Journal of Crystal Growth 326 (2011) 152–156

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

The analysis of CdS thin film at the processes of manufacturing CdS/CdTe solar cells

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ARTICLE INFO

Available online 23 February 2011

Keywords:
A1. Structure properties
A1. Optical properties
A3. Chemical Bath Deposition
B1. CdS thin film
B1. Manufacturing process

ABSTRACT

In sequence, the deposited CdS thin film had undergone physical and optical changes by the processes of manufacturing CdS/CdTe solar cells. CdS thin film was manufactured by the Chemical Bath Deposition (CBD) method. The aqueous solution was based on ammonia solution. The temperature of bath system was 75 °C and deposition time was 50 min. The thickness of deposited CdS thin film was about 200 nm. The substrate was the glass coated with SnO_2:F thin film.

The following process was the deposition of CdTe thin film by the Closed-Space-Sublimation (CSS) method. The final process was the $CdCl_2$ heat treatment at N_2+O_2 atmosphere, and the contrast experiment progressed for $CdCl_2$–CdS thin film after CSS process at N_2 atmosphere.

The phase transition of CdS thin film, stress relaxation and optical band gap narrowing were developed by each process. And so, the formation of cadmium oxide was detected after the $CdCl_2$ heat treatment. It influenced to increase the optical band gap of CdS thin film.

The variation in the structure properties, optical properties and residual stresses of CdS thin film was analyzed by X-ray diffractometer (XRD), Raman spectroscopy and ultraviolet (UV)–visible (VIS) spectroscopy.

1. Introduction

CdS thin film is suitable for window layer of CdS/CdTe solar cells and has been manufactured by various techniques. It is one of the metal chalcogenide semiconductors (II–vi) used in CdS/CdTe solar cells. It has wide and direct band gap (2.4 eV) [1–4], and is suitable for developing junction effect for CdS/CdTe solar cells due to an n-type material. The lattice mismatch between CdS and CdTe was reported about 10% [5]. It has also been used in other applications including Cu(In,Ga)Se_2 (CIGS).

Various methods employed for fabricating CdS thin film were electrodeposition [1,6], RF sputtering [7,8], chemical vapor transport [9] and Chemical Bath Deposition(CBD) [4,10–16].

Among all the available techniques, Chemical Bath Deposition (CBD) method was suitable for manufacturing CdS thin film for commercial CdS/CdTe solar cells. CBD method was successful for the low cost devices. CBD method did not require complicated equipments for manufacturing CdS thin film. Beakers, holders, stirring and heating systems were only necessary. The Simplicity of process and equipments decreased the production cost.

CdS thin film had undergone physical and optical changes by lots of manufacturing processes for CdS/CdTe solar cells. CdTe thin film was deposited by Close Spaced Sublimation (CSS). $CdCl_2$ heat treatment could not be omitted for increasing the properties of solar cells. It helped recrystallization, grain growth, improved the electronic properties in CdTe thin film, influenced the morphology of CdTe surface, caused smoothing of the CdTe surface and made deep crevasses at the grain boundaries [17–22]. This paper deals with the structure and optical analyses of CdS thin film at each manufacturing process.

2. Experimental

2.1. Fabrication CdS thin film by CBD method

The substrates were glasses coated with SnO_2:F thin film. The overall thickness of SnO_2:F was about 500 nm. The substrates had high transparency and high thermo-stability. SnO_2:F thin film, which was deposited on glass had a sheet resistance of 10 Ω/cm^2. The transmission of SnO_2:F/glass is about 84% at 500 nm. The substrates were cleaned acetone, ethanol and deionized water with ultrasonicator for 1 min.

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doi:10.1016/j.jcrysgro.2011.01.086

CdS thin films were grown in a beaker and the beaker was capped with the holder. The substrates were kept vertically in the solution by the cap with holder. Deposition time was 20 min. Solution bath system consisted of magnetic stirring and heating system. The beaker was immersed insilicon oil. Temperature was maintained at 75 °C by the silicon oil and the hot plate. The solution consisted of $CdCl_2$(0.002M), thiourea($SC(NH_2)_2$(0.003M)), NH_4Cl(0.015M), NH_4OH(0.640M) and deionized water. pH of the ammonia based aqueous was about 11. Cadmium chloride was used as Cd precursor and thiourea was used as S precursor. Ammonia was used as a complexing agent. To ensure a stable complex, ammonium chloride was used as NH_3 buffer [11].

After deposition process, the back side of the substrate was cleaned by dilute hydrochloric acid. CdS thin film, which was deposited on the back side of the substrate absorbed the photons and decreased conversion efficiency of CdS/CdTe solar cells.

2.2. Fabrication CdTe thin film by CSS method

CdTe thin film was deposited on CdS thin film by CSS in Ar atmosphere. The pressure of CSS chamber was 0.5 Torr. At this process, the substrate was heated from room temperature to 550 °C for 9 min and the source was heated from room temperature to 600 °C for 10 min.The maintain time of the substrate and source was 6 min and 5 min, respectively. The thickness of CdTe was about 5–7 μm.

2.3. $CdCl_2$ heat treatment and N_2 annealing

After this process, $CdCl_2$ heat treatment was carried out. Cadmium chloride was dissolved in methanol. CdTe/CdS thin film was immersed in saturated cadmium chloride+methanol solution for 10 times. Then, CdTe/CdS thin film was heated by furnace at 400 °C and N_2+O_2 atmosphere for 20 min.

N_2 annealing experiment was designed for the comparison of $CdCl_2$ heat treatment. It was performed at the same time and temperature. However, cadmium chloride dipping step was omitted and the atmosphere was changed from N_2+O_2 to nitrogen.

2.4. Characterization of CdTe thin film and nanopattern

An X-ray diffractometer (Rigaku Model D/MAX-2500 V/PC) with Cu$K\alpha$ radiation and Raman spectroscope (LabRam High-Resolution), which has a monochromator with a focal length of 800 mm, and liquid nitrogen cooled charge-coupled device multichannel detector and Ar-ion laser with a wavelength of 514 nm were used for structural research. Additionally, a UV–vis spectrometer (JASCO, V-670) was used to measure the transmission, absorbance at room temperature and calculate the optical band gap of CdS thin film.

3. Results and discussion

3.1. Structure properties of CdS thin film

Fig. 2 shows X-ray diffraction patterns of CdS thin film at each process. The analysis of X-ray diffraction patterns is difficult. The substrate peaks appear at all patterns. It is difficult to interpret X-ray diffraction patterns of CdS thin film. The pattern of as-deposited CdS thin film was similar to that of the substrate (SnO_2:F/glass). CdS thin film, which was made by the CBD method was influenced highly by the substrate than CdS thin films, which were made by other methods. The X-ray diffraction pattern of as-deposited CdS was similar to that of the substrate (SnO_2:F/glass). However, Broad peak (cubic (2 0 0) or HCP (1 1 0)) appeared at 44.3° in Fig. 2, and the peak that appeared at 27° in Figs. 1 and 2 was believed to be cubic (1 1 1) or HCP (0 0 2) of CdS thin film on the substrate.

It was reported that the as-deposited CdS thin film has the mixtures of cubic and hexagonal structures. It is difficult to distinguish between cubic (1 1 1) and HCP (0 0 2), cubic (2 2 0) and HCP (1 1 0). However, after high temperature process, new peaks of hexagonal structure appealed at X-ray diffraction patterns. This phenomenon was thought to be the phase change of CdS thin film by heat treatment. It was believed that the mixtures of hexagonal and cubic phase were changed to hexagonal phase by the heat treatment. Generally, the hexagonal phase of CdS thin film is more thermodynamically stable than the cubic phase of CdS thin film [23].

Bulk hexagonal (0 0 2) peak was reported to appear at 26.507° (JCPDS No. 41-1049). The position of HCP (0 0 2) peak was changed from 27.2° to 26.8°. The position of CSS–CdS thin film corresponded to the position of JCPDS card. It may be due to the relaxation of tensile stress. The tensile stress of the as-deposited CdS thin film was developed by lattice mismatch of the hexagonal structure of CdS thin film and tetragonal structure of SnO_2. Lattice parameters of hexagonal structure of CdS thin film were reported to be a=4.140 Å and c=6.719 Å (JCPDS NO. 41-1049), and those of tetragonal structure of SnO_2 were reported to be a=4.737 Å and c=3.186 Å (JCPDS No. 88-0287). The schematic diagram of crystal structures is shown in Fig. 3. HCP (0 0 2) plane of CdS thin film was parallel to x–y plane. Since lattice parameter (a=4.140 Å) of CdS thin film is shorter than that (a=4.737 Å) of SnO_2, it is thought to be the origin of tensile stress development at HCP (0 0 2) plane.

After $CdCl_2$ heat treatment, the Cubic (2 2 0) of CdO has appeared and we believed the existence of the cubic (2 0 0) at 38°. However, we did not distinguish the CdO (2 2 0) and the peak of the substrate. The formation of oxide phase was for O_2 atmosphere and high temperature process. After $CdCl_2$ heat treatment, HCP (1 0 2) and HCP (1 0 3) have appeared. It is thought to be the re-orientation of CdS hexagonal structure

$$t = (K\lambda)/(B\cos\theta) : \text{Scherrer's formula} \quad (1)$$

The individual crystalline size (t) was determined using Scherrer's formula, where K is Scherrer's constant, which is a reference value corresponding to the quality factor of the apparatus measured with a reference single crystal and dependent on

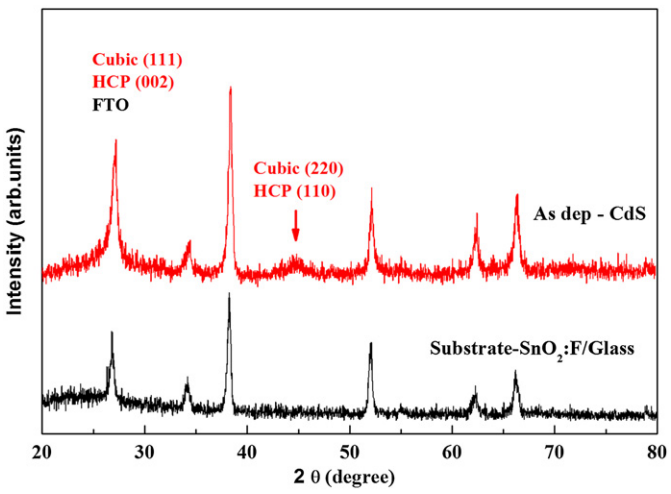

Fig. 1. XRD patterns of substrate (SnO_2:F/Glass) and as-deposited CdS thin film.