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Deposition Methods and Properties of Polycrystalline CdS Thin Films

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Abstract: CdS thin film was used as a suitable window layer for CdS/CdTe solar cell, and the properties of CdS thin films deposited by pulsed laser deposition (PLD), chemical bath deposition (CBD) and magnetron sputtering (MS) were reported. The experimental results show that the transmittances of PLD-CdS thin films are about 85% and the band gaps are about 2.38-2.42eV. SEM results show that the surface of PLD-CdS thin film is much more compact and uniform. PLD is more suitable to prepare the CdS thin films than CBD and MS. Based on the thorough study, by using totally PLD technique, the FTO/PLD-CdS(150 nm)/CSS-CdTe solar cell (0.0707 cm^2) can be prepared with an efficiency of 10.475% .

Key words: CdS thin film; pulsed laser deposition; solar cells

1 Introduction

In the last two decades, a large amount of work has been devoted to the study of the cadmium sulfide (CdS) thin films due to their potential applications in solar cell devices, including thin film transistors for flat panel display, sensors and other optoelectronic device[1]. CdS thin film is often used as window layer in hetero-junction solar cells based on CdTe, due to its band gap (E_g=2.42 eV) and low-cost fabrication process[2].

CdS has been used as hetero-junction partner in the fabrication of CdTe solar cell for many years. A variety of physical or chemical methods have been used to prepare CdS thin films, such as chemical bath deposition (CBD), magnetron sputtering (MS), chemical vapor deposition (CVD), *etc*. And the pulsed laser deposition (PLD) method has also been adopted because it has several advantages of the thin film composition even for a multi-component system, and multi-layers thin films of different target compositions[2-6]. Using the PLD method to fabricate CdS is suited for small area solar cells in lab for its lower deposition temperature (T_{su}), little pinholes and even deposition thin film with stoichiometry same to the target. The focused pulsed laser beam produces such a rapid temperature rise (>10^{11} Ks^{-1}) on the target that the stoichiometry of the target is maintained in the growing film[7] and superlattice or multilayer devices can be easily fabricated by PLD because of its flexibility in using multiple targets[8]. Compared with PLD-CdS, CBD-CdS and MS-CdS usually have uncontrolled deposition rate and some more pinholes in its surface. Therefore, pulsed laser deposition (PLD) is a reliable and promising method to grow the CdS thin film.

The process of PLD is affected by many parameters, such as substrate temperature, pressure, laser energy, which have important influences on the growth of the films. And by using the different preparation methods to grow CdS thin films, for example PLD, CBD and MS, the properties are different.

2 Experimental

In the present study, CdS thin films were fabricated by PLD method on the FTO substrates which were cleaned by normal cleaning procedure before deposition. The details of PLD method are introduced

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as shown in Fig.1.

Fig.1 is the diagram of KrF-PLD. The samples were grown by pulsed laser deposition (PLD) standard method. The Kr: F excimer laser with the wavelengh of 248 nm was used for ablation of the CdS target (purity 99.999%). The laser energy and repetition rate were 60 mJ and 10 Hz, respectively. And the chamber was evacuated to 10^{-3} Pa. The target and substrate were placed in the smaller, quasi-closed growth chamber; the substrate-target distance was 3-4 cm. In order to avoid the local overheating to the target, the CdS target needed to bond on a rotating target holder. The substrates which were FTO-coated glass slices with resistance of 15-20 Ω, sustained the temperature at 150 (sample PLD-1) and 200 ℃ (sample PLD-2) during the deposition process.

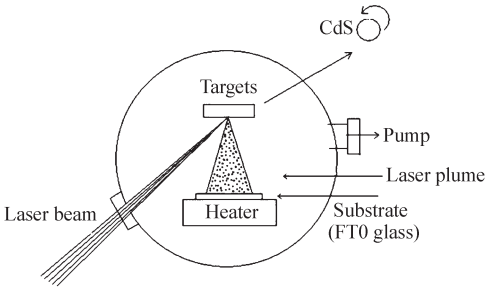

Fig.1 The diagram of KrF-PLD

In addition to the contrast with the PLD samples, the other two CdS thin films were prepared by CBD and MS respectively. The optical properties and morphology of CdS thin films grown by different methods were investigated and compared.

In this work, the three methods (PLD, MS, CBD) were used to prepare CdS thin films (Table 1).

As a contrast, CBD-CdS was prepared at T_{su}=80 ℃ for 50-60 minutes. MS-CdS was prepared at the room temperature for 20 minutes.

The thickness of the films was measured by using a surface profilometer (model No. Ambios XP-2), scanning electron microscopy (SEM) images and transmission spectra were obtained using a scanning electron microscope (HITACHI S-3000 H) and a UV-Vis-NIR double beam spectrophotometer (LAMBDA-35), respectively. The transmission spectroscopy was recorded in the range of 300-800 nm. All the measurements were carried out at room temperature.

3 Results and discussion

3.1 Deposition rate

The dependence of films thickness by different methods and at different substrate temperatures can be found in Table 1. Firstly, as the substrate temperature increases from 150 to 200 ℃, there is a corresponding increase in the film deposition rate from 8n m/min to 9nm/min. This is mainly because the higher T_{su} is, the higher energy the FTO surface particles can gather, which means that the nucleation of the particles is easier to be realized[9]. Table 1 shows that the deposition rate of the CdS thin film via PLD is slower than that of MS technology. The deposition rate of CdS thin film grown by MS technology is influenced by deposition power and atmosphere, and faster than that of CBD which is affected by the rate of chemical reaction[10].

3.2 Optical properties

The optical properties of the CdS films were performed using the transmission and absorption spectra in the wavelength range of 400-800 nm. Fig.2 shows the transmittance data of only the CdS layers already corrected for the glass and FTO absorption deposited by PLD, CBD, and MS, respectively.

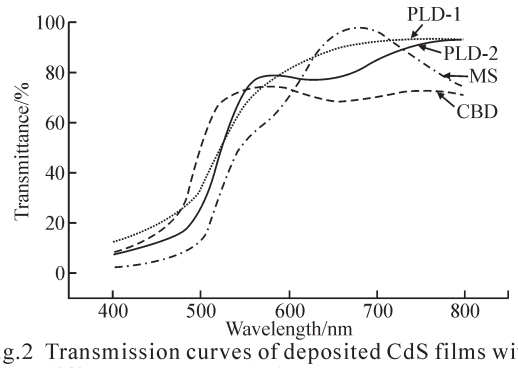

Fig.2 Transmission curves of deposited CdS films with different grown methods

Firstly, all the as-deposited CdS thin films were found to be highly transparent in the visible wavelength region (Fig.2) with an average transmittance of 85%, layers deposited by PLD at 200 ℃ show a sharp decline, whereas the other films have a more gradual decline, which can be attributed to sub-band-gap absorption due to the defect states located in the band gap. The defect states may originate from the bulk or the FTO/CdS interface[11]. Secondly, in comparison

Table 1 Deposition rate of CdS films by different methods and different substrate temperatures (T_{su})

Sample	Layer	Deposition time /min	Deposition temperature, T_{su}	Average thickness/nm	Deposition rate/(nm/min)
PLD-1	CdS	12	150 ℃	98	8
PLD-2	CdS	12	200 ℃	108	9
MS	CdS	20	25 ℃	235	11.025
CBD	CdS	50-60	80 ℃	200	2.5

with the samples PLD-1 and PLD-2, the spectra of the MS-CdS have a slightly Red shift and that of CBD-CdS have a slightly blue shift, which is probably because of the existence of the lattice stress in the samples[12]. Finally, for the samples grown by PLD, with the temperature increased from 150 to 200 ℃, the change is shown clearly in the curves, the CdS thin film deposited at the temperature of 200 ℃ has a well-defined semiconductor band gap than that of the temperature 150 ℃, which can be attributed to the increase of carrier density with the temperature, another reason could be the improving crystallinity with increasing grain size[13].

The optical energy gap Eg was derived assuming a direct transition between the edges of the valence and the conduction bands. Then, the dependence of the absorption coefficient upon the incident photon energy, in semiconductors takes the form below[10]:

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

where, k is a constant related to the effective masses associated with the bands and n is a constant which is equal to one for a direct-gap material and four for an indirect-gap material. As we know, CdS is a direct band gap semiconductor, so the pattern of $(\alpha h\nu)^2$ versus $h\nu$ is depicted in Fig.3.

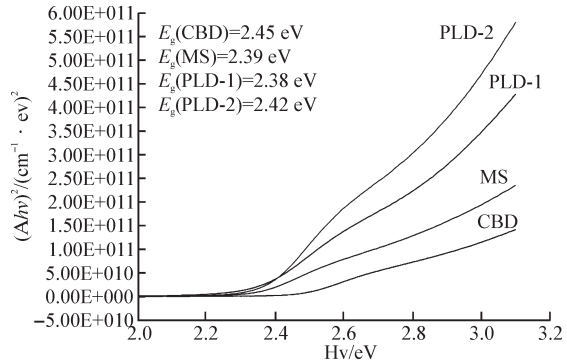

Fig.3 Plots of $(\alpha h\nu)$ *vs* $(h\nu)$ for CdS films with different growth methods

The straight-line portions were extrapolated to the energy axis at α=0, to obtain band gaps of the CdS thin films. First of all, it is seen that the optical band gap of the films slightly increases (from 2.38 to 2.42 eV) with increasing substrate temperature. It is clear from the $(\alpha h\nu)^2$-hν plots that the band gaps of as-deposited CdS thin films by CBD and MS are 2.42 and 2.39 eV, respectively.

3.3 Surface morphology

Scanning electron microscopy (SEM) was used to investigate the surface properties; meanwhile the surface properties directly affect the electrical and optical properties of the films. Fig.4 shows the SEM images of the surface morphologies of the CdS films deposited by PLD at substrate temperatures of 150 and 200 ℃, respectively. And the SEM images of the other two contrast samples are shown in Fig.4.

The morphology of CBD-CdS is shown in Fig.4 (c), with big crystal grain, and the surface is loose and sound. While the MS-CdS (Fig.4 (d)) has smooth surface, and the crystal grains are small. However, the surfaces of PLD-CdS thin films (Figs.4(a), 4(b)) are much more compact and uniform than that of the samples deposition by CBD and MS (Figs.4(c), 4(d)). As can be seen from Figs.4(a) and 4(b), two films are dense and have strong adherence to the substrate. The films are fairly uniform with some fine textures. The texture size is considerably larger at the higher growth temperature, which is not surprising if considering the promoted grain growth at elevated substrate temperature. No obvious pinholes can be observed on CdS films, whose grain size is about 100 nm[10].

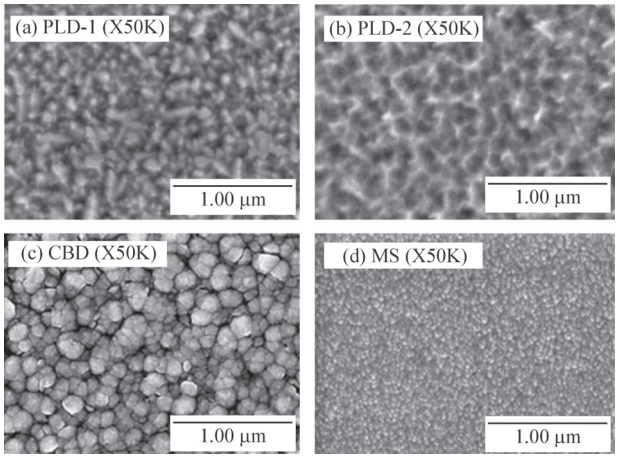

Fig.4 SEM images of the surfaces of CdS films grown by (a) PLD at substrate temperature of 150 ℃; (b) PLD at substrate temperature of 200 ℃; (c) CBD; (d) MS

As is well known, decreasing the thickness of the CdS window layer is one of the important ways to improve the efficiency of CdS/CdTe solar cells[14]. And to sum up, for the CBD-CdS thin film with big crystal grain, loose connection surface, it is difficult to decrease the thickness, and MS-CdS thin film with high growth rate leads to some more pinholes on its surface, so it is unsuitable to be the window layer of CdS/CdTe solar cells. However, PLD-CdS thin films with suitable crystal size, good uniformity, high compactness and strong interfacial adhesion, its thickness can be made as thin as 100 nm in solar cells. Obviously, PLD is a proper method to decrease the thickness of CdS thin films.

3.4 PLD-CdS/CdTe thin films solar cell

Based on the thorough study of CdS deposited by PLD in vacuum condition, relatively low T_{su} (200 ℃)PLD-CdS film was firstly deposited on FTO glass and the chamber pressure was maintained in vacuum ($<10^{-3}$ Pa), and then, The high-efficiency ultra-thin film solar cell was fabricated. Fig.5 shows the structure of FTO/PLD-CdS (150 nm)/CSS-CdTe / graphene/Au

solar cell.

As can be seen in Fig.5, the CdS layer was firstly deposited on FTO glass, then the CdTe layer onto the as-deposited CdS layer.

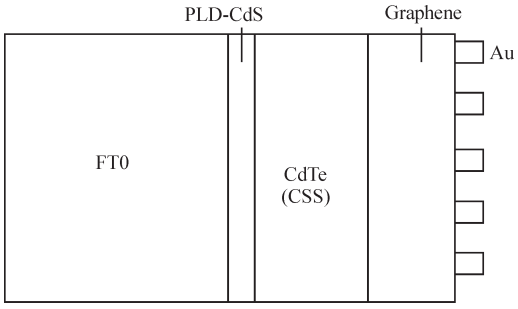

Fig.5 Structure of the thin film cell

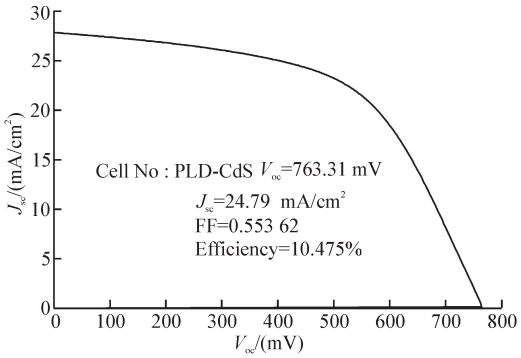

Fig.6 J-V curves for the Ultra-thin PLD-CdS/CdTe cell

The (J-V) measurement for the ultra-thin PLD-CdS/CdTe solar cell is plotted in Fig.6. As can be seen in Fig.6, the cell with an efficiency of 10.475% (V_{oc}=763.31 mV, J_{sc}=24.79 mA/cm^2, FF=0.553 62) has been fabricated.

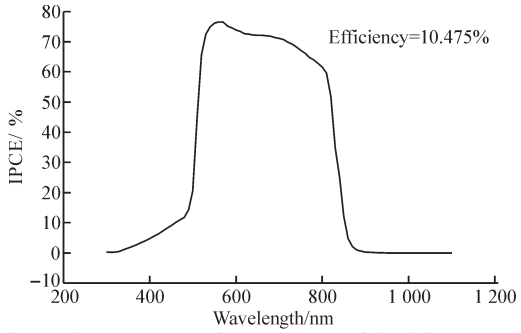

Fig.7 Photocurrent action spectrum of the thin PLD-CdS/CdTe cell

In addition, the solar cell performance has evaluated by recording the incident photon-to-charge carrier conversion efficiency (IPCE) at different incident wavelengths as shown in Fig.7 with an IPCE maximum of about 77% at 567 nm.

4 Conclusions

CdS thin films were deposited by CBD, MS, and at different substrate temperatures by PLD. The dependences of the properties of the films on the substrate temperature and on the grown method were investigated. As the substrate temperature increased, a sharp decline and a more fine texture for the as-deposited CdS films were observed. So the layers deposited by PLD at the temperature of 200 ℃ are more suitable for the ultra-thin films application. Comparing with the CdS thin films grown by CBD and MS, the films deposited by PLD methods have sharp decline are more compact and uniform. And at the same time, the efficiency of PLD-CdS/CdTe solar cell up to 10.475% was firstly demonstrated. Therefore PLD is a better method to decrease the CdS thickness.

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