Preparation and Characterization of Pulsed Laser Deposited a Novel CdS/CdSe

Composite Window Layer for CdTe Thin Film Solar Cell

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Abstract: A novel CdS/CdSe composite window structure was designed and then the corresponding films were prepared by pulsed laser deposition as an improved window layer for CdTe-based solar cells. Two types of this composite window structure with 5 cycles and 10 cycles CdS/CdSe respectively both combined with CdS layers were prepared at 200°C compared with pure CdS window layer and finally were applied into CdTe thin film solar cells. The cross section and surface morphology of the two composite window layers were monitored by using scanning electron microscopy and the result shows that the pulsed laser deposited composite window layers with good crystallinity are stacking together as the design. The devices based on CdS/CdSe composite window layers have demonstrated the enhanced photocurrent collection from both short and long wavelength regions compared to CdS/CdTe solar cell. The efficiency of the best reference CdS/CdTe solar cell was 10.72%. And the device with 5 cycles CdS/CdSe composite window showed efficiency of 12.61% with V_{OC} of 772.92 mV, J_{SC} of 25.11 mA/cm² and FF of 64.95%. In addition, there are some differences which exist within the optical transmittance spectra and QE curves between the two CdS/CdSe composite window samples, indicating that the volume proportion of CdSe may influence the performance of CdTe thin film solar cell.

Key words: CdS/CdSe; window layer; cycles; pulsed laser deposition; solar cell;

1.Introduction

Cadmium telluride (CdTe), with its direct band gap of ~ 1.5 eV which matches pretty well with the solar spectrum and high optical absorption coefficients ($>10^5 \text{ cm}^{-1}$), is considered one of the most promising thin film solar cell materials dated back to 1950s [1]. The theoretical conversion efficiency of CdTe polycrystalline thin-film solar cell is as high as 28% [2]. The n-type CdS window layers are widely applied to form hetero-junctions with p-type CdTe in high efficiency solar cells [3]. However, when the sunlight passes through the CdS window layer, the photons in short-wavelength regions ($<510 \text{ nm}$, defined by its band gap of $\sim 2.42 \text{ eV}$) will be mostly absorbed by CdS layer due to its high absorption coefficient and the carriers generated by those short wavelength photons in the window layer are far away from the depletion region and recombine quickly in the window layer [4]. Thus, these carriers have no contribution to the photocurrent. Besides, inter-diffusion occurs at CdS/CdTe interfaces during CdTe depositions and then CdCl_2 annealing treatments will result in forming $\text{CdS}_{1-x}\text{Te}_x$ in window layer and $\text{CdTe}_{1-y}\text{S}_y$ in absorber layers while photons absorbed by $\text{CdS}_{1-x}\text{Te}_x$ will not generate any photocurrent due to its high defect and photo inactivation [5]. One way to solve those problem is to reduce the thickness of CdS layer directly. CdSe, with its direct band gap of ~ 1.7 eV, has less size mismatch with CdTe than CdS which can improve the solubility of Se in CdTe [6,7]. The $\text{CdTe}_{1-y}\text{Se}_y$ usually shows a narrower band gap than that of CdTe due to the bowing effects [8]. Therefore, alloying of the CdTe absorber with Se during preparation process can enhance photocurrent collection in the long wavelength region ($>960 \text{ nm}$).

Multilayer structure attracts much attention recently, since the optical properties can be enhanced and charge transfer characteristics in the surface and interface regions of hetero-structure can also be improved [9]. Therefore, we designed a novel composite window structure for CdTe thin film solar cells. Two types of this composite window structure include 5 cycles and 10 cycles CdS/CdSe, and the sub-layer thickness of CdS and CdSe are 2nm and 4nm respectively. In the composite window, CdS and CdSe are stacking together layer by layer alternately, combined with CdS layers and one function of this combined CdS layer is to prevent the formation of a $\text{SnO}_2/\text{CdTe}_{1-y}\text{Se}_y$ interface, which can improve the p-n junction and, therefore, shunt resistance of the CdTe-based solar cells [10]. Moreover, CdS/CdSe multilayer actually forms a super-lattice structure. According to the value of energy bands of these two semiconductors [11], the energy band structure of CdS/CdSe super-lattice was represented in the schematic diagram (shown in fig.1). In the super-lattice structure, CdS is the barrier, while CdSe is the well. The ultrathin CdS barrier in each cycle leads to the formation of sub-bands in the conduction and valence bands, enabling electrons and holes to tunnel through the entire barriers (CdS). Therefore, applying this novel composite window in CdTe thin film solar cell will promote charge transfer, resulting in higher J_{SC} and better quantum efficiency of the solar cell.

Pulsed laser deposition (PLD) has been proved to be an excellent technique to deposit high-quality thin films of II–VI compound semiconductors [12]. Thin films with complex chemical constituents can be congruently ablated then we can obtain stoichiometric films with properties comparable to those prepared by molecular beam epitaxy (MBE) technology [13]. Furthermore, the thickness of pulsed laser deposited film can be fine adjust even to a single atomic layer, thus, it is easy for PLD to deposit multilayer with thin thickness on the order of a few nanometers [14]. In this work, two types of

CdS/CdSe composite window layer were prepared by PLD. CdTe solar cells modified with these composite window layers compared with pure CdS window layer were fabricated and the performance of three solar cells are compared and discussed.

Fig.1 The energy band structure and deposition sequence for the growth of CdS/CdSe super-lattice

2. Experimental details

In this work, A KrF Excimer Laser (Lambda Physik Compex 201, $\lambda = 248$ nm, pulse duration = 20 ns) was used to ablate the CdS and CdSe targets alternately inside the vacuum chamber which is maintained at $\sim 10^{-5}$ torr by using a molecular pump together with a mechanical pump. The substrates were 25 mm $\times$ 60 mm commercial FTO (surface conductivity is $20 \Omega/\text{cm}^2$) glass. As shown in fig. 2, the angle of incident laser beam was $\sim 30^\circ$ from the surface normal. The incident laser pulse energy and repetition rate for films deposited on FTO substrate was fixed at 90mJ and 6Hz respectively. The distance between the target and the substrate holder inside the vacuum chamber was ~ 7 cm. The laser beam was focused on the target rotating at 4 rpm. There was a resistive type heater to heat the substrate temperature to reach the set value. Before deposition, the CdS and CdSe targets (purity 99.99 at. %) was irradiated by pulsed laser for ~ 30 s to remove the oxides and contaminations. During this process, there was no other reactive gas in the vacuum chamber.

Fig.2 The diagram of KrF-PLD

Fig.3 Schematic illustration of the three window layer on FTO glass: (a) pure CdS window layer (A-1), (b) and (c) composite window layers containing 5 cycles(A-2) and 10 cycles(A-3) of CdS (2nm)/CdSe (4 nm), respectively

Fig.3 displays the schematic illustration of three window layers prepared in this work. Sample A-1 is the pure CdS window layer. Sample A-2 and sample A-3 are composite window layers containing 5 cycles and 10 cycles CdS/CdSe respectively combined with CdS layers, and have the total thickness of 70 nm which is same with the sample A-1. CdS and CdSe layers are alternately deposited on FTO substrate by PLD at a low growth temperature (200°C). Fig.1 also shows the film deposition sequence for the growth of (CdS/CdSe)₅ multilayer.

Scanning electron microscopy (SEM) (Hitachi S-4800) was used to monitor the cross section and surface morphology of the three window layers. The crystal structure of those window layers was

investigated by using X-ray diffraction (XRD) (DanDong HaoYuan DX-2700) with Cu K α of 1.54 Å wavelength and an incident X-ray beam angle of 1.5° with the sample. The three window layers were characterized for optical transmittance by UV/Vis spectrophotometer (PerkinElmer Lambda 950), within the spectral range of 300~1000 nm. The above characterizations were done at room temperature.

Based on the above study, CdTe thin film solar cells modified with these composite window layers compared with pure CdS window layer were then manufactured by the following process. After three window layers were prepared by PLD, the CdTe layers were deposited on those different window layers by close-space sublimation (CSS) under the reactive gases of Ar and O₂ maintained at 3kPa. During deposition, the substrate temperature and the source temperature were set at 540°C and 620°C respectively. The thickness of CdTe polycrystalline layer was about 6μm for 3 min deposition. Then three samples were annealed in CdCl₂ atmosphere at 382°C for 35 min and subsequently etched in bromine-methanol solution to remove the oxides and contaminations. The co-evaporated Cu-doped ZnTe back contact layer and Au electrodes were used to complete those cells. The completed solar cells were characterized by current density–voltage (J – V) measurements under an AM 1.5 illumination and external quantum efficiency (EQE) both at room temperature.

3. Results and discussion

3.1 Scanning electron microscopy (SEM) of window layers

Fig.4 (a) SEM cross-sectional view and (c) SEM surface morphology view of the composite window layer with 5 cycles CdS/CdSe(sampleA-2); (b) SEM cross-sectional view and (d) SEM surface morphology view of the composite window layer with 10 cycles CdS/CdSe (sample A-3)

The cross-sectional views and surface morphology views of the composite window layers were monitored by using scanning electron microscopy (SEM) (Hitachi S-4800). Fig. 4(a) and (b) show cross-sectional views of these two composite window layers. It is observed that CdSe and CdS layers are stacking together. The total thickness for 5 cycles of CdS/CdSe layers is about 30nm which can be recognized in the fig.4(a), and about 60 nm for 10 cycles of CdS/CdSe layers in the fig.4(b) which correspond to our original design. The results indicate that the thickness of pulsed laser deposited film can be fine control, makes PLD technology suitable for the preparation of multilayer with thin thickness.

The surface morphology views of two composite window layers are shown in fig.4(c) and (d). The upper layer of these two samples is CdSe. It can be observed that the grains size is uniformly distributed on the surface of the two samples. Besides, no pinholes and cracks among grains can be seen from the SEM images, thus the two samples present continuous and compact surface, which will benefit the performance of the solar cells.

3.2 X-Ray diffraction pattern of window layers

Fig.5 X-ray diffraction patterns of pure CdS window layer and composite window layers (together with the spectrum of FTO)

The crystal structure of the three window layers together with that of FTO was investigated by using X-ray diffraction (XRD) (DanDong HaoYuan DX-2700). As shown in fig.5, we can observe that the relatively higher and narrower peaks which are related to tetragonal SnO_2 of FTO glass: (200) and (211) located at 37.74° and 51.42° , respectively. The (002) peaks labeled in the figure is from CdS with the hexagonal structure. The (002) peak of hexagonal CdS is relatively strong besides the overlapping of SnO_2 (110) peak, revealing that pulsed laser deposited CdS thin film with fine crystallinity oriented growth in the (002) direction. However, the intensity of (002) peak is slightly weakened as the volume

proportion of CdS is decreased. Besides, it is difficult to distinguished the peaks of CdSe from noise peaks maybe due to the sub-layer thickness of CdSe is only 4 nm thick, leading to poor crystallinity along with relatively low intensity of the peaks, thus those peaks are hardly recognized from the XRD spectra. However, it can be confirmed that the existence of CdSe layers in the composite window layers from the SEM cross-sectional views.

3.3 Optical transmittance of window layers

Fig.6 Transmittance spectra of pure CdS window layer and CdS/CdSe composite window layers

The optical properties of three samples were studied by analyzing the spectroscopic optical transmittance using UV/Vis spectrophotometer (PerkinElmer Lambda 950). Fig.6 shows the optical transmittance spectra of these three window layers which have the same total thickness of 70 nm and deposited on FTO at 200°C. Apart from overlying FTO's absorption, the pure CdS window layer exhibits a typical absorption edge located in the range of 480–580 nm which is defined by its band gap $E_g \sim 2.4$ eV. Compared with pure CdS window layer, the absorption edges of two CdS/CdSe composite window layers show a red-shift due to the narrower band gap of 1.7 eV for CdSe; the transmittance of the composite window layers is a little poor within the visible range due to the higher absorption

coefficient ($>10^5\text{cm}^{-1}$) of the CdSe than CdS, and those additional photons absorbed by composite window layers can contribute to photocurrent. It is obvious that the optical transmittance curves of the two composite window layers are different since the volume proportion of CdSe is the key distinction between the two composite window layers, thus, the volume proportion of CdSe in the composite window layers influences the optical transmittance behavior.

3.4 Energy conversion efficiency

Fig. 7 J-V curves of solar cells with pure CdS window layer and CdS/CdSe composite window layers

Table 1 Main performance parameters of CdTe solar cells with pure CdS window layer and CdS/CdSe composite window layers

Window layer	Efficiency %	Voc [mV]	Jsc [mA/cm ²]	FF%
CdS	10.72	707.72	24.10	62.84
CdS/(CdS/CdSe) ₅	12.61	772.92	25.11	64.95
CdS/(CdS/CdSe) ₁₀	11.47	746.56	25.20	61.18

The photovoltaic properties of the completed CdTe solar cells was tested by using a Solar Cell Tester (Gsolar XJCM-9) under AM1.5illumination. Fig. 7 shows the $J-V$ curves of CdTe cells with pure CdS window layer and CdS/CdSe composite window layers. Table 1 summarizes the main performance parameters of CdTe solar cells with those three different window layers.

The CdTe solar cell with pure CdS window layer obtains the energy conversion efficiency of 10.72 %, with short circuit current (J_{SC}) of 24.10 mA/cm² and open circuit voltage (V_{OC}) of 707.72 mV. The performance of CdTe solar cells with the two composite window layers is improved obviously especially in V_{OC} , which maybe caused by the higher solubility of Se in CdTe improving the p-n junction properties. It is noticed that the J_{SC} in the solar cell with CdS/CdSe layers is better than that in the solar cell with CdS layer; the solar cell modified with composite window layer containing 5 cycles CdS/CdSe layers obtains the best energy conversion efficiency of 12.61% and a J_{SC} of 25.11 mA/cm², higher than that in the CdS/CdTe solar cell maybe due to the CdS/CdSe composite window structure which can enhance the transportation of photon-generated carriers and reduce recombination in the carrier transportation process.

3.5 Quantum efficiency

Fig.8 Quantum efficiency of solar cells with pure CdS window layer and CdS/CdSe composite window layers

The external quantum efficiency (EQE) of the three solar cells with different window layers are displayed in fig.8. For the two solar cells with composite window layers, the absorption edge in EQE has a large blue shift and the external quantum efficiency increase drastically in the range of 300–500 nm maybe due to the composite window structure which can improve the carrier transportation and collection. With high temperature close-space sublimation (CSS) CdTe deposition followed by the CdCl₂ activation process, Se diffuses into CdTe and forms a CdTe_{1-y}Se_y alloy in absorption layer, resulting in producing an obvious red shift in the absorption edge compared with that in pure CdS window layer cell and leads to an enhanced current collection in the long wavelength region [15].

The EQE of sample A-2 (5 cycles) is better than sample A-3 (10 cycles) in the range of 500–800 nm which deserves our close attention because the J-V measurements show an opposite trend on J_{sc} , indicating that the volume proportion of CdSe should be seriously regarded as a key factor that influences the EQE and J_{sc} of the solar cells. Therefore, the further optimization of the volume proportion of CdSe is deserved to improve the performance of CdTe solar cell.

4 Conclusion

In this study, two novel CdS/CdSe composite window layers containing 5 cycles and 10 cycles CdS/CdSe multilayer respectively were deposited at 200°C by PLD using a KrF excimer laser. The CdTe solar cells were modified with this novel CdS/CdSe composite window layers, resulting in a J_{sc} enhancement in both the short and long wavelength regions. The essential mechanism is that CdS/CdSe superlattice structure leads to the formation of sub-bands in the conduction and valence bands, enabling

electrons and holes to tunnel through the entire barriers (CdS), promoting the carrier transportation and collection, thus improving the blue response obviously. In addition, the CdSe/CdTe interfaces exhibit much stronger inter-diffusion than CdS/CdTe interfaces during the CdTe synthesis process and then CdCl₂ activation process. The inter-diffusion allows alloying of the CdTe absorber with Se and promotes the formation of CdTe_{1-y}Se_y with narrower band gap than CdTe, which can produce a large red shift in the absorption edge. Therefore, realizing higher J_{SC} and better quantum efficiency of the solar cells than CdS/CdTe cells. Meanwhile, there are some obvious differences in the optical transmittance spectra and QE curves between the two CdS/CdSe composite window samples, mainly caused by the different volume proportion of CdSe. Therefore, the further optimization of the volume proportion of CdSe is deserved to improve the performance of CdTe solar cell. Our results suggest a viable structure of the window layer which has positive impacts on the performance of CdTe solar cell.

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