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Effects of CdS substrates on the physical properties of polycrystalline CdTe Films

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Abstract

In this study, CdS thin films were deposited by thermal evaporation, close spaced sublimations, and solution growth methods, respectively, and the effects of the deposition methods on the physical properties of polycrystalline CdS deposited on ITO/glass were investigated. In addition, the effects of variously deposited CdS on the physical properties of thermally evaporated CdTe were also investigated. XRD results showed that CdS thin films deposited by solution growth, thermal evaporation, and close spaced sublimation (CSS) had a hexagonal structure with a random orientation of , (002) and (103) preferred orientation, respectively. All of the CdTe thin films deposited on those CdS substrates had the same cubic zincblende structure, however, they showed a little different crystal orientation relationship depending on the underlying CdS deposition method. Cross-sectional TEM showed that CdTe grain sizes of the furnace annealed CdTe grown on the CSS-CdS was the smallest among the furnace annealed CdTe thin films deposited on the variously prepared CdS substrates.

Keywords: CdS; CdTe; Rapid thermal annealing

1. Introduction

In CdTe or $CuInSe_2$ solar cells, polycrystalline CdS thin films are generally used as the window material for transmitting the light absorbed by CdTe or $CuInSe_2$ and also as the n-type material for p–n junctions of the solar cells [1–4]. To fabricate CdS thin films for the solar cells, deposition methods such as sputtering, spray pyrolysis, close spaced sublimation, thermal evaporation, solution growth, etc. have been used [3,5–7]. Currently, CdS thin films grown by the solution growth method are the most widely used for the fabrication of highly efficient CdTe solar cells, however, the effects of CdS growing methods on the physical and electrical properties of CdTe deposited on the CdS are not well investigated.

In this study, the effects of CdS growing methods on the physical properties of the CdS thin films deposited on ITO glass substrates and the effects of those CdS deposited substrates on the physical properties of CdTe were investigated.

2. Experiment

To deposit different types of CdS, deposition techniques such as thermal evaporation, solution growth, and close spaced sublimation (CSS) were used. Thermal evaporation was conducted in vacuum less than 7×10^{-2} Pa while the substrate temperature was maintained at 200°C. In case of the solution growth method, a solution consisted of 0.025M $Cd(AC)_2$, $(NH_3)CS$, 0.6M NH_4OH, 0.1M $NH_4(AC)$, and 0.025M $(NH_2)_2CS$ at 70°C was used and, for the close spaced sublimation, CdS was deposited at 500°C in the H_2 environment while the source temperature was maintained at 700°C and the spacing between the source and the substrate was kept at 5 mm. The deposited CdS thickness were in the range from 100–300 nm. The variously deposited CdS thin films were annealed in hydrogen for 20 min at 400°C for thermally evaporated and solution grown CdS thin films and at 500°C for CSS-CdS thin films after being dipped in a $CdCl_2 + CH_3OH$ solution.

To study the effects of the variously prepared CdS thin films on the physical properties of CdTe, CdTe thin films were deposited on those annealed CdS after the treatment using hydrazine hydrate (H_6N_2O) for 2 min to remove oxides possibly formed on the annealed CdS. CdTe thin films (3–4 μm thick) were deposited at 280°C using thermal

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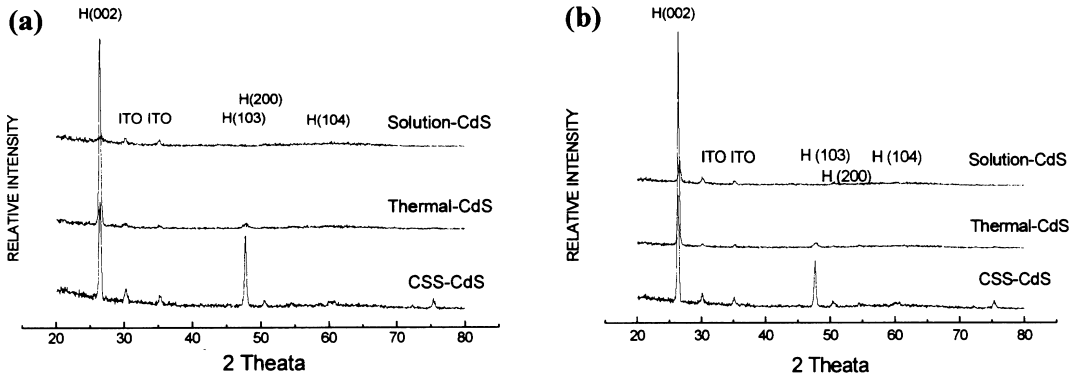

Fig. 1. X-ray diffraction data of CdS thin films deposited variously (a) and annealed thin films in the H_2 environment (b).

evaporation. Rapid thermal annealing at 550°C for 2 min in the air environment was carried out to anneal the deposited CdTe and some of the CdTe thin films were also annealed using a three-zone tube furnace at 400°C for 30 min after treatment in a $CdCl_2$ + CH_3OH solution to compare with the rapid thermally annealed CdTe.

The physical properties of deposited and annealed CdS and CdTe thin films were investigated using X-ray diffraction to study the preferred orientation and the crystal structure, Auger electron spectroscopic depth profiling was used to study the surface and the bulk composition of the deposited and annealed CdS thin films, and cross-sectional transmission electron microscopy was used to study the grain size, the grain structure, defects, etc.

3. Results and discussion

Crystal structures and preferred orientations of the CdS thin films deposited variously and annealed were investigated using X-ray diffraction and are shown for the deposited CdS thin films (Fig. 1a) and for the annealed thin films (Fig. 1b). As shown in the figure, all of the deposited CdS thin films had a hexagonal structure with different orientations, that is solution grown CdS showed random orientation, thermally grown CdS showed a (002) preferred orientation, and CSS-CdS showed a (103) preferred orientation, and the annealing process used in the experiment did not change the structure and the orientation relationship.

Table 1
Surface and bulk composition of variously deposited and annealed CdS thin films measured by Auger electron spectroscopy

Experiment		As-deposition		After annealing	
		Cd	S	Cd	S
Evaporation	Surface	52.4	47.6	57.2	42.8
	Bulk	51.2	48.8	52.9	47.1
Solution	Surface	54.2	45.8	56.2	43.8
	Bulk	51.8	48.2	51.7	48.3
CSS	Surface	52.7	47.3	57.9	42.1
	Bulk	50.5	49.5	49.2	50.8

The surface and bulk compositions of the deposited and annealed CdS thin films were investigated using Auger electron spectroscopy and the results are summarized in Table 1. The bulk compositions were obtained from the Auger depth profiling. In general, the surface and the bulk compositions of CdS thin films fabricated in our experiment were Cd-rich and more Cd-rich compositions was obtained on the surface compared to the inside of the film. After the annealing in the H_2 environment, the surface of the CdS thin films became increasingly Cd-rich, however, the bulk compositions remained the same as those of the as-deposited CdS. The increase of Cd on the CdS surface after the annealing appears to be related to the formation of H_2S during the annealing in H_2.

CdTe thin films were thermally evaporated on those annealed CdS thin films and the effects of the variously deposited CdS thin films on the structural properties of the CdTe thin films were investigated using X-ray diffraction, and the results are shown for the rapid thermally annealed CdTe thin films (Fig. 2a) and for the furnace annealed CdTe thin films (Fig. 2b). As shown in the figure, CdTe thin films possessed the cubic zincblende structure and showed a (111) preferred orientation. However, depending on the orientation of the underlying CdS thin films, different degrees of the preferred orientations were shown. In case of the CdTe thin films grown on the thermally evaporated CdS, a (111) preferred orientation was shown while, for the CdTe thin films grown on the solution grown CdS, a rather random orientation was obtained, however, in case of CdTe thin films deposited on the CSS grown CdS, a (111) orientation with rather broad X-ray diffraction peaks between (220) and (311) were obtained. This broadening appears to be related to the lattice mismatch stress between the deposited CdTe and the underlying CdS and the rapid thermal annealing used in the experiment appears not to remove the stress completely. When the furnace annealing was performed as shown in Fig. 2b, the broad peaks were removed and sharp cubic zincblende (220) and (311) peaks were restored.

Cross-sectional transmission electron microscopy of the

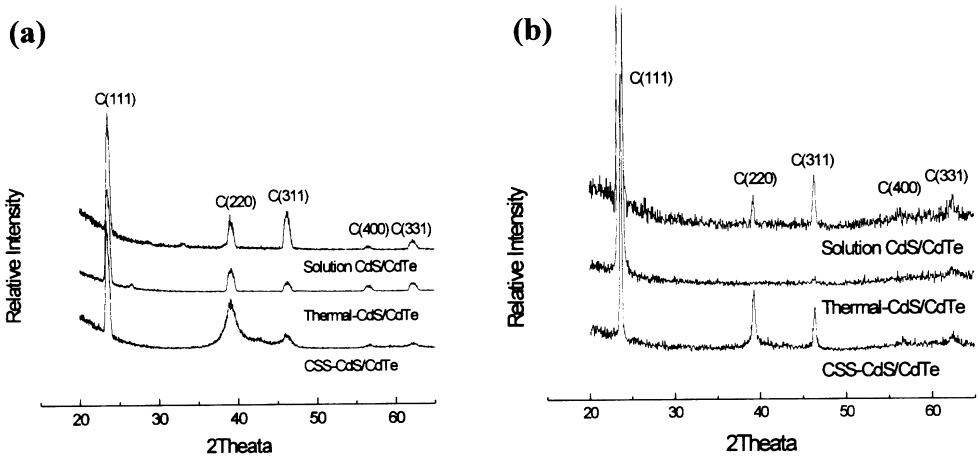

Fig. 2. X-ray diffraction data of CdTe thin films deposited on the variously prepared CdS thin films. CdTe thin films were annealed at 550°C using rapid thermal annealing (a) and at 400°C using furnace annealing after the treatment in $CdCl_2$ + CH_3OH solution (b).

CdTe/CdS junction was investigated and the results for the furnace annealed CdTe deposited on the solution grown CdS and on the CSS grown CdS are shown in Fig. 3a,b, respectively. Cross-sectional transmission electron microscopy of the furnace annealed and the rapid thermally annealed CdTe thin films deposited on the thermally evaporated CdS was also investigated (not shown). The CdTe deposited on the thermally evaporated CdS showed a columnar structure and the grains ($\sim$ 200 nm) were epitaxially related to the underlying CdS grains ($\sim$ 200 nm). The rapid thermal annealing of the CdTe did not change the grain structure while reducing some of the observed defects such as dislocations and micro-twins in the CdTe grains. However, the furnace annealing of the CdTe removed the columnar structure and a recrystallized structure ($>$ 1) was emerged. The furnace annealed CdTe thin films deposited on the solution grown CdS and on the CSS grown CdS in Fig. 3a,b also showed the recrystallized CdTe grains. The grain sizes ($\sim$ 200 nm) of CdS grown by CSS were similar to those by the thermal evaporation and these were larger than those ($\sim$ 10 nm) of CdS by the solution growth method. However, as shown in the figure, the furnace annealed CdTe deposited on the CSS grown CdS showed smaller recrystallized CdTe grains (100 nm) compared to the same furnace annealed CdTe grains ($>$ 1) deposited on the solution grown CdS and on the thermally evaporated

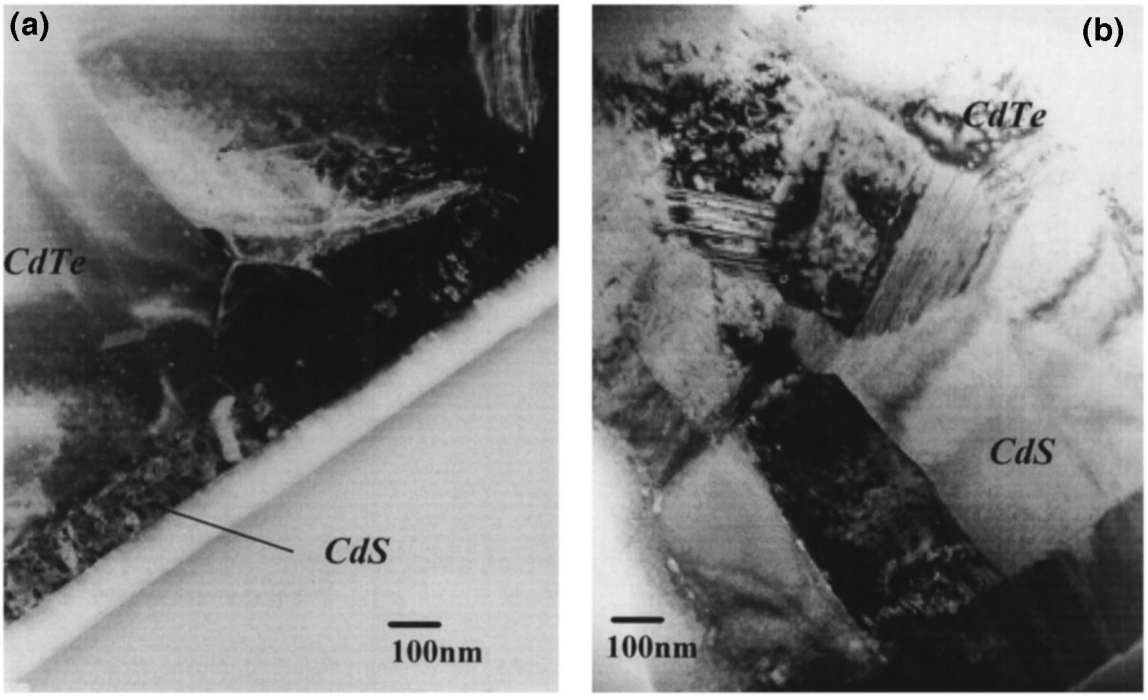

Fig. 3. Cross-sectional TEM micrographs of the furnace annealed CdTe/Solution grown CdS (a) and the CdTe/CSS grown CdS (b).

CdS. The small grain size of the furnace annealed CdTe deposited on the CSS grown CdS appears to be related to the stress observed from the X-ray diffraction as shown in Fig. 2. With micro-energy dispersive X-ray spectroscopy (micro-EDX), the degree of sulfur diffusion through the CdTe/CdS junction was also investigated (not shown). More sulfur diffusion through the furnace annealing compared to the rapid thermal annealing was observed.

The structural and the compositional variation of CdTe depending on the physical properties of previously deposited CdS and the annealing methods of the deposited CdTe could change the electrical properties of polycrystalline CdTe/CdS thin film solar cells and, therefore, affect the solar conversion efficiency of the solar cells, and which is currently under investigation.

4. Conclusion

XRD results of the CdS deposited variously on the ITO glass and annealed in the hydrogen environment showed that CdS thin films showed the same hexagonal structure, however, the preferred orientations of CdS deposited on the ITO glass were different depending on the deposition method. The furnace annealing in the hydrogen environment did not change the preferred orientation and the composition of the deposited CdS thin films did not change except for the surface composition.

CdTe deposited on those variously prepared CdS showed the same cubic zincblende structure with little different orientation. Also, the broadening of the XRD peaks between (220) and (331) possibly related to the little mismatch stress was observed for CdTe deposited on the CSS grown CdS. This broadening of XRD peaks was removed after the furnace annealing, however, cross-sectional transmission electron microscopy showed that, even though the underlying grain sizes of CdS grown by the CSS was comparable to those of CdS grown by the thermal evaporation and larger than those of CdS grown by the solution growth method, the furnace annealed CdTe deposited on the CSS grown CdS showed the smallest grain size near the junction possibly due to the recrystallization process related to the removal of the stress.

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