers, deteriorating the short-circuit current (J_{SC}) and the fill factor (FF) of the device.

Fig. 3 Box charts of main photovoltaic parameters obtained from 15-20 dot cells of the four CdTe cell samples with PLD-CdS window layer prepared at various temperatures

Fig. 4 J-V curves of the best dot cell on the four samples with PLD-CdS window layer prepared at various temperatures

Table 1 main performance parameters of the best dot cell on the four samples with PLD-CdS window layer prepared at various temperatures

Sample	Efficiency(%)	FF	V _{OC} (mV)	J _{SC} (mA/cm ²)
RT	9.06	0.57	683.66	23.24
200°C	10.07	0.60	739.74	26.17
300°C	9.58	0.55	706.81	24.65
400°C	8.09	0.52	654.91	23.55

Fig. 5 Quantum efficiency of the best dot cell on the four samples with PLD-CdS window layer prepared at various temperatures

The external quantum efficiency (QE) was evaluated by QE/SR Measurement System (PV Measurements QEX-10) and the results on the best dot cells of four samples shown in Fig. 4 are depicted in Fig. 5. The QE of all these four cells is about the same at $\sim 76\%$ between 500 nm-800 nm. Interestingly, the CdTe cell with

200°C-deposited CdS window layer shows relatively higher QE values between 300-500nm. Thus it can be speculated that it is the best short-wavelength spectral response that contributes to its highest J_{SC} among these four solar cell samples.

From the above discussion, it can be seen that the deposition temperature does have a great impact on pulsed laser deposited CdS films in terms of the crystallinity and optical transmittance. However, the observation of a better performance in the CdTe solar cell with the 200°C-deposited CdS window rather than the one with 400°C-deposited CdS window suggests other factors may be also important in consideration of the CdS/CdTe solar cell in device form, such as various recombination losses of photon-generated carriers in the carrier transportation process and the density of defects within the solar cell, which need further in-deep study.

2. Effects of $CdCl_2$ annealing treatment

Fig. 6 X-ray diffraction pattern of annealed and as-deposited PLD-CdS films prepared at 200°C and 400°C respectively

Fig. 6 shows the XRD patterns of $CdCl_2$ annealed and as-deposited PLD-CdS films deposited at 200°C and 400°C respectively. After the $CdCl_2$ annealing treatment of the CdS polycrystalline films prepared at either 200°C or 400°C, the hexagonal crystalline phase persisted. However, the original (110) peak of the as-deposited CdS film prepared at 200°C disappeared after the annealing, implying a better crystallographic orientation is acquired. This argument seems consistent with the more intensified (002) diffraction peaks of annealed samples, which became much sharper than that of the as-deposited CdS. These results clearly indicate that $CdCl_2$ annealing treatment leads to better crystallinity in the pulsed laser deposited CdS polycrystalline thin films.

Fig. 7 Optical transmittance spectra of both annealed and as-deposited PLD-CdS films prepared at 200°C and 400°C respectively.

Fig. 8 re-plotted $(\alpha h\nu)^2$ - $h\nu$ curves of both annealed and as-deposited PLD-CdS films prepared at 200°C and 400°C respectively

The transmittance spectra of annealed CdS samples are compared with that taken on their as-deposited counterpart in Fig. 7. A major effect of the annealing is the blue shift of the absorption edge. Since the location of absorption edge is mainly determined by the band gap (E_g), this result clearly shows that the band gap of CdS changes after CdCl_2 annealing treatment.

As CdS is direct band gap semiconductor, the band gap can be estimated by the Tauc formula [15]:

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$

Where α is absorption coefficient which can be figured out from the formula $\alpha = -(\ln T)/d$, $h\nu$ is the incident photon energy. According to the re-plotted $(\alpha h\nu)^2 - h\nu$ curves (Fig. 8), the band gap of annealed CdS samples prepared at 200°C and 400°C were both increased to 2.44 eV. Besides, the absorption edges of the annealed CdS films become sharper than that of the as-deposited films. This indicates fewer defect and impurity energy levels in the annealed PLD-CdS films [16].

Fig. 9 SEM images of both annealed and as-deposited PLD-CdS films prepared at 200°C and 400°C respectively. (a) 200°C-deposited; (b) 200°C-deposited, followed with the CdCl₂ annealing; (c) 400°C-deposited and (d) 400°C-deposited, followed with CdCl₂ annealing.

Fig. 9 shows surface morphology images measured using a HITACHI S4800 Scanning Electron Microscope (SEM). The grain size of the as-deposited PLD-CdS films prepared at both 200°C and 400°C is only several nanometers, rendering CdS grains difficult to be recognized from the SEM image (Fig. 9a and Fig. 9c). Also it can be observed that parts of CdS grains are agglomerate (white dots on the surface) in the as-deposited samples prepared at both 200°C and 400°C, but much more severely in the latter sample. However, after the CdCl₂ annealing treatment, CdS grains grew drastically as shown in Fig. 9b and Fig. 9d. For the 200°C-deposited CdS sample, the grain size increased to 50-100nm after CdCl₂ annealing based on the SEM image; and for the 400°C-deposited CdS sample, the grain size reached even over 100nm in the lateral direction. The growth of the CdS grain indicates the reduction of grain boundary, which acts as a recombination interface for electrons and holes. Thus the annealing treatment of PLD-CdS window layer could help reduce the recombination loss of photon-generated carriers and improve the short-circuit current consequently.

Fig. 10 (a) XPS spectra and (b) Cd 3d core levels of CdCl_2 annealed and as-deposited PLD-CdS films prepared at 200°C and 400°C respectively

X-ray photoelectron spectra (XPS) were measured using the Kratos AXIS Ultra DLD, and survey scan spectra were shown in Fig. 10a. From survey scan spectra, all films are confirmed to be composed of Cd and S atoms. The C 1s peak is utilized for calibration of XPS spectra, which is supposed to be originated from the CO_2 molecule absorbed on the surface of CdS, since all CdS samples were exposed to air for extended periods before XPS measurement.

The core level spectra of Cd 3d are shown in Fig. 10b. After annealing, the core levels of CdS shifted to higher binding energies. The variation of the binding energies indicates that the Fermi level becomes closer to the conduction band. The move of Fermi level is most probably resulted from a higher n-doping in PLD-CdS layer after the CdCl_2 treatment. Such a Fermi level shift might cause a higher band bending at the CdS/CdTe interface and consequently higher built-in potential in the CdTe film. In addition, higher n-doping of the window layer can extend the depletion width in the CdTe layer and increase the photoelectrons collection, which is beneficial to the performance of solar cells. This observation is important considering CdCl_2 annealing is applied typically after CdTe absorption layer is deposited on CdS window layer, which may prevent optimal doping of the CdS layer.

Fig. 11 Box charts of main photovoltaic parameters obtained from 15-20 dot cells of the four CdTe cell samples with CdCl₂ annealed and as-deposited PLD-CdS window layers

Fig. 12 J-V curves of the best dot cell on the four samples with CdCl₂ annealed and as-deposited PLD-CdS window layers prepared at 200°C and 400°C respectively

Table 2 main performance parameters of the best dot cell on the four samples with CdCl₂ annealed and as-deposited PLD-CdS window layers prepared at 200°C and 400°C respectively

Sample		Efficiency(%)	FF	V _{OC} (mV)	J _{SC} (mA/cm ²)
CdS deposited at 200°C	As-deposited	10.07	0.60	739.74	26.17
	Annealed	12.63	0.64	747.31	26.38
CdS deposited at 400°C	As-deposited	8.09	0.52	654.91	23.55
	Annealed	11.21	0.59	695.81	27.14

Fig. 11 shows the box chart of the main photovoltaic parameters comparison of CdTe dot cells with CdCl₂ annealed and as-deposited CdS windows (based on 15-20 dots). It is obvious that the average performance of CdTe solar cells with annealed PLD-CdS window layer is enhanced significantly. Fig. 12 shows the J-V curve of the best dots on these four samples. Table 2 compares the major parameters of the best solar cells made with as-deposited and CdCl₂ annealed PLD-CdS windows. The best dot cell with CdCl₂ annealed window layer deposited at 200°C has improved energy conversion efficiency (12.63%), as compared to its as-deposited counterparts (10.07%), due to higher J_{SC} and V_{OC}. For the best dot cell with annealed window layer deposited at 400°C, the improvement of the overall performances is more significant. The energy conversion efficiency is increased from 8.09% to 11.21%, by almost 40%. J_{SC} was increased from 23.55mA/cm² to 27.14mA/cm², and the main reason is that the recrystallization of CdS film after CdCl₂ annealing leads to the improved crystalline quality, as well as reduced grain boundaries and exhausting of defects in the lattice, thus effectively reduce the photon-generated carrier recombination. V_{OC} increased from 654.91mV to 695.8mV, due to the enhancement of built-in potential resulted from Fermi level shift as a consequence of CdCl₂ n-doping. Also, fill factor (FF) of CdTe cell with annealed PLD-CdS window becomes much better, which is another key to high energy conversion efficiency.

These results clearly prove CdCl₂ annealing treatment on the pulsed laser deposited CdS layer does really work on the promotion of the performance of CdTe solar cell, which conforms to our anticipation. However, the energy conversion efficiency of CdTe solar cell with 200°C-deposited and annealed CdS window is still better than that of the one with 400°C-deposited and annealed CdS window. The difference was mainly originated from the relatively lower V_{OC} and fill factor of the latter cell, which may possibly be resulted from excessive carrier recombination in the in the depletion region [17].

Conclusion

In summary, this work explores optimization of the CdS layer fabricated using PLD for CdS/CdTe solar cells applications. Specifically, the effect of PLD growth temperature in the range of room temperature to 400 °C and the post CdCl₂ annealing has been investigated on CdS films as well as the CdS/CdTe solar cells. We have found the PLD growth temperature has a profound effect on the crystallinity and transmittance of the CdS films with a monotonic improvement with increasing temperature. Interestingly, the best solar cell performance was obtained with CdS

window made at 200°C, which is primarily attributed to the cells higher quantum efficiency in 300-500 nm, despite the best optical transmittance in the CdS film prepared at 400°C. An additional post CdCl₂ annealing treatment on the PLD-CdS film prepared at 200°C and 400°C revealed further improvement on CdS films via promoted grain growth and n-type charge doping, both are beneficial to the solar cell performance as manifested in enhanced energy conversion efficiency up to 12.63%. This result is important towards understanding the role of the PLD-CdS window layer and reveals considerable rooms for further improvement of the CdTe thin film solar cells.

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Graphical Abstract

1.Effects of deposition temperature

2.Effects of CdCl2 annealing treatment