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Optimized chemical bath deposited CdS layers for the improvement of CdTe solar cells

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ABSTRACT

CdS layers grown by chemical bath deposition (CBD) are treated in different ways to improve the performance of CdS/CdTe solar cells. It has been found that the open circuit voltage of the CdS/CdTe solar cell increases when the CBD CdS is annealed with $CdCl_2$ before the deposition of CdTe by close spaced sublimation (CSS). A thin CBD CdS (~80 nm) with bi-layer structure can significantly improve the short circuit current of the CdS/CdTe solar cells.

1. Introduction

CdS is one of the group II–VI compound semiconductors with a direct optical band gap of 2.4 eV, used as a suitable window layer for CdTe based photovoltaic devices. The CdS/CdTe contact is the energy converting interface in the CdTe solar cell. Due to large lattice mismatch at the CdS/CdTe interface, good solar cells are obtained by controlling inter-diffusion of S and Te [1,2].

Chemical bath deposition (CBD) is a popular way to deposit CdS films [3]. 16.5% efficiency of CdS/CdTe solar cell was made by NREL using CBD CdS [4]. However, CBD CdS films tend to form the cubic phase, and thus show poor crystalline quality, which makes an annealing treatment necessary in order to improve the optical and electronic properties. Annealing of the CBD CdS films in $CdCl_2$ atmosphere has been certified as an effective method [5]. After the $CdCl_2$ treatment, these films recrystallize into the hexagonal phase, resulting in better crystalline quality and a lower density of defects [6]. Such treatment can also enhance n-type doping of the CdS films. High n-doping of the CdS layer should result in a higher built-in potential in the CdTe film and consequently lead to a higher photovoltage [7]. Less severe $CdCl_2$ treatments have also been effective in limiting the subsequent CdTe–CdS inter-diffusion [8].

The performance of CdTe solar cells is strongly limited by the thickness of CdS. Though higher short circuit current can be achieved by reducing the CdS thickness directly, open circuit voltage and fill factor can suffer from pinholes and leakage along grain boundaries. Ideally, the CdS films should be thin enough to allow high transmission and uniform to avoid short circuit effects [9]. This requirement can be obtained from the bi-layer CBD CdS [10]. The second layer is composed of small grains and is expected to fill the pinholes. The bi-layer CdS film is more compact and uniform than a single CBD CdS layer.

In this work, CdS films were prepared by a standard CBD method and $CdCl_2$ annealed under ultrahigh vacuum (UHV) conditions. Chemical, electronic, morphological and optical properties were investigated using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), atomic force microscopy (AFM) and UV–vis spectroscopy. Bi-layer CBD CdS films were prepared as a further improvement in the window layer. The total thickness of the bi-layer CdS is about 80 nm. All CdS films were finished into solar cells.

2. Experimental

The substrates used were 2×2 cm^2 soda lime glasses coated with fluorine doped SnO_2. A standard CBD CdS film (sample A) was prepared in liquid chemical solution, which contained 1.5×10^{-3} mol/L cadmium acetate and 5×10^{-2} mol/L thiourea. Ammonia was employed to adjust the solution pH to 11 at room temperature. The bath temperature was kept constant at 75 °C for a deposition time of 60 min. The thickness of the standard CBD CdS film was about 150 nm. Sample B was prepared by the standard process, followed by annealing in UHV using $CdCl_2$ vapor at 300 °C for half an hour. The thickness of sample B was around 150 nm, which was almost the same as that of the standard CBD CdS film. Sample C was made first by the standard CBD CdS process with

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reduced deposition time (20 min) and then an additional low temperature chemical bath of CdS layer. The solution temperature of the second treatment was kept at 55 °C for 20 min. The final sample C had the same $CdCl_2$ annealing treatment as sample B. The total thickness of the bi-layer CdS film was about 80 nm. All the CdS films were finished into solar cells.

When all CdS films finished CdTe/CdS solar cell devices were fabricated. A 5 μm CdTe layer was deposited by close space sublimation at source and substrate temperatures of 600 and 520 °C, respectively. This was followed by an ex-situ $CdCl_2$ treatment, NP etching and gold back contact deposition. Finally the 2×2 cm^2 coated glass sheets were scribed using stainless steel needles into cells of 5×5 mm^2 dimension.

Morphological properties were obtained by atomic force microscope using an AC mode (Asylum research MFP-3D). Optical properties were analyzed by UV–vis–IR transmittance (Perkin-Elmer Lambda 900). The crystallographic structure of the films was studied by X-ray diffraction (Rigaku). X-ray photoelectron spectroscopy (XPS) studies have been performed using an Escalab 250 spectrometer with a monochromatized Al anode X-ray source ($h\nu = 1486.6$ eV). The thickness of CdS films was measured by a white light interferometer. Performances of CdTe/CdS solar cells were characterised by J–V curve and quantum efficiency. The cell efficiency was measured under AM1.5 (100 mW/cm^2) illumination using a solar simulator.

3. Results and discussion

3.1. Morphology and structure

From AFM images (see Fig. 1), the roughnesses of sample A (standard CBD CdS) and sample B (CBD CdS with $CdCl_2$ annealing treatment at 300 °C) are 12.2 and 14.6 nm, respectively. The grain sizes also increase with increase in roughness of the CdS films after the annealing treatment. Cracks among grain boundaries are found in these 3D pictures. These are evidently the reasons for reducing device open circuit voltage and fill factor. Sample C has a second CdS on top, which has a small grain size. No pinholes and cracks among grain boundaries are observed. The surface is smoother than that of a single layer and the roughness is reduced to 7.2 nm even with the subsequent $CdCl_2$ treatment, which tends to increase the grain size. As a window layer, the bi-layer CdS is free of holes with a uniform grain size distribution, which has a positive effect on the performance of the final device.

Fig. 2 shows XRD patterns for the deposited CBD CdS films before and after $CdCl_2$ treatment. The identification and assignments of the observed diffraction patterns are made using the JPDS data. The (1 0 0) and (1 0 1) reflections at 24.8° and 28.2° belong to the hexagonal phase of CdS and appear only in the diffractogram of sample B. The (2 2 0) reflection at 44.1° of the cubic CdS phase shifts to the hexagonal peak (1 1 0) at 43.7°; the reflection intensity is also reduced. This indicates the transition of CdS film from the metastable cubic structure to the stable hexagonal structure produced by annealing in $CdCl_2$ atmosphere. The sharp peaks indicate good crystallinity of CdS film after $CdCl_2$ annealing. The decrease in the main peak (0 0 2) width is associated with an increase in grain size, which is also shown in AFM pictures (Fig. 1(a) and (b)).This change in crystalline structure is characteristic of the recrystallization process: a new, low-stress, larger grained structure is formed [11].

3.2. Optical property

The optical transmittance spectra of different CdS films are shown in Fig. 3. The absorption edge of sample B in the range of 450–550 nm is sharper than that of sample A. Sharper absorption edge indicates fewer defect and impurity energy levels in the film [12]. Better crystallinity of CdS film with $CdCl_2$ treatment is also indicated from this analysis. The bi-layer CdS film (sample C) has higher transmission at energies above E_g than the standard CBD CdS film due to the lower film thickness. Thereby more photons of the short wavelength range can pass through the window layer and contribute to the photocurrent. As shown in Fig. 4, the band gap (E_g) values can be calculated by plotting $(\alpha h\upsilon)^2$ against $h\upsilon$ of the graph at the beginning of band to band absorption and taking the intersection of the tangent to the $(\alpha h\upsilon)^2$ axis: $E_g = 2.38$ (sample A), 2.43 (sample B) and 2.24 eV (sample C). With $CdCl_2$ annealing treatment, the band gap of the CdS layer shifts to a higher value.

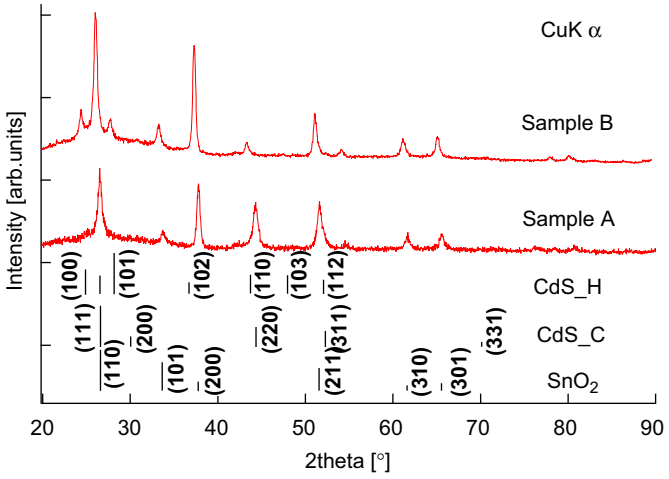

Fig. 2. XRD diffraction patterns of CBD CdS films deposited before and after $CdCl_2$ treatment: sample A, standard CBD CdS; sample B, CBD CdS with $CdCl_2$ annealing treatment at 300 °C. (CdS_H, hexagonal phase of CdS; CdS_C, cubic phase of CdS).

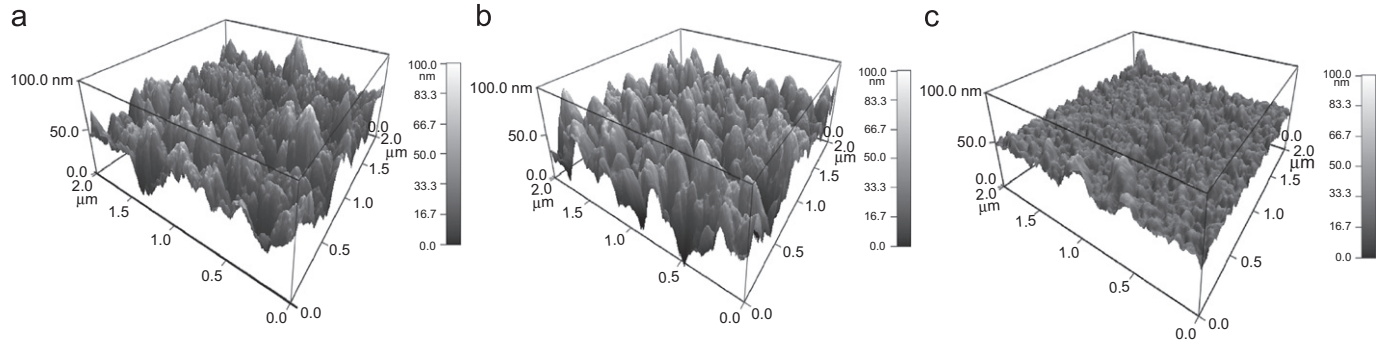

Fig. 1. AFM of different CdS films: sample A, standard CBD CdS, the roughness is 12.2 nm; sample B, CBD CdS with $CdCl_2$ annealing treatment at 300 °C, the roughness is 14.6 nm; sample C, bi-layer CdS with total 80 nm thickness, the roughness is 7.2 nm.