



Utilization of residual CdCl₂ in CBD-CdS to realize grain growth in CdTe: A novel route



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ABSTRACT

CdTe films were deposited by thermal evaporation onto chemical bath deposited CdS (CBD-CdS) films. The composite films were subjected to rapid thermal annealing (RTA) to observe simultaneous grain growth in both the CdS and CdTe layers. The films were characterized by measuring the compositional, microstructural and photoluminescence (PL) properties. PL spectra is dominated by the characteristic peaks (~ 1.42 eV and ~ 1.26 eV) associated with the virgin CdTe film. Additional features located at ~ 2.56 eV and ~ 1.99 eV could also be detected. The Fourier Transform Infra Red (FTIR) peak at ~ 482 cm⁻¹ appeared due to the simultaneous presence of absorption peaks for CdTe stretching mode as well as Cd-S modes. Appearance of the broad peak between 1000 cm⁻¹ and 1165 cm⁻¹ may be an indication of interfacial alloying. Secondary ion mass Spectroscopy (SIMS) measurements were done to observe the compositional uniformity in the film and to measure the interfacial mixing behaviour.

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1. Introduction

CdTe is one of the primary candidates in the field of photovoltaic energy conversion due to its specific advantages and currently leading the thin-film photovoltaic industry due to its low-cost fabrication. The advantageous properties include the near ideal band gap energy ~ 1.45 eV for the achievement of the theoretical maximum photovoltaic conversion efficiency of 31% and a high optical absorption coefficient of over 99% of the incident sunlight with only about 2 μ m of active thickness [1–7]. Cadmium sulfide (CdS) is generally used as a window layer for CdTe/CdS heterostructured solar cells [2,6]. The highest efficiency, 16.5%, was recorded with laboratory for CdTe/CdS heterostructured samples, which had the potential for further improvement to realize efficiencies close to 20% [5,6].

Properties of the as deposited films can be modified by various chemical, physical methods and post-deposition treatments. To improve the electronic parameters of devices, a few post

deposition treatments are necessary. Especially, a CdCl₂ solution treatment on CdTe film has been routinely used to enhance the electronic properties of CdTe through associated grain growth. But there seems to be ample potential for improving the process steps to reach this end-goal [5–7]. In this report we have clearly shown that additional CdCl₂ treatment is not needed in imparting the grain growth in CdTe layers in CdTe/CdS based solar cells. Residual CdCl₂ present in chemically bath deposited CdS is sufficient enough which can be fruitfully utilized to initiate the desired grain growth in CdTe layer. This would significantly eliminate an additional process step regarding CdTe grain growth with CdCl₂ treatment.

In this communication, studies on CBD-CdS/CdTe structures realized by depositing CdS by wet chemical route on glass substrate and then depositing CdTe layer thermal evaporation on Glass/CBD-CdS have been presented. Unlike previous reports, we have used unwashed CdS layer which contained useful CdCl₂ for initiating grain growth in CdTe layer. The films were characterized for their compositional structures by secondary ion mass spectrometry and also by measuring microstructural, photoluminescence and Fourier transformed infrared (FTIR) properties.

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2. Experimental details

CBD-CdS films were deposited onto glass substrates by adopting the method of Chopra et al. [8]. The experimental jig for CdS deposition consisted of a reaction kettle with a water sealed condenser fitted at the top to prevent loss of ammonia. The sample holder could be lifted outside the bath fluid whenever required. Direct heating of the bath fluid was avoided by placing the kettle in an oil bath which could be heated by a magnetic stirrer-cum-heater. CdS films were deposited onto glass substrate from a bath containing aqueous solution of 0.01 M CdCl₂, 0.1 M NH₄Cl and 0.05 M thiourea (NH₂CSNH₂). The bath was constantly stirred and the films were deposited at bath temperatures ~80 °C and the time of deposition was ~45 min. The pH value of the precursor was maintained at 10. The pH value and the temperature of the bath were constantly monitored during the whole experiment. NH₄OH solution was added drop wise to maintain the pH of the solution at ~10. The water sealed condenser of the reaction kettle prevented loss of ammonia.

CdTe layer was then deposited onto the CBD-CdS by thermal evaporation of CdTe powder (99.995%) from an alumina crucible, indirectly heated by a heavy duty tungsten heater. The as-deposited CBD-CdS and CBD-CdS/CdTe films were then subjected to rapid thermal annealing (RTA) at 400 °C for 4 min in argon atmosphere with a temperature ramp of 10 °C/s followed by another 4 min at 460 °C.

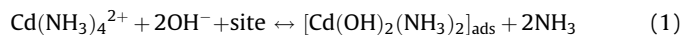
Microstructural properties were studied for all the individual films like CBD-CdS and CdTe as well as for as-deposited and rapid thermally annealed (RTA) CBD-CdS/CdTe structures deposited onto glass substrates. Atomic force microscope (AFM) pictures were recorded by using a Nanosurf Easy Scan2 in contact mode. A Carl Zeiss SUPRA[®] 55 field emission scanning electron microscopy (FESEM) was used to record the surface morphology at an operating voltage of 10 kV in secondary electron mode. X-ray diffraction (XRD) studies were carried out by using Rigaku MiniFlex XRD (0.154 nm Cu K α line) to obtain the micro-structural information. FTIR spectra were recorded in the range of 400–4000 cm⁻¹ by using a Nicolet[™]-380 FTIR. Photoluminescence (PL) measurements were recorded at 300 K by using a 300 W xenon arc lamp as the emission source. A Hamamatsu photo multiplier along with a 1/4 m monochromator was used as the detecting system.

A time of flight secondary ion mass spectrometry (TOF-SIMS 5) of ION TOF GmbH, Germany was used to study the compositional depth profile of the film. A 25 KeV liquid metal ion gun (LMIG) of Bi was used as a pulsed primary ion source to produce the secondary particles from the sample surface. The primary ion beam current was kept at 1.05 pA. The secondary ions were analyzed through a reflectron type time of flight mass analyzer in positive mode. For the depth profile of the samples, 1 KeV Cs⁺ source having beam current of 120 nA was used to sputter out the materials with respect to the film depth. The sputtering area was kept at 300 μ m \times 300 μ m while the analysis area was kept at 100 μ m \times 100 μ m to avoid any crater edge effect. The actual crater depth was measured using a Stylus type profilometer and the time scale in the original intensity (I) vs. time data was converted into I versus depth data using the crater depth value.

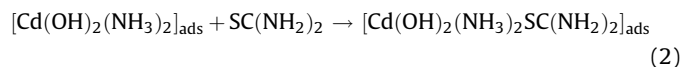
3. Results and discussion

Chemical bath deposition (CBD) process involves the slow release of sulfide ions via the controlled hydrolysis of thiourea in the presence of a cadmium salt and a chelating agent (commonly NH₃) which results in the precipitation of CdS on glass substrates as indicated in the earlier section. The nature of colloidal CdS particles depended critically on ammonia content regulating the pH value of the bath solution. In addition, ammonia also acts as a

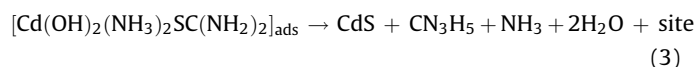
complexing agent such that in addition to Cd(NH₃)₄²⁺ complex in the solution, one also have complementary Cd-anion complex which culminated in precipitation of colloidal CdS particles [9,10]. Following Dona and Herrero [11], the mechanism for reversible adsorption of dihydroxodiammino-cadmium complex may be expressed as:



Adsorption of thiourea would culminate in the formation of a metastable complex:



Formation of CdS and site regeneration by the metastable complex decomposition as:



The basic final step adopted by earlier workers was to wash out the CdS film after deposition and then dry it in nitrogen flow by which additional colloidal CdS layer along with residual CdCl₂ and the metastable complex shown in expression (3) get washed away leaving behind a thin layer of CdS film. The CdS films, thus obtained, was amorphous consisting of nearly nano-dimensional CdS particles. We have tried to utilize the additional CdS colloidal particles along with the residual CdCl₂ by subjecting the as-deposited and unwashed CBD-CdS to rapid thermal annealing (RTA) to initiate grain growth in CdTe. A typical ramp of 10 °C/s was used to perform RTA at 400 °C for 4 min followed by a second ramp at 460 °C for 4 min at partial argon atmosphere were utilized to impart grain growth in CBD-CdS/CdTe films. The first ramp would initiate typical grain growth due to the presence of CdCl₂ vapour and the second ramp would take away the residual CdCl₂ vapour from the CBD-CdS/CdTe film. In this study, CBD-CdS films were deposited with the right molar concentration and with slightly higher and lower molar concentration of CdCl₂, to substantiate the role of CdCl₂ released from as-deposited and unwashed CBD-CdS.

3.1. Microstructural studies

Microstructures of the as-deposited and unwashed CBD-CdS films, as observed (not shown here) by FESEM, represent a compact amorphous film having featureless texture. The FESEM picture of the same film, when subjected to RTA as discussed in earlier section, is shown in Fig. 1a. A substantial grain growth (~150 nm) in this film was observed, which could be ascribed to the CdCl₂ mediated grain growth in the film. The EDAX spectra of the CBD-CdS film are shown in the inset of Fig. 1a which indicated the films to be sulphur deficient. The corresponding XRD trace shown in Fig. 1(b) indicated a peak located at $2\theta = 26.84^\circ$ corresponding to reflections from (1 1 1) planes of cubic CdS. The AFM picture of the same CBD-CdS film has been shown in the inset of the above XRD trace (Fig. 1b). From the SEM and the AFM micrographs, it may be observed that the films are compact and the average surface roughness ~10 nm. It may be mentioned here that the washed CBD-CdS films prepared as above did not indicate such grain growth upon annealing.

The micrographs of as-deposited CdTe on glass at 100 °C is shown in Fig. 1(c) while the bottom inset of Fig. 1(c) shows the morphology of the same film when subjected to RTA. It may be observed that the as-deposited films are composed of relatively smaller grains (~20 nm) as compared to that (~40 nm) of the annealed film. The EDAX spectrum of the CdTe film is shown in the top inset of Fig. 1(c) which indicated the films to be cadmium deficient. The XRD trace for CdTe films after subjecting to RTA is

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